Physical properties of lead free solders in liquid and solid state

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General introduction

Liquid metals and alloys are the subject of many studies. Applications of molten metals can be found in many fields (metallurgy, nuclear thermal power stations and geophysics, among others). Work by Ziman on liquid metals and by Faber and Ziman on alloys have largely contributed to the study of electronic transport properties by using the concepts of structure factor and form factor. The structure factor, which represents atomic interactions, can be determined from scattering experiments or from analytical models (for example, the hard sphere model). The form factor describes electron-atom interaction and can be represented by simple analytical "pseudo-potential" models, or by the scattering t matrix, which requires ab-initio calculations to produce the "muffin-tin" potential. The Animalu-Heine pseudo-potential form factor and the Ashcroft-Lekner hard sphere structure factor allow a successful semi-quantitative interpretation of the electronic transport properties of simple metals. The scattering t matrix approach developed by Evans et al. and based on the collision theory, contributes to the understanding of complex metals, especially noble metals, transition metals, heavy metals and semi-metals. This approach consists of replacing the square of the form factor entering Ziman’s formula by the square of the scattering t matrix element.

Our research team at Metz is mainly interested in the experimental studies of electrical resistivity and of the absolute thermoelectric power of liquid metals and alloys. Measurement devices for electronic transport properties have been developed, enabling many liquid metals and alloys to be studied.

In this work, two complementary research projects have been undertaken. The first one consists of studying the electronic transport phenomena of cadmium-antimony alloys and to use the transport properties to examine if hysteresis may exist in liquids. The second one, which is being carried out as a collaborative research project between Metz University and Chemnitz University, deals with the study of the lead-free solders. Solder must
conduct electricity and heat well. The electronic transport properties of different lead-
free solders (Sn-Ag-Cu, Sn-Cu, Sn-Ag, Sn-Sb) were measured at the LPMD laboratory
(Metz) in both liquid and solid states. These results were compared to the lead-tin solder
(Sn-Pb) ones. The compositions studied during this thesis are those expected to replace
lead-tin solders. At Chemnitz, surface tension and density are measured for both types
of alloys with and without lead by a tensiometer, and their wettability is measured using
the sessile drop method. Viscosity is also measured for these alloys with and without
additives, particularly nickel.

The first part of this thesis covers the fundamental study of the electronic transport prop-
erties of liquid metals and alloys. This part is organized into three chapters. The first
chapter will give a description of the experimental device and of electrical resistivity and
absolute thermoelectric power measurement methods. The second chapter covers what is
known about electronic transport properties from both the macroscopic and the micro-
scopic points of view. In the third chapter, our experimental results of pure antimony
and Cd-Sb alloys will be presented. The \( Cd_{40}Sb_{60} \) hysteresis phenomenon of the electronic
transport properties will then be discussed. These experimental results will be compared
to both earlier results and theoretical calculations.

The second part of this thesis is devoted to the study of the physical properties of indus-
trial solders. In the fourth chapter, we will present the problems that arise from using
lead-based solders and the medical risks of lead. In the fifth chapter we will present our
experimental results on electrical and thermal conductivity and the absolute thermoelec-
tric power of tin-based solders. These experimental results were compared to theoretical
calculations using the Ashcroft potential. Chapter six will present the experimental de-
vices used to measure surface tension and wettability, as well as the corresponding results
of the experiments carried out in Chemnitz. In the seventh chapter we will present the
viscosity measurements of the lead-tin and lead-free solders, which were also measured
in Chemnitz. A very small quantity of nickel can be added to improve the mechanical
properties of lead-free solders. The influence it has on the flow and on the viscosity of the
solder was checked.

Lastly, we will reach the conclusion of this thesis.
Chapter 1

Principle and experimental techniques of measuring of the electronic transport properties

1.1 Introduction

In general, experimentally determining resistivity and absolute thermoelectric power (ATP) is difficult to achieve. Many problems of a technological nature have to be overcome. Indeed, a liquid does not have a defined geometrical shape; it is thus essential to give it a shape by putting it in a suitable cell. The constituent materials of the cell must be selected among those which do not react with molten metals. These materials must retain the property of electrical insulators even at high temperature. Molten metals are good electric conductors, it is thereby essential to employ an experimental device to measure low levels of resistances. Other problems are related to the choice of refractory materials: from thermal shock resistance to low vapour pressure of molten metals and electrode oxidation. It is consequently necessary to work under controlled or vacuum atmospheric conditions. In our laboratory, we use an automated device that enables the resistivity and absolute thermoelectric power with a silica cell to be measured simultaneously.
1.2 Principle and experimental methods of measuring resistivity

The measurement technique used in this work, known as "the four-point probe technique", was first used by Gasser [1] in a fused silica cell. It used a volt-amperometric method with four wires and consisted of passing a current at the ends of the molten metal by two electrodes and to note the voltage at the terminals of the two other electrodes. The direct application of the Ohm law \( U = R_m I \) gives the resistance of the molten metal. This resistance is linked to the resistivity by:

\[
R = \rho \int_0^L \frac{dl}{S(l)} = \rho C
\]  

To accurately determine the resistivity, these three parameters are needed:

- The current, \( I \), through the sample.
- The voltage, \( U \), at the terminals of the sample.
- The constant, \( C \), depending only on the geometry of the sample.

The principle here in measuring (fig. 1.2.1) is to pass a constant current through our sample (of which resistance is unknown) and then through a standard resistance. The voltage is noted at the terminals of unknown resistance and standard resistance. Then, these same voltage levels are measured after having reversed the direction of the current. This method of measurement allows parasitic e.m.f. of thermoelectric origin to be eliminated, regardless of the current’s direction. After having taken into account the algebraic difference divided by two of the voltages obtained before and after inversion of the current, the intensity crossing the circuit is obtained by carrying out the ratio of the voltage at the terminals of the reference resistance value. With data on the current passing through the circuit, Ohm's law enables us to determine the value of the unknown resistance \( R_m \). To find out the electrical resistivity, constant \( C \), often known as constant of the cell, needs to be determined. Since the capillary containing the liquid alloy does not have a regular shape, the geometrical constant of the cell is defined by \( C = \int_0^L \frac{dl}{S(l)} \cdot S(l) \), in the section of the conductor (which is not constant) at position \( l \). An accurate determination of \( C \) by measuring the dimension of the cell is not possible. Thus the constant \( C \) was calibrated by measuring the resistance of the cell filled with triple-distilled mercury whose resistivity is well known.
1.3 Absolute thermoelectric power "ATP"

1.3.1 Background on thermoelectric phenomena

1. The Seebeck Effect

Electricity and heat are two types of energy expected to give rise to various phenomena in conductors. The Seebeck effect is the direct conversion of temperature differences into electricity. In 1821, Seebeck noted that a closed loop formed of two different metals, or alloys A and B, and whose two junctions $S_0$ and $S_1$ are held at different temperatures $T_0$ and $T_1$, produce the voltage difference $dV$. This circuit (fig. 1.3.1) called a thermocouple is frequently used. A voltmeter is inserted in the circuit. For reasons of simplicity, it is often placed at $S_0$. The electromotive force
obtained depends only on the nature of the conductors in contact and on the temperatures of the two junctions. This effect is characterized by the Seebeck coefficient which can be defined as the ratio of the voltage by the difference in temperature when both values are infinitely low. This coefficient is often measured by using one of the junctions to a known temperature (as a reference - generally 0°C-) and the other to a variable temperature (measurement junction). The Seebeck coefficient of a couple is given by the derivative of the electromotive force as a function of temperature.

2. The Peltier Effect

The Peltier effect is (approximately) the reverse of the Seebeck effect: a creation of a (algebraic) heat release from an electric current. When an electrical current is passed through the junction between two dissimilar conductors, heat is produced or absorbed at the junction, according to the direction of the current. The quantity of heat dQ absorbed or produced per unit of time dt is proportional to the intensity of the electrical current I as the following equation:

\[ dQ = \pi_{A/B} I dt \]  

\( \pi_{A/B} \) is the Peltier coefficient for the combination of conductors A/B. The direction of heat transfer is controlled by the polarity of the current; reversing the polarity will change the direction of heat transfer and thus the sign of the heat absorbed or produced (fig. 1.3.2). At a uniform temperature, the direct measurement of the Seebeck coefficient of couple \( S_{A/B} \) is not possible because of Volta’s metal chain law: a heterogeneous metallic circuit at a constant temperature is not crossed by a current (the Peltier coefficient of a couple is measurable, that of one of the elements is not). In such a circuit, the algebraic sum of the contact difference of the potential is zero.

3. The Thomson Effect

The Thomson effect describes the heating or cooling of a current-carrying conductor with a temperature difference (in addition to the Joule effect). In conductor ‘A’, which was subjected to a difference in temperature (dT) (fig. 1.3.3), the electrons move and create an electric field. One can note an e.m.f. proportional to the
variation in temperature $dT$: $dV = h_A(T)dT$ where $h_A(T)$ is the Thomson coefficient of conductor A, expressed in V/K. This effect is reversible like the Peltier effect: the Thomson heat changes in sign when the direction of the current $I$ changes contrarily to Joule effect. The Thomson effect is typical of a single conductor. The Seebeck effect is a combination of the Peltier effect (of a couple) and Thomson effect (of two single conductors). The Seebeck effect gives rise to the e.m.f. of thermocouple A/B (fig. 1.3.1). Conventionally, one starts from an unspecified point of this circuit in a chosen direction, with the measured e.m.f. corresponding to these two phenomena. This electromotive force, which depends only on the temperature of the junctions and the nature of the materials, is given by the following expression:

$$
E_{T_1}^{T_0} (A/B) = \pi_{A/B} (T_1) - \pi_{A/B} (T_0) + \int_{T_0}^{T_1} [h_A (T) - h_B (T)]dT = \int_{T_0}^{T_1} [S_A (T) - S_B (T)]dT
$$

(1.3.2)

$S_A$ and $S_B$ are the Seebeck coefficients of elements A and B.

1.3.2 Applications of these thermoelectric effects

In practice, these thermoelectric phenomena can be used for measuring temperature by thermocouple (Seebeck effect). The Peltier effect is used to work out thermoelectric generators which allow electricity to be converted into "heat" or, more interestingly, into "cold" (as refrigeration or thermoelectric heater). As for the thermocouples, the insertion of a third metal of a different nature in any part of initial circuit A/B does not at all modify the e.m.f., provided that the connections are at the same temperature. This property is called "intermediate metal law", which is very important from an experimental point of
view. This law enables a wire (generally copper) to be inserted at the cold junction so as to connect it to a measuring apparatus without distorting the results. Taking into account these laws, there are two types of possible circuits for measuring thermoelectric effects depending on the point where the apparatus is inserted. In our laboratory, an open circuit is used at the cold junction. The voltmeter is connected to the thermocouple by copper wire, whose cold junction is adjusted to the temperature $T_0$ (generally 0°C) and the hot junction at $T_1$.

### 1.3.3 Methods of measuring ATP

The thermoelectric power $S_{AB}$ of a circuit consisting of two dissimilar conductors A and B is the derivative related to the temperature of the electromotive force $E_{AB}$ delivered by the couple AB. This e.m.f. comes from the superposition of the Peltier and Thomson effects that appear in the circuit: this is the Seebeck effect (eq. 1.3.3).

$$S_{AB}(T) = \frac{dE_{AB}(T)}{dT} = \lim_{\Delta T \to 0} \frac{\Delta E_{AB}(T)}{\Delta T}$$

There are two relations between the various thermoelectric coefficients (chap. 2). These relations, called Kelvin laws, tie together the Peltier ($\pi$), Seebeck (S) and Thomson (h) coefficients, giving us equations from 1.3.4 to 1.3.6.

$$S_{AB}T = \pi_{AB}$$  \hfill (1.3.4)  

$$h_A - h_B = T \frac{dS_{AB}}{dT}$$  \hfill (1.3.5)  

we can also write it as:

$$S_{AB} = \int_0^T \frac{h_A - h_B}{T} dT$$  \hfill (1.3.6)  

$$S_A = \int_0^T \frac{h_A}{T} dT$$  \hfill (1.3.7)  

$$\pi_A = T.S_A$$  \hfill (1.3.8)  

By definition, the Seebeck coefficient $S_{AB} = S_A - S_B = \frac{dE_{AB}}{dT}$ shows that this coefficient of a wire (pure metal or alloy) cannot be measured. The difference of the two "absolute thermo-electric powers" of two wires can only be measured by realising a thermocouple.
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This is the same for the Peltier effect. To get the "absolute" thermo-electric power of a wire, it is necessary to measure the electromotive force of a couple, and to derive it in respect to the temperature in order to subtract the "absolute" thermo-electric power of the second wire constituting the couple. It is thus necessary to know the absolute thermo-electric power of at least one element. Roberts [2], at the National Bureau of Standards, measured the Thomson coefficient $h$ of very pure platinum (called "platinum 67") from 0 Kelvin to 1900 Kelvin. Then, using Kelvin's second law, he determined by integration, the absolute thermoelectric power $S$ of very pure platinum, which is now considered as the reference. The Thomson coefficient is the only "absolute" coefficient of a wire that is directly measurable (it does not need a junction). If a current passes through a wire where there is a temperature gradient, there will be a release or absorption of heat, proportional to the Thomson coefficient. The experimental determination is however very difficult since the Thomson heat value for metals is proportional to the current $I$, and is generally about 100 times lower than the quadratic Joule effect. The Thomson effect is measured by very accurate calorimetry, changing the direction of the current $I$. All the other wires can be calibrated by realising a couple with platinum 67. In our laboratory, we systematically calibrated all the wires that we use for thermo-electric power measurements. In this research, this was done for pure tungsten and tungsten-26% rhenium.

To determine the ATP of the element $A$ in the laboratory, it is necessary to know the ATP of $B$ and to measure the e.m.f. $E_{AB}$ according to the temperature $T$. It is thus of primary importance to have a reference element. The ATP of an unknown metal at the temperature $T$ can be given starting from a traditional assembly of thermocouple (fig. 1.3.4) where one of the conductors is an unknown metal (or alloy) (M) studied and the other (A) is a reference element whose ATP is well-known (Example: Platinum). The Seebeck e.m.f. of the couple is measured when the temperature of one of the junctions varies.

At the time of the various assemblies used in our laboratory, the following essential points were stressed in order to have accurate measurements:

- Good homogeneity of alloys.
- Calibration of the reference.
- Elimination of the parasitic voltages effects during the measurement.
Two "practical" methods to determine the thermoelectric power $S$, starting from the assembly of the thermocouple (reference conductor/ metal or liquid alloy/ reference conductor), are used according to the importance of the temperature gradient between the junctions:

**a-Great temperature gradient method**

The reference junction is maintained at a constant temperature $T_0$ (typically $0^\circ$C) and the temperature of the other junction varies widely in temperature. The thermoelectric power is given by the slope of the Seebeck e.m.f. as a function of temperature. This method known as "of large $\Delta T$" is generally used for the calibration of the thermocouple wires and for solids.

**b-Small temperature gradient method**

It requires the introduction of a second wire of a different nature into the assembly (fig. 1.3.5). Wire A is used to measure the Seebeck effect of an unknown alloy and couple AB is used to measure the temperature. A variation of the temperature difference of about 2 to $5^\circ$C was created between the junctions (the temperature of one junction is fixed to $T_1$ and the other is a variable depending on the time from $T_1 - \Delta T$ to $T_1 + \Delta T$). This method has been adapted for the measurement of the absolute thermoelectric power of
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liquid metal alloys, because an overly important heat gradient can be the reason for the diffusion of atoms of a different nature, which modifies the composition of the alloy locally.

We employed this method to determine the ATP of our liquid systems.

1.3.4 Principle of the employed method

The device used is represented on the figure 1.3.5. Moreover, circuits \( A - M - A' \) and \( B - M - B' \) simultaneously give two e.m.f. between wires of the same nature ((\( V_{13} \) and \( V_{24} \)), which are measured during the variation of the temperature of the right junction. On this small temperature range, it can be postulated that the e.m.f. varies linearly with temperature. Supposing we break up the fem. \( V_{12} \) and \( V_{34} \) in their various terms. At the temperature \( T_1 \) for the left junction, the voltages would be written as such:

\[
V_{13}(T_1) = \int_{T_R}^{T_1} h_A(T) dT + \pi_{AM}(T_1) + \int_{T_1}^{T} h_M(T)dT + \pi_{MA'}(T_1) + \int_{T}^{T_R} h_{A'}(T)dT \quad (1.3.9)
\]

At the temperature \( T_2 \), the expression of the voltage \( V_{13} \) changes to give:

\[
V_{13}(T_2) = \int_{T_R}^{T_2} h_A(T) dT + \pi_{AM}(T_2) + \int_{T_2}^{T} h_M(T)dT + \pi_{MA'}(T_2) + \int_{T}^{T_R} h_{A'}(T)dT \quad (1.3.10)
\]

The same calculation is used to determine \( V_{24}(T_1) \) and \( V_{24}(T_2) \). The similar wires are marked differently (A and A’) because their characteristics are never completely identical. Indeed, it can be noted that even if the two junctions are maintained at an identical temperature, a parasitic e.m.f. due to the difference in pairing of similar wires can be observed. During the experiment, these e.m.f.s can vary somewhat according to time.

Figure 1.3.5: ATP measurement scheme (small \( \Delta T \))
It is the sign of a degradation of the thermoelectric characteristics of the reference wire. This parasite e.m.f. is written:

$$V_{13}(T) = \int_{T_R}^{T} (h_A(T) - h_{A'}(T)) dT + \pi_{AM}(T) + \pi_{MA'}(T)$$  \hspace{1cm} (1.3.11)

The same expression is obtained for $V_{24}(T)$. Voltages $V_{13}$ and $V_{24}$ vary linearly with the temperature but can not exactly equal to zero when the junctions are at the same temperature. The method that we describe below makes it possible to correct the errors resulting from these drifts. A variation in temperature is carried out over a short time during which the thermoelectric characteristics is considered to be constant. The slope of the straight line is measured as $V_{24} = f(V_{13})$. This is expressed as:

$$p = \frac{\Delta V_{24}}{\Delta V_{13}} = \frac{\int_{T_1}^{T_2} (h_B(T) - h_M(T)) dT + \pi_{BM}(T_2) - \pi_{BM}(T_1)}{\int_{T_1}^{T_2} (h_A(T) - h_M(T)) dT + \pi_{AM}(T_2) - \pi_{AM}(T_1)} = \frac{\int_{T_1}^{T_2} (S_B(T) - S_M(T)) dT}{\int_{T_1}^{T_2} (S_A(T) - S_M(T)) dT}$$  \hspace{1cm} (1.3.12)

Using Kelvin's law and the approximation of the linearity of the e.m.f. on T interval relations (2.2.10, 1.3.8), we arrive at the following equation:

$$S_{MB}(T_1) = S_{MB}(T_2) \approx S_{MB}(T_m)$$  \hspace{1cm} (1.3.13)

$T_m$ is the average temperature. By using the preceding concepts, the slope $p$ becomes:

$$p = \frac{S_{MB}(T_m)}{S_{MA}(T_m)}$$  \hspace{1cm} (1.3.14)

This expression shows that the measurement of $V_{24}$ in accordance with $V_{13}$ gives a straight line with the slope $p$. After decomposition of this relation, the expression of the ATP of the metal M is written as:

$$S_M(T_m) = \lim_{\Delta T \to 0} \frac{S_{BA}(T_m)}{p - 1} + S_A(T_m)$$  \hspace{1cm} (1.3.15)

In conclusion, the determination of $S_M$ by this method requires to know the thermoelectric characteristics of reference metals A and B. Depending on the temperature, a preliminary calibration of these conductors will provide us:

- The ATP of the metal A according to temperature $S_A(T)$. 

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- The ATP of the couple A/B according to temperature $S_{AB}(T)$.

- The temperature of the couple A/B according to the e.m.f. $T(E_{AB})$.

The role of metals A and B can be inverted. The measurement of this e.m.f. provides the temperature $T_m$ of the experiment. The measurements of $V_{24}$ and $V_{13}$ determine the slope $p$. To determine the thermoelectric power of our liquid metal (or alloy), it is necessary to carry out the calibration of our various reference wires.

1.4 Measuring cell

The cell that we retained for our simultaneous measurements of the resistivity and the absolute thermoelectric power is derived from that described by Gasser [1] (fig. 1.4.1). The fused silica cell was selected for its characteristics. It has little chemical reaction with the metals studied; it can quickly be implemented and used up to 1200°C. Moreover it has a very low expansion coefficient. It is represented on the figure 1.4.1. It consists of a 10 mm diameter silica tube going out of the furnace. This makes it possible to modify the composition of an alloy during measurement, to make a vacuum or to apply an inert atmosphere of argon. This principal tube is connected by a capillary to a smaller secondary tank. The liquid metal is contained in a fused silica cell equipped with sealed pure tungsten and tungsten-rhenium 26% wires to measure the resistivity and the thermopower. The temperature is measured inside the cell using non-standard W-WRe26, and outside the cell with a K thermocouple. A heating element (standard "Thermocoax") is affixed on a small tank in order to create a small temperature gradient, which is essential for ATP measurements. Before and during the heating stage, the cell and metal are carefully outgassed by pumping except when the vapour tension is too important (to avoid distillation). In order to carry out electrical contact between the electrodes and a reading of the potential difference at the ends of the capillary, argon pressure is applied, which fills the capillary and the small tank with molten metal.

1.5 The furnace

The heating system was made using a furnace (height: 60 cm, external diameter: 30 cm). It is shown in figure 1.5.1. An A1 Kanthal heater is wound on a central ceramic
1.6 Vacuum /pressure device

To avoid the oxidation of metal and electrodes as well as the elimination of gases dissolved in metals and to ensure the sealing of the cell, before and after heating, a good vacuum within the cell is necessary. This vacuum-pressure device consists of:

tube, which can be heated up to approximately 1300°C. The temperature of the furnace is controlled by a programmable regulator (PID). During the experiment, the slope in rise and descent of temperature should not exceed 2°C per minute in order to remain in quasi-equilibrium.

Figure 1.4.1: fused silica cell for simultaneous resistivity and ATP measurement
Chapter 1. Principle and experimental techniques of measuring of the electronic transport properties

Figure 1.5.1: measurement furnace

- A primary vacuum pump, providing a pressure limit of 10^{-3} Torr. This verifies the proper sealing of the cell as well as the connections between this cell and the vacuum system

- An argon bottle allows pressure of up to 10 bars to be applied in the cell. Here, we did not exceed 5 bars

- A series of pressure gauges, gauges, filters, valves and stainless steel canalisation

1.7 Measuring equipment

An automated device measures both electrical resistivity and absolute thermopower. It includes a PC computer that manages the various stages of a measurement and saves the results. With an I.E.E.E. card, the computer uses a model 2000 Keithley scanning voltmeter of great input impedance. The scanner is connected to the reference junction of
the thermocouples (which is maintained at 0°C in a Dewar vessel containing a mixture of ice and water) by copper wire (as short as possible to reduce the parasitic potentials). The wires of thermocouple (W/WR26) of our cell are also connected to this junction. This makes it possible to read all the voltages necessary so as to find the ATP, the resistivity and the temperature of a liquid alloy. In addition, using a PCPIA card, the computer controls:

- The commutation between a measurement of resistivity and a measurement of A.T.P.,
- The choice to apply or not apply power on the auxiliary heater in order to create a temperature gradient $\Delta T(\pm 5^\circ C)$,
- Inversion of the current coming from the generator to eliminate the influence of the parasitic voltages during resistivity measurements.

To measure resistivity, the electrical current comes from a stabilized D.C. current generator. It passes through a standard resistor ($0.1 \Omega$) and is directly injected at the exit point of the cell on the tungsten electrodes. The scanning voltmeter, which has a high degree of accuracy, notes the e.m.f. at the terminals of the cell ($V_{24}$) and the standard resistor.

### 1.8 Preparation of alloys

The cadmium-antimony alloys are prepared from pure metal in the form of grains or of bars of great purity (99.999%). Before each experiment, metals are cleaned, dried then weighed accurately in order to obtain the exact composition of desired alloy before introducing it into the cell. The composition of the liquid alloy is expressed in its atomic concentration. The other industrial alloys based on tin (tin-copper, tin-silver, tin-antimony, tin-silver-copper, tin-lead), are provided in bar form with well-defined compositions. After an analysis of these industrial compositions by scattering electronic microscopy, lead and other traces of metals were found. These alloys are intended more for the industrial application of "lead-free solders". Once that cell is calibrated and the mercury is eliminated by vacuum distillation, the measurement process comprises these steps:

- Fixing the thermocouples.
Chapter 1. Principle and experimental techniques of measuring of the electronic transport properties

- Introduction the solid metal.
- Fixing the cell in the furnace so that the higher part is initially at a temperature lower than that of the big tank.
- Evacuating the cell as well as the remainder of canalisations, carrying out a leak test of the assembly and degassing the metal. Once the vacuum is reached, the furnace is started.
- Applying argon pressure once those metals are melted and outgassed. Metal rises in the small tank and the electrical contact is achieved.
Chapter 2

Theory

2.1 Introduction

In this chapter, we will briefly point out the electronic transport properties in a metal by examining it first from a macroscopic point of view using the thermodynamics of irreversible phenomena; then from a microscopic point of view using the Boltzmann equation. The resistivity and the thermoelectric power were expressed by using Ziman’s formalism developed by Ziman [3] within the framework of the perturbation theory for pure, simple amorphous and molten metals. This calculation was extended to noble and transition metals through an extended version of Ziman’s formula [4, 5, 6], where the square of the form factor is replaced by the square of the $t$ matrix determined from a muffin-tin potential. This second approach is considered better than that of the model potential for higher valence noble and transition metals. It was generalized to include binary alloys of simple metals by Faber and Ziman [7] as well as noble and transition metal alloys (Dreirach et al. [8]) by the extended Faber-Ziman formula. The theoretical calculation of the potentials and after that of electronic transport properties depends on the scattering mode. A metal in the liquid state is a disordered system where there is free electron gas or conduction electron gas (ion drowned in a cloud of nearly free electrons). Two types of scattering can be distinguished: weak scattering and strong scattering.
2.2 Macroscopic aspects: thermodynamic treatment of the thermoelectric effects

The transport phenomena of heat and electricity in the conductors give rise to various phenomena known as "thermoelectric effects". Indeed, these effects do not exist separately and are the consequences of two transport phenomena (heat and electricity) occurring simultaneously. The study of these phenomena by the thermodynamics of irreversible phenomena leads to two relations between the absolute thermoelectric power $S$, or Seebeck coefficient, the Thomson coefficient $h_T$ and the Peltier coefficient $\pi$. These relations are known as Kelvin relations. In this approach, where entropy plays a central part, the system is divided into subsystems. Each subsystem is supposed to be in local equilibrium. The intensive parameters thus depend on the co-ordinates of position (of under systems) and of the gradients $F^*$ of these parameters (generalized forces) which produce irreversible phenomena, which result in flux densities of current $\vec{J}$ or of heat (particles, heat, and so forth). If equilibrium is not far off, the generalized forces are weak, resulting in a linear relation between the densities of fluxes and forces.

$$\vec{J}_i = \sum_j L_{ij} \vec{F}_j$$ (2.2.1)

The $L_{ij}$ coefficients depend on the nature of the conductor and on the temperature. Onsager and Casimir gave the following phenomenological equations:

$$\vec{J}_n = eL_{11} \left( -\nabla V \right) T - L_{12} \frac{\nabla T}{T^2}$$ (2.2.2)

$$\vec{J}_Q = eL_{21} \left( -\nabla V \right) T - L_{22} \frac{\nabla T}{T^2}$$ (2.2.3)

with $L_{12} = L_{21}$

1. Electrical conductivity

With zero variation in temperature (isothermal system $\nabla T = 0$), the potential's gradient induces a density of the current. Electrical conductivity $\sigma$ is defined from the first equation:

$$\vec{J} = e\vec{J}_n = e^2 L_{11} \frac{1}{T} \left( -\nabla V \right)$$ (2.2.4)
The relation 2.2.4 is none other than the Ohm law \( \vec{J} = -\sigma \nabla \vec{V} = \sigma \vec{E} \). Isothermal electric conductivity is given by equation

\[
\sigma = e^2 \frac{L_{11}}{T} \quad (2.2.5)
\]

2. **Thermal conductivity**

A variation in temperature creates heat flux density. With zero density of current \( \vec{J} \) (open circuit), one determines thermal conductivity \( \lambda \). The Fourier Law expresses this by:

\[
\vec{J}_Q = -\lambda \nabla T \quad (2.2.6)
\]

From this expression and the two equations (eq. 2.2.3, 2.2.3) thermal conductivity is obtained, written as this formula:

\[
\lambda = \frac{1}{T^2} \left( L_{22} - \frac{L_{12}^2}{L_{11}} \right) \quad (2.2.7)
\]

3. **Absolute thermoelectric power "A.T.P." (Seebeck coefficient).**

Let us suppose now that an open circuit is created; the two wires constituting the thermoelectric circuit are open (this can be realized by connecting the two ends to a voltmeter of infinite impedance, so that the current in the circuit becomes zero). If the current is zero, there exist nevertheless a gradient of electrochemical potential at any point where the variation in temperature is different from zero. This gradient of electrochemical potential is related to the variation in temperature by the relation obtained while making the density of the current equal to zero (\( \vec{J}_n = 0 \)).

\[
S = \frac{1}{eT} \frac{L_{12}}{L_{11}} \quad (2.2.8)
\]

where \( S \) is Seebeck coefficient.

4. **Peltier coefficient**

The Peltier coefficient is the heat flow available per unit of an electrical current at a uniform temperature (\( \nabla T = 0 \)): \( \vec{J}_Q = \pi e \vec{J}_n \). From (eq. 2.2.3), there is the equation:

\[
\pi = \frac{1}{e} \frac{L_{21}}{L_{11}} \quad (2.2.9)
\]
By comparing formulas (eq. 2.2.8 et 2.2.9), and while taking into account the
equation in the Onsager symmetry of $L_{12} = L_{21}$, the first Kelvin equation is
deduced:

$$\pi = TS \quad (2.2.10)$$

This relation is a direct consequence of the Onsager equation. The four kinetic
coefficients associated with thermoelectric effects can be expressed using the three
independent dissipative coefficients $\sigma$ (electric conductivity), $\lambda$ (thermal conductivity
in open circuit), and $S$ (thermoelectric power), which can be obtained through experimentation.

5. **The Thomson coefficient**

To determine this coefficient, the quantity of heat emitted (absorbed) must be mea-
sured in a conductor in which a current passes through with a temperature gradient.
The power released per unit of volume is given by the equation:

$$\frac{dQ}{dt} = \nabla \cdot \lambda \nabla T - T \frac{\partial S}{\partial T} \nabla T \cdot \vec{J} + \frac{1}{\sigma} \vec{J}^2 \quad (2.2.11)$$

There are three contributions of heat transfer with the external medium. The first
term is the contribution of thermal conduction. The third term is the power dis-
sipated by the Joule effect, produced by an electrical current even if there is no
temperature gradient. The second term corresponds to the Thomson effect and
gives the power absorbed by the external medium per unit of time when an ele-
ctrical current of density $\vec{J}$ crosses the temperature gradient. The proportionality
factor is the Thomson coefficient, given by:

$$h_T = T \frac{\partial S}{\partial T} \quad (2.2.12)$$

This expression is the second Kelvin law.

The Kelvin relations show that it suffices to know one of the coefficients $h_T$, $\pi$ or $S$
according to the temperature (between 0 K and the temperature considered) to be
able to determine the two other coefficients. From an experimental point of view and
for an isolated element (pure metal or alloy), the only measurable thermoelectric
transport coefficient is the Thomson coefficient. On the other hand, only the Peltier
2.3 Electronic transport theory of metals: The microscopic aspect

After having examined the macroscopic form of the transport equations, we will make a connection between the experimental properties $h_T$, $S$ and $\lambda$ to the microscopic theory of electronic transport in liquid or amorphous metal and alloys.

2.3.1 The Boltzmann equation

The demonstrations and the development were carried out in the book by Smith et al. [9]. We will only present their results. The movement of the electrons is described by using a distribution function $f$ which, in theory, suffices for our purposes. It follows the generalized Boltzmann transport equation:

$$\frac{\partial f}{\partial t} + \frac{\mathbf{d}r}{dt} \cdot \nabla_r f + \frac{\mathbf{d}k}{dt} \cdot \nabla_k f = \left( \frac{\partial f}{\partial t} \right)_{coll}$$ (2.3.1)

$f$ represents the probability of occupation by the electronic states. The variation of the distribution as function of time results in two opposite effects in the displacement of electrons in metal. On one hand, the external macroscopic fields tend to draw the equilibrium system aside. On the other hand, the collisions between electrons and scattering sites bring the system to back equilibrium. When the external perturbations are removed, these collisions bring the system back to equilibrium and $f$ becomes the Fermi-Dirac distribution $f_0$:

$$f_0(E) = \frac{1}{1 + \exp \left( \frac{E - \mu}{k_B T} \right)}$$ (2.3.2)

The equation (eq. 2.3.1) is reduced to $\left( \frac{\partial f}{\partial t} \right)_{coll} = 0$. $\mu$ is the electrochemical potential in the presence of an external field, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. A system placed out of equilibrium, in absence of external forces, returns exponentially to its position of equilibrium at a speed proportional to the remaining difference $(f - f_0)$. The effects of the internal fields are
Chapter 2. Theory

represented by:
\[
\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \frac{f - f_0}{\tau} = \frac{g}{\tau} \tag{2.3.3}
\]

\(\tau\) is the relaxation time which characterizes the speed which equilibrium is restored to. In the particular case of the stationary regime, the development of the Boltzmann equation is quite detailed by Smith et al. [9]. It leads to the linearized Boltzmann equation:
\[
\left( \frac{\partial f_0}{\partial E} \right) \bar{v} \left[ \nabla \mu + \frac{E - \mu_e}{T_k} \nabla T \right] = -\frac{f - f_0}{\tau} \tag{2.3.4}
\]

where \(\mu_C\) is the chemical potential at equilibrium and \(e\) the electrochemical potential. The result is: \(\mu_e = \mu_C + eV\), with \(V\) as the applied external potential.

2.3.2 Calculation of the relaxation time

To be able to calculate the electronic transport properties for molten metals, it is necessary to determine the relaxation time at Fermi energy. The existence of a single relaxation time is justified when the collisions are elastic and when the conductor is isotropic. One expresses the collision term \(\left( \frac{\partial f}{\partial t} \right)_{\text{coll}}\) according to the transition probability density \(P(\vec{k}, \vec{k}')\) per unit of time so that an electron in the state \(\vec{k}\) is scattered in the initially empty state \(\vec{k}'\). The following equation is obtained:
\[
\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \frac{\Omega}{8\pi^3} \int P(\vec{k}, \vec{k}') \left[ f(\vec{r}, \vec{k}') - f(\vec{r}, \vec{k}) \right] d^3k' \tag{2.3.5}
\]

Smith et al. [9] and Makradi [10] show that the relaxation time can be expressed as such:
\[
\frac{1}{\tau} = \frac{k_F n \Omega}{2\pi \hbar^3} \int_0^1 8 \left\langle \left| \vec{k} + q \right| V \left| \vec{k} \right| \right\rangle^2 \left( \frac{q}{2k_F} \right)^3 d \left( \frac{q}{2k_F} \right) \tag{2.3.6}
\]

with \(V\) being the total scattering potential.

2.3.3 Transport coefficients

The density of current is the sum of the currents transported by all the electrons of speed \(\bar{v}\). It is written by:
\[
\vec{J} = \frac{e}{4\pi^3} \int \bar{v}.f(\vec{r}, \vec{k}, t) \, d^3k \tag{2.3.7}
\]
According to the equation 2.3.3, \( f = f_0 + g \). Let us consider that \( g(\vec{r}, \vec{k}) \) is a first order perturbation of the distribution function, induced by a weak electric field. The density of the current thus becomes:

\[
\vec{J} = \frac{e}{4\pi^3} \int \vec{v}.f_0 d^3k + \frac{e}{4\pi^3} \int \vec{v}.gd^3k
\]

(2.3.8)

\( f_0 \) is an even function of \( \vec{k} \) and \( g \) is an odd function of \( \vec{k} \). This cancels the first integral of the current’s density. We reach the following equation:

\[
\vec{J} = \frac{e}{4\pi^3} \int \vec{v}.gd^3k
\]

(2.3.9)

It is postulated that the temperature and the electrochemical potential are uniform. The integration of this equation for an isotropic medium (molten metals) leads to the expression of the electrical conductivity:

\[
\sigma = \frac{e^2}{12\pi^3\hbar} \int_{SDF} \tau.v.dS
\]

(2.3.10)

where \( \tau \) is the relaxation time defined in equation (eq. 2.3.6). Barnard [11] (eq. 3.57) pointed out that, after a complex calculation initially developed by Ziman, the Seebeck coefficient (absolute thermoelectric power) and thermal conductivity are written as:

\[
S = \frac{\pi^2 k_B^2 T}{3 e} \left( \frac{\partial\sigma(E)}{\partial E} \right)_E
\]

(2.3.11)

The Seebeck coefficient is proportional to the derivative in regards to the energy of the electric conductivity.

The thermal conductivity is written as:

\[
\lambda = \frac{(L_0 - S^2)T}{\rho} \approx \frac{L_0 T}{\rho}
\]

(2.3.12)

with \( L_0 = \frac{\pi^2 k_B^2}{3e^2} \).

The approximation in the formula of thermal conductivity is called the Wiedemann-Franz approximation. \( L_0 \) is the Sommerfeld value of the Lorentz number. This approximation is used when the values of the ATP are small or not known.
2.4 Liquid and amorphous states

As indicated previously, the electronic transport properties were explained by Ziman [3] for pure metals and by Faber Ziman [8] for metallic alloys. A liquid is defined by a grouping of ions where a local order of ions, drowned in a free electron conduction gas, is predominant. The Ziman formalism describes the scattering of an electron on an ionic core as an electron-ion potential interaction that takes into account screening by the other electrons. The screened form factor is introduced into a reciprocal space.

2.4.1 Relaxation time

The probability of transition per unit time so that an electron passes under the influence of a perturbation potential \( V(r) \), from a state \( k \) to a state \( k' \) (both on the Fermi surface), was expressed to the first order. The matrix of the potential responsible for the scattering is written as such:

\[
V(\vec{k}, \vec{k}') = \left\langle |\vec{k}'| V |\vec{k}\rangle \rightangle = \frac{1}{\Omega} \int_{\Omega} \exp\left( -i(\vec{k}' - \vec{k}) \cdot \vec{r} \right) V(r) d^3 \vec{r} \quad (2.4.1)
\]

It should be noted that the potential is important inside the ions and cannot be treated strictly as a perturbation. Free electron approximation finds its validity through the introduction of the pseudopotential concept. In the following paragraph, it will be shown that the true potential \( V \) can be replaced by a weak pseudopotential \( W \) with the same "scattering ability", in the vicinity of the ions, i.e. having the same spectrum of energies. The trade-off is that the pseudopotential becomes a function of the energy \( E \) of the electrons.

The (pseudo) potential can be broken down into a sum of individual ionic potentials centred on the ions at \( R_j \):

\[
W(r) = \sum_j w\left( \vec{r}, R_j \right) \quad (2.4.2)
\]

The following regrouping is carried out (assumption of factorization):

\[
\left\langle \vec{k} + \vec{q} |W| \vec{k}\right\rangle = \left( \frac{1}{N} \sum_j \exp(-i\vec{q}\vec{R}_j) \right) \frac{N}{\Omega} \int \exp(-i\vec{q}\vec{r}) w(r) d^3 \vec{r} \quad (2.4.3)
\]
in order to put the matrix element in the product form of two terms:

\[
\langle \vec{k} + \vec{q} | W | \vec{k} \rangle = S(q) w(q, E) \quad (2.4.4)
\]

with \( S(q) = \frac{1}{N} \sum_j \exp(-i\vec{q}\vec{R}_j) \) \hspace{1cm} (2.4.5)

\[
w(q, E) = \frac{N}{\Omega} \int \exp(-i\vec{q}\vec{r}) d^3\vec{r} \quad (2.4.6)
\]

we define \( w(q, E) \) as the "form factor"; it is independent of the individual position of the ions and characterizes the "scattering power" of electrons by the screened ions. \( S(q) \) is the structure factor; it depends only on the position of the ions. The interference function \( a(q) \) of a liquid can be written according to the structure factor:

\[
a(q) = N |S(q)|^2
\]

The relaxation time is written as:

\[
\frac{1}{\tau} = \frac{k_F m \Omega}{2\pi\hbar^3 N} \int_0^1 a(q) |w(q, E)|^2 \left( \frac{q}{2k_F} \right)^3 d \left( \frac{q}{2k_F} \right) \quad (2.4.7)
\]

2.4.2 Resistivity and absolute thermoelectric power "ATP"

This formalism is valid for molten and amorphous metallic alloys.

**Resistivity and absolute thermoelectric power of pure metals**

1. **Resistivity**: Electrical resistivity is connected to the relaxation time \( \tau_{k_F} \) at \( k_F \) by:

\[
\rho = \frac{m}{ne^2 \tau_{k_F}} = \frac{3\pi^2 m}{e^2 k_F^3 \tau_{k_F}} \quad (2.4.8)
\]

The resistivity \( \rho \) expressed by Ziman’s formalism, is written as:

\[
\rho = \frac{3\pi m^2 \Omega}{\hbar^3 e^2 k_F^2 N} \int_0^1 a(q) |w(q)|^2 \left( \frac{q}{2k_F} \right)^3 d \left( \frac{q}{2k_F} \right) \quad (2.4.9)
\]

or

\[
\rho = \frac{3\pi^2 m^2 \Omega q}{4e^2 \hbar^3 k_F^6} \int_0^{2k_F} a(q) w^2(q, k_F) q^3 dq \quad (2.4.10)
\]
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2. **A.T.P.**: The thermoelectric power is given according to the derivative of the resistivity to regard to energy by:

\[
S = \frac{\pi^2 k_B^2 T_k}{3|e| E_F} \chi
\]  

(2.4.11)

with \( \chi = -E_F \left( \frac{\partial \ln \rho(E)}{\partial E} \right)_{E_F} \)  

(2.4.12)

\( k_B \) is the Boltzmann constant, \( \chi \) is called the "thermoelectric parameter", which can be written in as:

\[
\chi = 3 - 2\alpha - \frac{\beta}{2}
\]  

(2.4.13)

where

\[
\alpha = \frac{w^2(2k_F, k)_{k=k_F} a(2k_F)}{(2k_F)^2} \int_0^{2k_F} \frac{4w^2(q, k_F)a(q)q^3dq}{\langle w^2(q, k_F)a(q) \rangle}
\]

and

\[
\beta = \frac{k_F \int_0^{2k_F} \frac{\partial w^2(q, k)}{\partial k}}{\int_0^{2k_F} \frac{4w^2(q, k_F)a(q)q^3dq}{\langle w^2(q, k_F)a(q) \rangle}}
\]

Term 3 comes from the free electrons (prefactor), term \( 2\alpha \) corresponds to the variation of the higher limit of integration of the resistivity, and finally \( \beta \) stands for energy dependence (coming from the form factor), which is a very difficult parameter to calculate for pure metals as well as for alloys. Thus, many authors incorrectly regard it as equal to zero.

**Extension to binary alloys**

The calculation of resistivity and thermoelectric power was extended by Faber [12] to include binary alloys. The general form of the resistivity and of the absolute thermoelectric power does not change with the proviso of taking several parameters into account:

- the atomic volume of alloy to correct the form factor,
- the effective number of conduction electrons,
- the modification of the Fermi wave vector (in particular within the limit of integration),
2.5 The case of semi-metals

- the modification of the static dielectric function,

- the modification of model potential parameters according to the energy of the electrons in the alloys.

The term \(a(q)w^2(q, k_F)\) in the resistivity formula (eq. 2.4.10) must be replaced by:

\[
c_1 w_1^2 [1 - c_1 + c_1 a_{11}(q)] + c_2 w_2^2 [1 - c_2 + c_2 a_{22}(q)] + 2c_1 c_2 w_1 w_2 [a_{12}(q) - 1]
\]  

(2.4.14)

c_i (i = 1, 2 for binary alloys) are concentrations of the two elements, \(a_{ij}\) (i and j = 1, 2 for binary alloys) are the partial structures factors of Faber-Ziman [12] while \(w_i\) are the form factors of elements i and j in the alloy.

The number of alloy conduction electrons will be taken as the average weight multiplied by the concentration of conduction electrons of the two elements \(N_{C_{moy}} = c_1 N_{c1} + c_2 N_{c2}\). The atomic volume of the alloy is the average weight multiplied by the atomic concentrations of the pure elements: \(\Omega_{moy} = c_1 \Omega_1 + c_2 \Omega_2\). It should be noted that the atomic volumes and not the densities are interpolated.

The presence of \(d\) levels in the conduction band for noble and transition metals greatly disturbs the free electron scheme. To better describe the electronic properties of these metals (extended Faber-Ziman formalism), Evans [4] and Dreirach et al. [8], replaced the form factor \(w_i\) with the \(t\) matrices \(t_i\) (\(t_i\) is a complex number).

\[
a(q)t^2(q) = c_1 t_1 t_1^* [1 - c_1 + c_1 a_{11}(q)] + c_2 t_2 t_2^* [1 - c_2 + c_2 a_{22}(q)] + c_1 c_2 (t_1 t_2^* + t_2 t_1^*) [a_{12}(q) - 1]
\]  

(2.4.15)

This formalism no longer needs the perturbation theory.

2.5 The case of semi-metals

2.5.1 Introduction

The Ziman theory is valid when the density of states at Fermi level is a free electron one. In semiconductors, the density of states can be zero (gap). There are also intermediate situations (pseudogaps). Mott et al. [13] introduced a corrective factor to the Ziman theory to calculate electronic transport properties in the case of pseudogap.
2.5.2 Mott’s model: transition semiconductor-metals?

Specifically, when the number of valence electrons and the atomic mass are high, a pseudogap appears, as demonstrated by Indelkofer. Electric conductivity and the ATP are expressed through a corrected Ziman theory. For a system from which the density of state at the Fermi level is very different from that of the free electrons, Mott proposes the relation:

\[
\sigma = \frac{e^2 L S_F}{12\pi^4 \hbar^2} g^2 = \frac{2\pi e^2 \hbar^3 L}{m^*} \langle n(E_F) \rangle^2 = \sigma_Z g^2
\]

(2.5.1)

\(S_F\) is the Fermi surface, \(\sigma_Z\) is the "Ziman conductivity", \(\sigma\) is the corrected conductivity and \(L\) is the mean free path, comparable to the average inter-atomic distance \((L \approx a)\). Mott identifies the corrective factor \(g\) to the ratio:

\[
g = \frac{n(E_F)}{[n(E_F)_{\text{electronslibres}}]}
\]

(2.5.2)

The absolute thermoelectric power is written by these authors [13] as:

\[
S = -\frac{\pi^2 k_B^2}{3|e|} \left\{ \frac{d\ln \sigma(E)}{dE} \right\}_{E=E_F}
\]

(2.5.3)

The limit between metal and non-metal conduction mechanisms is given for \(g \approx 0.3\), using the Anderson model [14, 15] for the localization. This model is also applied to the liquid alloys whose electrical conductivity \(\sigma\) lies between \(500 \leq \sigma \leq 5000 \, \Omega^{-1}.cm^{-1}\). These liquid alloys often have a temperature coefficient of \(d\sigma/dT > 0\) and a positive ATP \((S > 0)\). This category of alloy is often referred as poor molten metals or semi-metal liquids.

2.6 Modelling of the potentials in metals

2.6.1 Different scattering modes

a- Weak scattering mode or metallic mode

The mean free path is definitely higher than the average inter-atomic distance. The Ziman model of the nearly free electrons [3] is applicable here. The core electrons are separated from the conduction electrons, which are only responsible for the properties of metals. The conduction electrons are associated with wave functions close to those of plane
waves. Insofar as these electrons are slightly related to the cores, their density of states is of the type "free electrons" \( n(E) \approx E^{1/2} \). Electron-ion scattering is described within the framework of the Born approximation by using the concept of pseudopotential. Ziman’s theory \([3]\) effectively describes the liquid conductors and the amorphous metals whose electrical resistivity does not exceed 100 \( \mu\Omega.cm \). However, this theory is not well adapted to noble metals, transition metals or certain semi-metals. In this case, the extended Ziman formalism can be used by replacing the square of the form factor by the square of the \( t \) matrix expressed as phase shifts.

b- Strong scattering mode

According to the free electron theory, when the mean free path of the electrons is lower than or equal to the average inter-atomic distance, electron-ion interaction can no longer be considered in the perturbation theory. This can be found at the interface between metal and non-metal behaviour, where the resistivity lies between 200 et 3000 \( \mu\Omega.cm \). A pseudogap in the density of states appears. The parameter \( g = \frac{N(E_F)}{N_{\text{electrons libre}}(E_F)} \) is introduced at Fermi energy. The resistivity is proportional to \( 1/g^2 \). The sign of the thermoelectric power can be changed in reference to the concentration when the Fermi level passes through the minimum state density. The agreement between the Ziman model in the case of "pseudogap" remains qualitatively satisfying both for the resistivity and the ATP as will be demonstrated. As soon as one moves away from the metallic behaviour, there is no longer a general theory which allows a quantitative interpretation.

2.6.2 Concept of pseudopotential

The introduction of an (unscreened) electron-ion interaction is characterized by a Coulomb potential coming from the core. This potential is very deep inside the core. Thus the assumption of a perturbation potential (treatment in perturbation theory) is not valid. The problem can nevertheless be solved through the concept of pseudopotential. The adiabatic assumption is used, which makes it possible to separate the movement of the conduction electrons from that of the ions, presumably motionless. In this case, one defines the total Hamiltonian of homogeneous metal:

\[
H = H_e + T_i + V_{ii} \tag{2.6.1}
\]
Chapter 2. Theory

Where $H_e$ is the Hamiltonian of all the conduction electrons, $T_i$ and $V_{ii}$ are respectively the kinetic and potential energy of the ions.

$$H_e = T + V_0(r) + V_e$$  \hspace{1cm} (2.6.2)

$T$ is the kinetic energy of an electron of conduction, $V_0(r) = \sum_i v_0(\vec{r} - \vec{R}_i)$ (sum of the ionic sites) is the interaction potential between the conduction electrons and the ions; $v_0$ represents the potential of a single ion. $V_e$ represents the interactions with the other conduction electrons. The states of the conduction electrons $|\Psi_k\rangle$, are solutions of the equation:

$$H_e |\Psi_k\rangle = (T + V_0(r) + V_e) |\Psi_k\rangle = E_k |\Psi_k\rangle$$  \hspace{1cm} (2.6.3)

They have behaviour close to that of a plane wave out of the ionic core and have a strong oscillating wave function inside the core.

The pseudopotential theory suggests replacing the deep potential $V_0(r)$ of the ion core with another potential that is not very deep $W_0(r)$ and which has the same "scattering ability" on the electrons. The advantage of this new potential is that the perturbation theory can then be used. Having the same "scattering ability" results in an electronic spectrum of energy $E_k$, which is preserved and should be identical for $V_0$ and $W_0$. The wave function $\Psi_k(r)$ is replaced by a pseudo wave function $\varphi_k(r)$, which has the advantage of being softer inside the ionic core. Under these conditions, the Schrödinger equation for the pseudopotential is written as:

$$(T + W_0(r) + V_e) |\varphi_k\rangle = E_k |\varphi_k\rangle$$  \hspace{1cm} (2.6.4)

For the moment there is no approximation, but calculations remain very complex. The pseudopotentials are then replaced by "model potentials". Many authors have adopted these ideas to develop more or less exact models of potential. Among the models to take note are those of Heine, Abarenkov and Animalu [16, 17], and finally that of Ashcroft [18].
2.7 Models of Potential

2.7.1 The Heine and Abarenkov (HA) potential

The processes of building the model potentials were introduced by Heine and Abarenkov (fig. 2.7.1). It starts with constructing the model potential of the free isolated ion (an ion without its conduction electrons cloud). The ion is then placed in the condensed matter by adding gas from the conduction electrons. The interaction between the ions and conduction electrons gas is taken into account, as well as the interactions of these electrons with those of the core. That leads to a shift in energy (core shift). Lastly, the screening is taken into account. Heine and Abarenkov supposed that inside a sphere of radius \( R_M \), the potential is constant for each value of angular momentum \( l \). The potential is purely Coulombic (local term) outside the sphere of radius \( R_M \). The model of potential of H-A for the free ion is expressed by two terms:

**A local coulombic term:**

\[
w_L(r) = \begin{cases} 
0 & \text{si } r < R_M \\
-Z/r & \text{si } r > R_M 
\end{cases}
\]  
\[ (2.7.1) \]

\( Z \) is the number of conduction electrons.

**A non-local term:**

\[
w_{NL}(r) = \begin{cases} 
-Z \sum_{l=0}^{\infty} A_l(E)P_l & \text{si } r < R_M \\
0 & \text{si } r > R_M 
\end{cases}
\]  
\[ (2.7.2) \]

\( P_l \) is the operator projector which gives the component corresponding to the quantum number \( l \) in space of the spherical harmonics \( Y_{l}^{m} \). Parameters \( A_l \) are the function of the electrons’ energy. \( A_l \) must be adjusted to spectroscopic data in order to preserve the energy spectrum. The potential of H-A contains four parameters. It is known as a "first principle" potential.

2.7.2 The Ashcroft potential

Ashcroft simplified the preceding model by H-A. The Ashcroft potential (fig. 2.7.2) is a local potential (the parameters are independent of \( l \)) and has only one parameter: core
radius $R_C$. In this model, the interaction is purely Coulombic outside, the sphere of radius $R_C$; is null inside. The single parameter $R_C$ of this local model is determined by its adjustment on an experimental macroscopic property (resistivity, thermoelectric power, phonon spectrum, Fermi surface of pure metals) often measured experimentally. The Ashcroft potential is known as a "phenomenological" model potential.

## 2.8 Screening

In the various models presented, the interactions between conduction electrons were not taken into account. The expression of the unscreened form factor must be modified to introduce this new contribution. In the theory of linear screening, the screened form
factor corresponds to a local potential obtained simply by dividing the bare form factor by the dielectric function $\epsilon(q)$:

$$w(q) = \frac{w_0(q)}{\epsilon(q)}$$  \hspace{1cm} (2.8.1)

This expression can be used with the Ashcroft potential. The expression is much more complex when we have to deal with non-local pseudopotentials. This will not be developed in this research. The simplest screening theory was developed by Thomas-Fermi and makes it possible to write the screened potential of the ion $w(r)$ in real space from the bare potential of the ion $w_0(r) = -\frac{Ze^2}{r}$:

$$w(r) = w_0(r) \exp(-qr)$$  \hspace{1cm} (2.8.2)

The Thomas-Fermi dielectric function is defined by the Fourier transform of $w(r)$:

$$\epsilon_{TF}(q) = 1 + \frac{q^2_s}{q^2}$$  \hspace{1cm} (2.8.3)

Another dielectric function was described by Hartree as an equation:

$$\epsilon_H(q) = 1 + \frac{2me^2k_F}{\pi\hbar^2q^2} \left( 1 + \frac{4k_F^2 - q^2}{4qk_F^2} \ln \left( \left| \frac{2k_F + q}{2k_F - q} \right| \right) \right)$$  \hspace{1cm} (2.8.4)

The expression between brackets is from Lindhardt. The exchange and the correlation are introduced into the static dielectric function by means of the $G(q)$ function:

$$\epsilon(q) = [1 + G(q)] [\epsilon_H(q) - 1] + 1$$  \hspace{1cm} (2.8.5)

In our later calculations, the Vashishta-Singwi [19] expression, considered as one of the most accurate, was used:

$$G(q) = A \left( 1 - \exp \left( -\frac{Bq^2}{k_F^2} \right) \right)$$  \hspace{1cm} (2.8.6)

A and B are tabulated values.

### 2.9 The "t" matrix

The pseudopotential method is valid only in the case of a weak perturbation due to the Born approximation. This led to an expression of the transition probabilities based on
the golden rule of Fermi, which is only an approximation.

For certain elements including d and f electrons, such as transition, rare earth and noble metals, the pseudopotential method appeared to be inadequate. Evans [4] and Dreirach et al. [8], present an extended version of the Ziman formula. They replaced the scattering of an electron with a screened pseudopotential within the framework of the perturbation theory, by the real potential using the "\( t \)" matrix scattering formalism.

\[
t(q, k) = -\frac{2\pi \hbar^3}{m\sqrt{2mE}} \frac{N}{\Omega} \sum_l (2l+1) \sin(\eta_l(E)) e^{i\eta_l(E)} P_l(\cos(\theta)) \tag{2.9.1}
\]

\( \eta_l(E) \): are the phase shift functions of energy. The phase shifts characterize the behaviour of the scattered partial waves compared to the incident partial waves. They are calculated by the numerical integration of the Schrödinger equation with a muffin-tin potential, constructed following Mukhopadhyay et al.’s method [20] for the liquids.

2.10 Calculation of phase shifts

2.10.1 Construction of the muffin-tin potential

a- The muffin-tin potential

To be able to calculate phase shifts, it is necessary to know the scattering potential. Two approaches were developed, one by Dreirach et al. [21] (Quasi Crystalline Approximation) and the other by Mukhopadhyay et al. [20]. The latter was developed from the theory of Dreirach et al. and adapted to the disorder of molten metals. A sphere of radius \( R_{MT} \), is known as a muffin-tin radius. This radius is generally given as half of the distance between the origin and the first peak of the pair correlation function \( g(r) \) (half of the distance to the first neighbours).

Beyond the radius \( R_{MT} \) (outside of the sphere), the potential \( V(r) = V_0 \) is constant. \( V_0 \) is supposed to be the average of the \( V(r) \) potential between the muffin-tin radius RMT and the Wigner-Seitz radius \( R_{WS} \) (\( R_{WS} \) radius of a sphere specific to the molten metal, with volume \( \Omega_0 \), which is the atomic volume of the pure element):

\[
V_0 = \frac{3}{R_{WS}^3 - R_{MT}^3} \int_{R_{MT}}^{R_{WS}} V(r) r^2 dr \tag{2.10.1}
\]
On the other hand, inside the sphere, the two Coulomb contributions and the exchange contribution constitute the potential and are treated separately. The Coulomb contribution (the Coulomb attraction of the core with its neighbours) is that determined by the superposition of the Coulomb term of the atomic potential \( v^c_\alpha(r) \), and is given by:

\[
V^c(r) = v^c_\alpha(r) + \sum_i v^c_\alpha(r - R_i)
\]  \hspace{1cm} (2.10.2)

The summation is made on all the ionic sites. The contribution of the exchange potential, calculated within the framework of the Slater approximation [22], can be written as:

\[
V^{\text{exch}}(r) = \alpha V^{\text{Slater}}_{\text{exch}} = -3\alpha \left[ \frac{3}{8\pi} \rho(r) \right]
\]  \hspace{1cm} (2.10.3)

where \( \alpha = 1 \) following the Slater approach (for the purpose of our calculations) or \( \alpha = 2/3 \) following that of Kohn-Sham [23]. Other exchange-correlation approximations, based on the density functional theory (DFT) were used [24]. This calculation was developed by Makradi et al. [6] and was adapted to molten metals. Von Barth’s approximation of the local density (LDA) [25], which is very simple, is often used. This approximation consists of the assumption that the exchange and correlation energy \( E_{XC} \) is a local functional of the density, i.e. it depends only on the density at the point \( r \) [26, 27].

The purpose of GGA (Generalized Gradient Approximation) approximation is to correct deficiencies of the local functional calculus by including the gradient of the density in the exchange-correlation functional calculus (PW91). GGA, is used by Perdew and Wang [28]. Perdew and coll. [29] (PBE) proposed an improvement of the GGA model. \( \rho \) is the density of charge given as:

\[
\rho(r) = \rho_0(r) + \sum_i \rho_0(r - R_i)
\]  \hspace{1cm} (2.10.4)

The summation is carried out on the ionic sites. In a crystal, these sites are distributed periodically. In the liquid state, a metal preserves a local order described by the pair correlation function \( g(r) \) and which is taken into account by Mukhopadhyay.
Chapter 2. Theory

b- Mukhopadhyay approach

The method (quasi crystalline approximation) of constructing the muffin-tin potential was published by Dreirach et al. [21] to calculate the Coulomb potential and the density of charge in dense matter. This method was adapted by Mukhopadhyay [20] for disordered matter. In a molten metal, if a fixed atom at the origin is taken into account, another atom will be in an element of volume $d^3R$ at the distance $R$ with a probability $P(R)d^3R$ given as:

$$P(R)d^3R = \frac{4\pi R^2}{\Omega_0}g(R)dR$$ \hspace{1cm} (2.10.5)

The Coulombic contribution to the total potential (2.10.2) becomes:

$$V_c(r) = v_c^a(r) + \frac{1}{\Omega_0} \int_0^\infty v_c^a(r-R)g(R)dR$$ \hspace{1cm} (2.10.6)

In the same way, the density of charges is written:

$$\rho(r) = \rho_0(r) + \frac{1}{\Omega_0} \int_0^\infty \rho_0(r-R)g(R)dR$$ \hspace{1cm} (2.10.7)

2.10.2 Calculation of Fermi energy

Fermi energy plays a crucial role in calculating the electronic transport properties of molten metals. According to the Dreirach approach (1971) [8], Fermi energy is calculated from the bottom of the energy band $E_B$ (see fig. 2.10.1):

$$E_F = E_B + \frac{\hbar^2 k^2}{2m^*}$$ \hspace{1cm} (2.10.8)

Where $m^*$ is the effective mass deduced from the band structure analysis in the solid. This energy EB is often taken arbitrarily equal to 0; we calculated it in relation to muffin-tin zero energy, following the procedure suggested by Ziman [30]. Another approach in determining Fermi energy was developed by Esposito et al. [5] (figure 2.10.1). It consists of having $E_B=0$ and the effective mass equal to 1. But Esposito uses Lloyd’s method to calculate the real density of states, which introduces the concept of effective charge $N_C$. 

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2.11 Structure

The structure of a system is defined by the positions of the atoms forming this system. The position of the atoms results mainly from the influence of the interatomic forces which generate the order, and from the thermal movements which generate the disorder in the matter. At a low temperature, the interatomic forces prevail. The matter is completely ordered as it is for a crystal. On the other hand, at a very high temperature, thermal agitation creates total atomic disorder. The matter is in a gaseous state. In the case of liquids, the matter is in an intermediate state. The temperatures are such that the order of the ideal crystals is destroyed at a long distance; while at a short distance, a short range order persists. This situation is accurately described by the radial distribution function.

Figure 2.10.1: Muffin-tin potential, Dreirach and Esposito approaches to determine Fermi energy relative to the muffin tin zero potential
2.11.1 Radial distribution function and pair correlation function

The local order characteristic of liquids is generally described using the pair correlation function \( g(r) \). It is proportional to the probability of finding an atom at a distance \( R \) of an origin atom. More precisely, it describes the fluctuations of atomic density \( \rho(r) \), compared to the average atomic density \( \rho_0 = \frac{N}{V} \) of a liquid:

\[
g(r) = \frac{\rho(r)}{\rho_0}
\]

When \( g(r) \) is equal to 1, the fluid is in complete disorder (gas). For the crystals, peaks in all fields of distance are observed. In the case of the liquids, \( g(r) \) is represented by oscillations around the unit with a rapidly deadened amplitude when \( r \) becomes large. There is thus a first peak corresponding to the distance between the first neighbours; then a second less intense and broader peak, which represents the second neighbours; and so on. The pair correlation function has a value limit of 1 when \( r \) becomes large. At these distances, the positions are no longer correlated. It is zero at very small value of \( r \), which is explained by the non-interpenetration of the atoms.

The interference function \( a(q) \), characterizes the position of the atoms in a reciprocal space. It can be measured by X-ray, neutron or electron scattering. The function \( a(q) \) can be related to the pair correlation function \( g(r) \) by:

\[
a(q) = 1 + \rho_0 \int_0^\infty (g(r) - 1) 4\pi r^2 \frac{\sin(qr)}{qr} dr
\]

2.11.2 Hard sphere model

The structures of pure molten metals and binary alloys were studied theoretically by using the very simple hard sphere model. For pure metals, Ashcroft and Lekner [31] calculated the structure factor using the Percus-Yevick equation [32, 33]. In the case of binary alloys, the partial structure factors were determined by Ashcroft and Langreth [34], Enderby and North [35]. The analytic solutions were based on the exact solutions of the Percus-Yevick
equation obtained by Lebowitz [36].

\[ v(r) = \begin{cases} \infty & \text{si } r > \sigma \\ 0 & \text{si } r < \sigma \end{cases} \]  \quad (2.11.3)

\( \sigma \) is the hard spheres diameter. We deduce \( \sigma \) from experimental data such as the density of metal compiled by Crawley [37] and from the packing fraction given by Waseda [38].
Chapter 3

Electronic transport properties of Cd-Sb alloys

Scientific problems

The Cd-Sb alloy is a semiconductor in the solid state. The boiling point of cadmium is 760°C. The melting point of antimony is 630°C while that of cadmium is 320°C. We wish to study these alloys up to a temperature of 850°C. At high temperatures, it is difficult to make measurements because of the cadmium vapour "bubbles" formed in the liquid, which modify the "cell constant", and of the cadmium evaporation and its condensation in colder zones (modification of the composition). In its liquid state, Cd-Sb is rather metallic, although at low temperature, it maintains a semiconductor character similar to that of the solid [1]. Indeed, at low temperatures, we observe a decrease in resistivity when the temperature increases, which is characteristic of semiconductors. It is worth noting the transition between this semiconductor characteristic at low temperatures (an exponential like decrease of resistivity vs temperature) and a metallic characteristic at high temperatures (a nearly linear increase of resistivity vs temperature). The resistivity as a function of composition presents a maximum. At a low temperature, it is found around the $Cd_{48}Sb_{52}$ composition, whereas at a high temperature, the same effect was observed for an alloy close to $Cd_{40}Sb_{60}$.

Miller, Paces and Komarek [39] noted an influence of the history of a melt on the electrical resistivity of liquid alloys. They attributed this phenomenon to the presence of aggregates.
(clusters), which may persist in the liquid state. The purpose of this chapter is to check this behaviour and the corresponding assumptions. We will briefly present our results for pure antimony and will compare them to the calculations. We will reproduce the publication corresponding to the study of the history of a molten alloy measured by carrying out increasing cycles of temperature. We will extend the existing results to large temperatures ranges and to other concentrations. Finally, we will develop the calculations of electronic transport properties and will try to interpret the differences between the experimental and calculated results.
I: Pure antimony
3.1 Introduction

In the first part of this chapter, we will present the experimental study of pure antimony, which is of particular interest in the field of physics. We were interested in antimony because it is present in several alloys that our laboratory studied. Antimony is a semi-metal (a "bad" metal), and has a particular density of states. The electronic transport properties of pure antimony were first interpreted using the Ziman formalism described in chapter 2. In theory, the ATP (Absolute Thermoelectric Power or Thermopower) of pentavalent metals should be negative. We found a positive experimental ATP like Bath [40, 41] and Benazzi [42]. To explain this, we remember that antimony is a semi-metal with a pseudogap between the two s and p bands [43]. Consequently, it is necessary to correct our theoretical ATP and resistivity results obtained from the Ziman formalism. We used a corrective factor $g^2$ introduced by Mott [13] that we made energy dependent. In this chapter, we will compare our experimental results with those of Gasser [1] and Benazzi [42], and the calculated transport properties with a corrected Ziman formalism. We believe that this is the first time the Ziman formula has been corrected by the factor $g$ and its derivative in regards to energy to interpret the ATP.

3.2 Experimental results

The resistivity and the absolute thermoelectric power of antimony were measured simultaneously from 650 to 1020°C. These measurements were carried out in a fused silica cell described in the first chapter.

3.2.1 Electrical resistivity of antimony

Figure 3.2.1 compares our results of electrical resistivity to those of other authors. Our measurements coincide well with those obtained by Gasser [1]. In comparing the results of Benazzi [42] and Roll and Motz [42], our resistivity curve is located below their measurements between 700 and 850°C, but the difference decreases above 850°C. However, the variation never exceeds 2%. Electrical resistivity of pure antimony shows a nearly parabolic behaviour without minimum. The resistivity values were fitted by a second order polynomial: $\rho_{Sb}(T) = 122,91524 - 0,04152 \cdot T + 4,25612E^{-5} \cdot T^2$
Figure 3.2.1: Electrical resistivity of liquid antimony as a function of temperature.

Figure 3.2.2: Absolute thermoelectric power of liquid antimony as a function of temperature.
3.2.2 Thermoelectric power of antimony

The experimental values of the thermoelectric power of pure antimony are slightly positive, whereas the free electron theory gives negative values. We deferred to figure 3.2.2 for the results of our ATP measurements of liquid antimony compared to those obtained by Benazzi [42] and Bath [40]. Our values frame those of Benazzi and Bath. Under specific measurement conditions (K2000 Voltmeter of resolution 0.1 $\mu V$), the accuracy obtained is estimated at $\pm 0.5 \mu V.K^{-1}$ for the systematic error (calibration of the couple) and at 0.2 $\mu V.K^{-1}$ (accidental error: dispersion of the results).

3.3 Theoretical interpretation

3.3.1 Calculation with pseudopotential: bibliographical study

We wondered if the Ziman theory developed for metals applies to antimony, which is a semi-metal. Antimony has an experimental resistivity about $117 \mu \Omega.cm$ at 800°C and a positive ATP about $+0.3 \mu V/K$, whereas calculations by various methods using the pseudopotential formalism underestimate the resistivity and give a negative ATP, which is contrary to the experiment. Before developing our new approach, we will present in table 3.1 the results of the various "traditional" calculations carried out on this metal. The resistivity and the ATP were calculated as a function of temperature with various pseudopotential models. We will quote three types of calculation [44] which use:

- The Heine-Abarenkov-Animalu potential (S.M.P.) with a hard spheres interference function and a valence $Z=5$.

- The Shaw-Hallers potential with 5 valence electrons.

- Lastly, the t matrix using the parameters from the Waseda table (8-6, page 207) [38] (without taking into account the energy dependence for the ATP calculation).

From these results (tab. 3.1), it was noted that the resistivity was systematically under-valued when using the model potentials. With the t matrix formalism and the Waseda parameters, a value of calculated resistivity of $107 \mu \Omega.cm$ is obtained, which is close to the experimental value $117 \mu \Omega.cm$. The Waseda bottom of the free band is highly negative, with a value of $E_B=-0.301$ Ry. Deferring to the same table, the absolute thermoelectric
### Table 3.1: Experimental and calculated resistivity and ATP’s calculated with different theoretical models

<table>
<thead>
<tr>
<th>Models</th>
<th>Experimental resistivity and ATP’s</th>
<th>calculated resistivity and ATP’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard sphere/800°C</td>
<td>S.M.P.</td>
<td>Shaw-Hallers</td>
</tr>
<tr>
<td>Resistivity ($\mu\Omega.cm$)</td>
<td>117</td>
<td>68.19</td>
</tr>
<tr>
<td>A.T.P. ($\mu V/K$)</td>
<td>+0.3</td>
<td>-4.46</td>
</tr>
</tbody>
</table>

Powers were calculated from the same models as those used to calculate the resistivity (S.M.P. and Shaw-Hallers model potentials, t matrix with phase shifts of Waseda) at 800°C. We noted that the ATP values calculated from phase shifts were always positive with a bottom of free band $EB=-0.301$ Ry. Nevertheless, Waseda did not tabulate the $d\eta/dE$ coefficients. Due to this, the ATP energy dependent term has been omitted in the phase shift description, thus the calculation is false. The ATP values obtained from the model potentials were negative, contrary to the positive experimental values.

#### 3.3.2 Our approach

In this work, we used the program developed by Makradi (LDA), which is based on the extended Ziman formula using phase shifts. This calculation includes the energy dependent term which was absent in preceding calculation. The position of Fermi energy in regards to the muffin-tin potential plays a very important role in electronic transport properties. The key point is the position of the bottom of the conduction band compared to the muffin-tin zero potential and the shape of the density of states. In our new calculations, we used three approaches.

- Firstly, the Dreirach et al. approach [45] starts with a free electron density of states in which the band bottom is shifted by the energy $E_B$ from muffin-tin zero.

- Secondly, the Esposito et al. [5] approach supposes that the band bottom is at the same level as the muffin-tin zero potential; consequently the energy $E_B = 0$. However, Esposito et al. [5] take into account the true shape of the density of states by using Lloyd’s formula to calculate the integrated density of states (2.10.1).
With Esposito’s approach, we were able to calculate the resistivity according to energy (fig. 3.3.1). With 5 conduction electrons, a Fermi energy of 0.6964 Ry is obtained, which corresponds to a resistivity of 78.63 µΩ.cm. At this energy, the resistivity is a decreasing function of energy. Consequently the ATP, which is the logarithmic derivative of the resistivity relative to the energy, is negative. The resistivity and ATP values are very far from the experiment. However, Hafner [43] calculated the liquid antimony density of states and showed that the conduction band 3.3.2 includes a gap between the s and p bands. If this calculation represents physical reality, it would be advisable to take three valence electrons instead of five. This brings us to Fermi energy of 0.4523 Ry, which corresponds to a resistivity of 219.34 µΩ.cm and a negative ATP about -8.37 µV/K. The resistivity is much higher than the experimental one and the ATP still shows an erroneous sign and a numerical value very far from the experiment.

- We were also interested in the Dreirach approach described by Waseda. Calculations were carried out for \( E_B = -0.301 \text{ Ry} \). To understand the position effect of the
bottom of the energy band $E_B$ on the electronic transport properties, we deferred to figure 3.3.3 for resistivity as a function of energy for different values of $E_B$, considered here as a parameter, and to the corresponding ATP according to energy in figure 3.3.4. It is clearly shown that the maxima of the resistivity disappeared for all 3 negative values of $E_B$ presented on the figure 3.3.3. Consequently, it is not possible to obtain a positive ATP with negative values of $E_B$, especially with $E_B = -0.301 \text{ Ry}$ (fig. 3.3.4 and table. 3.2). It can also be observed that with positive values of $E_B$, a maximum will appear. But the Fermi energy, either with $Z = 3$ or $Z = 5$, also moves toward high energies and always remains in the decreasing part of the resistivity versus energy function. Neither the Dreirach nor the Esposito approaches may explain the experimental ATP (tab. 3.2).

- Thirdly. Mott introduced a corrective factor $g$, that was defined in chapter 2 (equation 2.5.2) in order to explain the properties of semi-metals and poor semiconduc-
3.3 Theoretical interpretation

Figure 3.3.3: Resistivity calculated by using Dreirach approach ($E_B = -0.301\text{Ry}$) compared to that obtained with different values of $E_B$.

Figure 3.3.4: ATP calculated by using Dreirach approach ($E_B = -0.301\text{Ry}$) compared to that obtained with different values of $E_B$. 

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Table 3.2: Resistivity and thermopower at Fermi energy for different values of $E_B$

<table>
<thead>
<tr>
<th>$E_B$ (Ry)</th>
<th>$E_F$ (Ry)</th>
<th>$\rho$ ($\mu\Omega.cm$)</th>
<th>A.T.P. ($\mu V/K$)</th>
<th>$E_F$(Ry)</th>
<th>$\rho$ ($\mu\Omega.cm$)</th>
<th>A.T.P. ($\mu V/K$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+0.301$</td>
<td>0.8579</td>
<td>104.78</td>
<td>-10.82</td>
<td>1.0838</td>
<td>39.16</td>
<td>-5.71</td>
</tr>
<tr>
<td>$+0.2$</td>
<td>0.7569</td>
<td>116.49</td>
<td>-10.38</td>
<td>0.9828</td>
<td>45.06</td>
<td>-5.67</td>
</tr>
<tr>
<td>$+0.1$</td>
<td>0.6569</td>
<td>125.25</td>
<td>-9.75</td>
<td>0.8828</td>
<td>53.82</td>
<td>-5.38</td>
</tr>
<tr>
<td>$0$</td>
<td>0.5569</td>
<td>134.43</td>
<td>-8.76</td>
<td>0.7828</td>
<td>61.68</td>
<td>-5.19</td>
</tr>
<tr>
<td>-$0.1$</td>
<td>0.4569</td>
<td>142.69</td>
<td>-7.8</td>
<td>0.6828</td>
<td>70.58</td>
<td>-4.79</td>
</tr>
<tr>
<td>-$0.2$</td>
<td>0.3569</td>
<td>161.64</td>
<td>-9.26</td>
<td>0.5828</td>
<td>85.83</td>
<td>-4.40</td>
</tr>
<tr>
<td>-$0.301$</td>
<td>0.2559</td>
<td>260.11</td>
<td>-17.91</td>
<td>0.4818</td>
<td>102.59</td>
<td>-4.26</td>
</tr>
</tbody>
</table>

Mott proposes to correct the resistivity expressions expressed according to the mean free path by a $g^2$ coefficient. Faber’s approach [12] differs from the traditional calculation of electrical conductivity. He uses a formula [5.42 of its book, [12]] which expresses conductivity as a function of the square of the density of states. After some calculations, we express the resistivity as: $\rho = \rho_Z/g^2$, where $\rho_Z$ is the Ziman resistivity calculated with the free electron density of states approach, while $g$ is the ratio of real density of states to free electron density of states. This is coherent with the term $g$ introduced by Mott and Davis (page 80) [13] which states that the mean free path in Ziman’s resistivity must be divided by $g^2$. The Faber approach is more rigorous and does not require the arbitrary substitution of the mean free path by the interatomic distance. Consequently, we propose to replace the resistivity calculated by the Ziman formula by that corrected by the $g$ factor introduced by Faber, Mott and Davis. To recalculate resistivity, it is necessary to know the real and the free electron densities of states at Fermi energy $E_F$. Recalculating ATP is more complex because it is necessary to know the energy dependence of $g$. This led us to record the density of states calculated by Hafner as a function of energy (fig. 3.3.2) and to define $g$ as a function of energy. For that, it is necessary to raise the same questions as was done for the Esposito and Dreirach approaches to know if 3 or 5 electrons must be considered in the conduction band when taking into account the Hafner
calculation, which notes a gap between the s and p bands. The determination of the g factor depends on this choice. Figure 3.3.5 shows factor g when 5 electrons are chosen. In figures 3.3.6 and 3.3.7, we deferred to the density of states and the g factor according to energy if three electrons are chosen.

- We initially considered that the band bottom is on the same level as the muffin-tin zero potential (Esposito approach) with 5 electrons in a free electron conduction band. We introduced this correction into our calculation. Figure 3.3.8 shows the resistivity calculated using the Ziman approach compared with the corrected version according to our proposal and to the corresponding ATP in figure 3.3.9. For Z=5 a resistivity of 68 $\mu\Omega.cm$ is obtained and can be compared to a Ziman resistivity value of about 61 $\mu\Omega.cm$. Moreover, there is still a negative ATP but with a near experimental value of -0.3 $\mu V/K$ when Ziman ATP’s is at about -5.19 $\mu V/K$.

- In our second calculation, we determine the ratio g by using a free electron density of states which has the same origin as the p band real density of states. The density of state in this assumption and the deduced function g(E) are shown respectively in figures 3.3.6 and 3.3.7. These curves enabled us to calculate the corrected resistivity (fig. 3.3.10) and the ATP (fig. 3.3.11) by taking into account the function g(E). With Z = 3, a corrected resistivity of 150 $\mu\Omega.cm$ and a positive ATP of 1.66 $\mu V/K$ is obtained. This calculation makes it possible to reach a resistivity near the experimental value and to find the correct sign for the ATP. This last approach is considered to be very satisfactory in comparison to previous approximations and is coherent with a physical description using 3 conduction electrons as suggested by Hafner’s state density.

- In conclusion, the former approach underestimates the resistivity and gives a false sign for the ATP. If a correction of density of states through a $g^2(E)$ term is taken into account, it is possible to approach resistivity considerably and to give a correct sign to the ATP. It validates the "extended-Ziman" approach with the proviso that there are 3 electrons in the conduction band, adhering to Hafner’s state density calculations.
Figure 3.3.5: The corrective Mott factor as a function of energy (if Z=5)

Figure 3.3.6: Hafner’s and free electron state densities in the hypothesis of 3 valence electrons

Figure 3.3.7: The corrective Mott factor as a function of energy (if Z=3)
3.3 Theoretical interpretation

Figure 3.3.8: Resistivity as a function of energy compared to the resistivity corrected by the energy dependent g factor if Z=5

Figure 3.3.9: ATP as a function of energy compared to that corrected by the energy dependent g factor if Z=5
Figure 3.3.10: Resistivity as a function of energy compared to the resistivity corrected by the energy dependent g factor if \( Z=3 \)

Figure 3.3.11: ATP as a function of energy compared to that corrected by the energy dependent g factor if \( Z=3 \)
II: Is there hysteresis in the liquid $Cd_{60}Sb_{40}$ alloy?
II: Is there hysteresis in the liquid $Cd_{60}Sb_{40}$ alloy?

For the alloy $Cd_{60}Sb_{40}$, Miller, Paces and Komarek (MPK) [39] noted an evolution of the resistivity depending on the history of the liquid alloy. They attributed this phenomenon to the presence of aggregates (clusters), which persist in the liquid state and which are destroyed at high temperatures. Here, they are small fields which have a similar configuration with an intermetallic phase with partial localization of electrons, and whose association is transitory. In this research, we supplemented the experimental work of MPK with a new experimental device to check if there was any resistivity hysteresis phenomena and to determine under which conditions it came about. To check this phenomenon, we made three major improvements over the experimental device used by MPK. Firstly, we replaced the pyrex cell by a quartz cell, to be able to exceed the temperature limit of 530°C reached by MPK. Secondly, we used an experimental device to mechanically homogenize the alloy. Lastly, we measured the resistivity of the melting point up to 850°C by carrying out cycles at increasing intervals of temperature. In MPK’s experiment, it was not possible to know if the hysteresis observed was due to a microscopic phenomenon or an experimental artefact with an initially non-homogeneous alloy. Our experimental device makes it possible to mix the alloy mechanically and should answer these questions about resistivity hysteresis phenomena (refer to [46]).
Influence of the history of a melt on the electrical resistivity of cadmium–antimony liquid alloys

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Abstract

Miller, Paces and Komarek (MPK) [Trans. Metall Soc. AIME 230 (1964) 1557] observed an influence of the history of a melt on the electrical resistivity of several cadmium–antimony alloys. In this work we complete the experimental work of MPK with new accurate experiments in order to verify the existence of the phenomenon and to precise by defining the conditions where it appears. We used three important improvements on the experimental design of MPK. First we used quartz cells instead of pyrex cells used by MPK so allowing the heating of the melt well above the temperature of 530 °C attained by MPK. Secondly our experimental design allows to mix mechanically the liquid alloy in order to achieve a macroscopic homogeneity of the melt. Finally we measure simultaneously the thermopower of the Cd$_{60}$–Sb$_{40}$ liquid alloy. The time evolution of our experiment is fully described with our conclusions.

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Keywords: Electrical resistance and other electrical properties; Thermoelectrical properties; Phase transformations

1. Introduction

In 1964, Miller, Paces and Komarek [1] reported an influence of the history of a melt on the electrical resistivity of several cadmium-antimony alloys. More recently physicists of different laboratories [2–7] worked collaboratively in the liquid metal field on “Phase transformations in liquids” (not only in pure liquid metals, but in liquid alloys too) and on “impurity effects” (again both in pure metals and in alloys). They introduced the concept of metastable micro-heterogeneity in liquid metals and alloys appearing in different other physical properties (especially density and viscosity). Dahlborg et al. [8] studied recently the influence of the history of the melt on the solidification process and the characterization of micro-heterogeneities using small angle neutron scattering. Thus the problem of clusters in liquids is an up to date important physical and industrial problem since it governs the solidification. These different authors showed that the solid alloys can have very different properties following the history of the melt.

The electrical resistivity and thermopower act as sensors of what is happening in the sample. The aim of this work is to complete the experimental work of MPK [1] by complementary experiments in order to check the existence of the phenomenon and to precise and define the conditions where it appears. We used fused quartz cells in place of Pyrex cells used by MPK. This allows us to heat the melt well above the temperature of 530 °C reached by MPK. In particular we can heat above the melting point of antimony (631 °C). The peculiar experimental design of our apparatus allows to mix mechanically the liquid alloy in order to achieve a macroscopic homogeneity of the melt (at low temperature only, because of the vapor pressure of cadmium).

The Cd–Sb alloy is a semi conductor in the solid state. In the liquid state it is metallic but maintains below 800 °C the semi conductor characteristic exponential decrease of resistivity with temperature [9]. The study of liquid cadmium – antimony at high temperatures is difficult because the boiling point of cadmium is 760 °C while the melting point of antimony is 631 °C. To measure properties at high temperature it is necessary to use a pressure of argon of about 7 bars to prevent the evaporation and the formation of vapor bubbles in the bulk of the liquid alloy. MPK [1] noted an evolution of the resistivity according to the history of the liquid alloy (hysteresis). They attributed this phenomenon to the presence of aggregates (clusters), which would persist in the liquid state. The objective of this work is:
(i) to check the influence of this behaviour on the resistivity and on the thermopower (which has never been reported to our best knowledge),
(ii) to examine the non-metal–metal transition,
(iii) to observe if some phenomenon occurs when passing, in the liquid state, from the stable to the metastable region of the phase diagram.

2. Experimental method

The experimental results here presented were obtained with an automated device which measures jointly the electrical resistivity and the absolute thermopower. This method has been completely described by Vinckel [10,11]. It combines the measurement of electrical resistivity using a four-point probe technique with the measurement of absolute thermoelectric power employing a small temperature gradient method. The liquid metal is contained in a fused silica cell (Fig. 2 of Ref. [12]) provided with sealed tungsten and tungsten—(26 wt.%) rhenium electrodes. The geometrical constant of the cell was calibrated by measuring the resistivity of triple-distilled mercury. The thermoelectric power of tungsten and tungsten—(26 wt.%) rhenium were previously calibrated [13] with a “platinum 67” standard wire (standard of absolute thermoelectric power). Its

![Temperature of the stable liquidus](image)

**Fig. 1.** Historical study of the resistivity of Cd$_{60}$–Sb$_{40}$ at low temperatures (400–550 °C).
absolute thermoelectric power was given by Roberts, Righini and Compton [13] and by Cusack and Kendall [14] after a careful measurement of the Thomson coefficient between 0 K and 1600 K. The Thomson coefficient was then integrated between 0 K and the considered temperature to get the absolute thermo electric power thanks to the second Kelvin law. The calibration is represented in Fig. 3 in the Sar et al.’s paper [12]. The error in the final results is estimated to be no more than ±0.5% for the resistivity and ±0.6 μVK⁻¹ for the thermoelectric power in the whole temperature range. Both A and B type of uncertainties have been used to determine these values. The metals employed were purchased from Roc/Ric and from Fluka respectively for antimony with purity of 99.95% for zinc with a purity of 99.999%.

3. Influence of the history of the melting process on the resistivity of the Cd₆₀Sb₄₀ alloy

The cadmium-antimony alloy presents a peculiarity. It has a stable and a metastable liquidus similar to the undercooling effect for pure metals. From the phase

![Fig. 2. Historical study of the resistivity of Cd₆₀–Sb₄₀ at high temperatures (400–850 °C). Observation of the non metal–metal transition.](image-url)
diagram of Hansen et al. [15] we observe that, at the composition studied (Cd$_{60}$–Sb$_{40}$), the stable liquidus state is met near 435 $^\circ$C, while the metastable liquidus is met near 417 $^\circ$C. As reported by MPK [1] the solidification occurs following the history of the melt.

Our experiments were carried out as follows:

1. The ingot of average composition Cd$_{60}$Sb$_{40}$ is introduced into the measuring cell and then heated at the temperature of 454 $^\circ$C, (20 $^\circ$C above the “stable liquidus” of Cd$_{60}$Sb$_{40}$). Being in its molten state, the capillary is filled by applying successively vacuum and pressure. Our curves are represented in Fig. 1 in an expended scale (400–550 $^\circ$C) and in Fig. 2 between 400 and 800 $^\circ$C.

2. Curves C, D, E, F, G. One makes two cycles of decreasing-increasing temperature starting between 454 and 414 $^\circ$C. 454 $^\circ$C is 2 $^\circ$C below the liquidus of the stable phase Cd$_{50}$Sb$_{50}$ and 20 $^\circ$C above the stable liquidus for the considered concentration Cd$_{60}$Sb$_{40}$. We mix the alloy several times by applying vacuum then pressure at 443 $^\circ$C, to eliminate bubbles, where present, and to homogenize the composition. Our four curves are overlapped.

3. Curves H, I, J, K. We apply vacuum then pressure and increase the temperature. We go up to

![Diagram of Cd$_{60}$Sb$_{40}$](image_url)

Fig. 3. Historical study of the thermopower of Cd$_{60}$–Sb$_{40}$ at all temperatures (400–850 $^\circ$C). A typical behaviour of the temperature dependence.
534 °C (curve H) decrease to 422 °C (curve I and J) and go up to 448 °C curve K. The curves are practically superimposed. We observe that the curves I, J, K are shifted compared to the curves C, D, E, F, and G, as in [1]. Are micrograins (clusters?) of solid Cd$_{50}$Sb$_{50}$ or Sb not entirely molten in the capillary during our experiments C, D, E, F, G though the experiments lasted approximately 2 days? The temperature of experiments H, I, J, K was higher than the melting point of the compound Cd$_{50}$Sb$_{50}$. It is necessary to remark that solid antimony has a resistivity 1.7 times higher than that of molten antimony. The compounds Cd$_3$Sb$_2$ and CdSb are semiconductors in the solid state and have also a higher resistivity than the liquid.

It is difficult to admit that more resistive solid matter constituents, after melting, raise the resistivity when they are located in the capillary. If nanograins uniformly distributed in the liquid cannot explain the variation of resistivity, it is possible to consider that the solid matter constituents “float” in the principal and auxiliary tanks or precipitate to the bottom according to the density of the solid compared to that of the liquid.

The melting point of cadmium is 320 °C, that of antimony 631 °C and that of Cd–Sb alloys 456 °C. Therefore it is sure that all free cadmium grains at this temperature are molten. But antimony or Cd$_{50}$Sb$_{50}$ can exist in the cell, at the surface or bottom, thus, the composition of the liquid in the capillary would be enriched in cadmium, and would have a resistivity lower than expected.

The rise of temperature to 530 °C would imply that the whole Cd–Sb alloy melts and that a slow diffusion occurs in the capillary which would be thus enriched in antimony. These considerations can also explain the increase in resistivity in the capillary.

(4) We mix the alloy at 443 °C by applying vacuum and pressure. This shifts the resistivity. Then we run the measurements (curves L, M, N, O, and P). Curves L, M, N and beginning of O are superimposed, but the end of the increase O and the decrease P are shifted.

(5) We mix the alloy again at 443 °C go down to 416 °C. Go up to 534 °C (curve Q) and go down again to 443 (curve R). The curves Q and R are practically superimposed.

(6) We mix the alloy at 443 °C. The resistivity increases again. We heat up to 663 °C, 32 °C above the melting point of antimony (no measurement). The descent (curve U, W) and the later rises up 800 °C and descents (curves X, Y, Z, and AA) are practically superimposed.

In conclusion of these various experiments, the observed phenomenon can be explained by a dissolution of Cd$_{50}$–Sb$_{50}$ and later, of antimony located at the surface or at the bottom of the auxiliary tanks and its migration in the capillary. Enrichment by antimony may be slow by diffusion towards the capillary or rapid following an operation consisting of cleaning the capillary by applying vacuum and filling it again by using pressure.

### 4. Theoretical interpretation

In the framework of the nearly free electron theory, the resistivity ρ and thermopower S are given by the Ziman formula recalled in Sar and Gasser’s paper [12] [Eqs. (13)–(15)]. We get an experimental resistivity value of 179.5 μΩ cm at 460 °C and of 149.7 μΩ cm at 800 Celsius to be compared with the calculated values of 90.6 and 95.1 μΩ cm, respectively at 460 and 800 °C by using the empty core pseudopotential of Ashcroft [16].

We first observe that, at low temperature, the experimental resistivity decreases with temperature in the same ways as that of a semiconductor, while the calculated resistivity increases like that of a metal. This is not surprising since the Ziman formula is valid only for metals. Secondly the Ziman formalism leads to too low results, but we must remember that the Ziman formalism has been obtained within a free electron theory with a free electron density of states. Mott et al. [17] proposed to correct the Ziman formula by taking into account the partial semi-conductor characteristic using the formula:

$$\rho_{\text{Mott}} = \left(\frac{1}{g^*}\right) \rho_{\text{Ziman}}\text{ where } g = \frac{N(E_F)}{N(E_F)_{\text{free-electron}}}$$

Indeed Cd–Sb is not fully metallic nor fully semi-conducting, thus a pseudo gap appears which closes with increasing temperature. At high temperature (above 800 °C) the experimental resistivity increases with temperature. Calculated values are still lower by 35% than the experimental value.

The thermopower is represented in Fig. 3. Like for the resistivity, an hysteresis effect of the history is observed on the thermopower. In principle thermopowers of metals are negative and have a negative slope. The thermopower of a semiconductor is positive or negative following the type of carriers (and the composition). But at a stoichiometric composition it passes to zero. Then, the only difference with metals is its slope. The temperature dependence is different from metallic alloys since it has a positive temperature dependence. Such behaviour has not been observed to our knowledge.
Some metals like cadmium and zinc can have a positive thermoelectric temperature coefficient [18] but it is clearly due to the fact that $2k_F$ with divalent metals is situated at the $q$ value where the structure factor presents its main peak which decreases with temperature. With the Cd$_{60}$–Sb$_{40}$ alloy the mean valence is 3.2 where this phenomenon no longer occurs.

5. Conclusion

The resistivity and the Absolute Thermo-electric power (ATP) are sensitive to the history of the alloy. The high resistivity in the middle of the phase diagram has no correspondence in the ATP. The anomalies of resistivity observed by MPK are also highlighted by our experiments. We cannot exclude that the results obtained can be due to the melting of clusters but we may also explain our observations by a progressive dissolution of antimony and Cd$_{50}$Sb$_{50}$ floating on the surface of the liquid in the principal and auxiliary storage tanks. This is however in contradiction with the observation of MPK that a seed of stable solid dropped in the alloy below 500 °C solidified the melt to the stable phase. The resistivity and its TCR do not have apparent discontinuity at the transition to the stable liquids. At high temperature ($T_c > 800$ °C) the alloy behaves as pure metals (i.e temperature coefficient of resistivity positive).

References

III: Electronic transport properties of the Cd-Sb System
3.4 Introduction

The $Cd - Sb$ system is at the border of a weak scattering mode. It has a maximum resistivity of about $200\mu\Omega.cm$ in the liquidus vicinity. We measured the resistivity and the absolute thermoelectric power (ATP) of $Cd_xSb_{100-x}$ alloys in a vertical fused silica cell. The study is different from earlier ones by the temperature and composition range. At low temperatures, the alloy preserves a semiconductor character similar to that of a solid state. A transition from a semiconductor character (negative temperature coefficient) to a metallic character (positive temperature coefficient) can be observed above $780^\circ C$. Furthermore, resistivity is at a maximum for the $Cd_{48}Sb_{52}$ composition (not far from the $Cd_{50}Sb_{50}$ observed by Gasser) at low temperatures and $Cd_{40}Sb_{60}$ at high temperatures. By using local pseudopotentials and hard sphere structure factors, the Faber-Ziman theory was able to interpret the experimental results on the whole phase diagram of the studied system.

3.5 Experimental results

3.5.1 Material and modification of the composition of alloys

The electronic transport properties were measured with a traditional fused silica cell equipped with sealed tungsten and tungsten/rhenium-26% electrodes. The temperature delivered by the standard 'internal' thermocouples W/WRe26% was checked using type K external thermocouples. Pure argon with a total pressure of 5 bars at high temperature was used to prevent the alloy from being distilled. Measurements were carried out, starting at pure cadmium (99.9999%), and going to $Cd_{40}Sb_{60}$. In a second cell, we studied antimony rich alloys. The resistivity and the ATP were measured simultaneously.

3.5.2 Resistivity

Measurements were carried out from the Cd-Sb alloy at fifteen different concentrations. Figure 3.5.1 shows the results of resistivity as a function of temperature. The Cd-Sb system has a maximum resistivity of about $200\mu\Omega.cm$ in the vicinity of the liquidus, and rather important negative temperature coefficients $d\rho/dT$ compared to the purely metallic systems. Three areas can be distinguished in figure 3.5.1: area 1, metallic behaviour
Figure 3.5.1: Experimental resistivity of liquid Cd-Sb as a function of temperature for different concentrations
(alloys rich in cadmium), area 2 semi conducting behaviour (with a negative temperature coefficient), and area 3 typical semi-metallic behaviour (alloys rich in antimony).

1. Area 1: purely metallic behaviour
   Resistivity of highly enriched cadmium alloys (fig. 3.5.2) (pure cadmium, Cd$_{93}$Sb$_7$, Cd$_{90}$Sb$_{10}$, Cd$_{80}$Sb$_{20}$ alloys), increase with the temperature. The temperature coefficients $d\rho/dT$ are positive. That corresponds to metallic behaviour: a parabolic curve without any minimum, except the concentration Cd$_{80}$Sb$_{20}$ for which the temperature coefficient is negative below 526$^\circ$C and which presents a minimum at this temperature.

2. Area 2: A strong decrease in resistivity as a function of temperature (fig. 3.5.3)
   The temperature coefficient is negative and the resistivity decreases. Nevertheless, at temperatures above 700°C-760°C (according to the compositions), we noted a change of slope with a slight increase in resistivity with the temperature, typical of metallic systems.
   This intermediate area retains some characteristics of semiconductors. The resistivity is at its highest in this concentration range and has a negative temperature coefficient ten times larger than that of metals.

3. Area 3: The liquid becomes again metallic
   Figure 3.5.4 shows the results of our measurements of antimony rich alloys (from Sb$_{100}$ to Cd$_{30}$Sb$_{70}$). They display usual metallic behaviour, with a positive temperature coefficient for most of these concentrations throughout the whole temperature range. The resistivity of Cd$_{30}$Sb$_{70}$ is a slightly decreasing function of temperature at low temperatures while it is an increasing one at high temperatures.

3.5.3 Absolute Thermoelectric Power

Measurements of the absolute thermoelectric power of these compositions are shown in figure 3.5.5. The ATP is positive for pure cadmium, pure antimony and the alloys whose atomic concentration of antimony is over 50%. The Cd$_{50}$Sb$_{50}$ alloy has a slightly positive ATP (near zero). It constitutes a borderline between a negative ATP for the alloys rich in cadmium and positive ATP for alloys rich in antimony. The ATP is parabolic for two alloys
3.5 Experimental results

Figure 3.5.2: Experimental resistivity of Cd-Sb alloys in a cadmium rich region

Figure 3.5.3: Experimental resistivity of Cd-Sb alloys in the middle of the phase diagram
Figure 3.5.4: Experimental resistivity of Cd-Sb alloys in an antimony-rich region
Figure 3.5.5: Experimental ATP of liquid Cd-Sb as a function of temperature for different concentrations
$Cd_{48}Sb_{52}$ and $Cd_{40}Sb_{60}$, the first having a minimum (from a negative slope to a positive slope) between 560-580°C and the second being between 700-720°C, which practically coincides with the position of both maxima of resistivity. It is essential to note that the ATP values are weak ($-2 < S < 4$), typical of the metallic mode, but it is important to remark the change of sign in the vicinity of $Cd_{50}Sb_{50}$. The variation of ATP as a function of temperature $dS/dT$ depends on the three aforementioned areas. In area (1), the ATP is negative and is strictly decreasing with a negative slope except for cadmium. In area (2), the ATP increases with temperature and with antimony concentration. The sign change is close to the concentration $Cd_{50}Sb_{50}$. Finally, in the last area, which is rich in antimony, the ATP is decreasing in regards to temperature and of concentration.

3.6 Calculating resistivity and ATP as a function of concentration

3.6.1 Calculating resistivity

Figure 3.6.1 presents the variation of experimental and calculated resistivity as function of the antimony concentration at two temperatures (500°C and 800°C). Calculations were based on the Faber-Ziman formalism with a "hard sphere" structure. We used the Ashcroft local energy dependent pseudopotential model and the Vashishta Singwi [19] dielectric screening function. The Parameter $R_C$ is the "core radius". The parameter $R_C$ of each metal has been chosen in order to fit the experimental resistivity of the pure elements at the chosen temperature. Two $R_C$ parameter values answer this condition. One of the values is not physical and is eliminated [47]. A second parameter [48, 47] is then adjusted on the experimental ATP of each pure element at the same temperature. We noted a difference between the theoretical calculations and the experimental results as well at low temperature (500°C) that at high temperature (800°C). By construction, the theoretical values are exactly the same as the experimental values for the pure metal compositions. This calculation did not reproduce the maximum in resistivity, nor the change in ATP’s sign. This is valid even at 800°C where the Faber Ziman theory should be better adapted. Nevertheless at this temperature, the experimental values of the resistivity approach the calculated values. A purely metallic model cannot explain the behaviour of a Cd-Sb alloy. On the other hand, it would be good to keep in mind Mott’s expression for pseudogaps.
3.6 Calculation of resistivity and ATP

Figure 3.6.1: Experimental and calculated resistivity as function of concentration

Figure 3.6.2: Experimental and calculated ATP as function of concentration
and the g parameter. The system leans towards a progressive metallization (the pseudogap is closed again) with an increase in temperature. A g value of 0.8 would be enough to obtain the experimental resistivity. The reduction of the pseudogap would explain the negative temperature coefficient of the resistivity. Moreover, the same pseudogap would explain the positive sign of the thermoelectric power of the alloys in the middle of phase diagram. At higher temperatures, the alloy has metallic characteristics, which result in a positive value of the resistivity temperature coefficient. The Ziman formula gives a result closer to the experiment. Nevertheless, there is still a difference between the theoretical curve and the experimental values. This difference can be explained by the fact that:

- The partial structure factors are calculated with a hard sphere potential which does not correctly represent the order in the alloy.
- The pseudopotential model is too simple.
- The closing of the pseudogap stops.

To confirm our experimental results, we compared these results with those of Gasser [1]. Our resistivity results were consistent with Gasser’s at both 500°C and 800°C.

### 3.6.2 Calculating ATP

The experimental and calculated values of absolute thermoelectric power are displayed in figure 3.6.2 as well as experimental values of other authors for the comparison. This is consistent with Bath’s experimental values at 500°C. On the other hand, the agreement between experiment and theory only works for concentrations close to pure elements. Taking a pseudogap into account makes it possible to explain a positive ATP.

### 3.7 Conclusion

Antimony is a semi-metal characterized by a pseudogap between the s and p bands. The Ziman formula does not accurately describe the ATP of this metal when there are five conduction electrons. The former Ziman approach over-estimates the resistivity and gives a false sign for the ATP. A density of states correction through a $g^2$ term makes it possible to approach considerably experimental resistivity and ATP (positive) and validate the "extended-Ziman" approach, provided that the real state density is taken into account.
In the second paragraph, phenomenon of hysteresis was covered similar to that observed by M.P.K for the $Cd_{60}Sb_{40}$ alloy. This is most likely due to the incomplete melting of the antimony. The maximum of resistivity moves with the temperature. At low temperatures the maximum is close to composition $Cd_{52}Sb_{48}$, close to that was already observed before by Gasser for $Cd_{50}Sb_{50}$. At high temperatures, the maximum is in the vicinity of composition $Cd_{40}Sb_{60}$. The electronic transport coefficients and their derivatives are continuous when passing from stable liquidus towards the metastable zone. At low temperatures the alloys display some remainders of the solid semiconductor state, which probably resulted in the existence of a pseudogap. At higher temperatures, the metallic behaviour corresponding to the increase in resistivity depending on temperature. The transition is observed for some alloys, between 700°C and 800°C. For these alloys, the resistivity changes its slope and goes through a minimum value. The Ziman formula underestimates experimental resistivity by 35%. We interpret this difference by the fact that the alloys Cd-Sb have a pseudogap state density type which was not considered in our calculation using the Faber-Ziman formalism. This pseudogap is closed by the temperature, which would explain the transition (minimum of resistivity depending on temperature) for some compositions.
Chapter 4

Lead-free solders: problems and properties
Lead and lead-free solders
Chapter 4. Lead-free solders: problems and properties

4.1 Introduction

Lead-tin solder, which melts at 180°C, has good mechanical characteristics and good adhesion to electronic circuits. In Europe, the WEEE Directive mandated lead-free welding by July 2006, and lead-free implementation is currently in force. While industrial lead-free solders still exist (for instance, tin-copper-silver alloy), unfortunately their melting point is 20% higher than tin-lead solders. Their mechanical properties are also inferior. These solders cause mechanical problems and have a weak adhesion to electronic circuits. Industrialists have expressed interest in the Sn-Cu-Ag alloy because metals with a low melting point are either neither as expensive nor as toxic as lead. Therefore we oriented our research towards how to improve the properties of Sn-Ag-Cu based solders. A solder must be a good conductor of electricity and heat. At the LPMD laboratory in Metz, France, the electronic transport properties were measured for different lead free solders (Sn-Ag-Cu, Sn-Cu, Sn-Ag, Sn-Pb) in both liquid and solid states, and were then compared to those of a tin-lead solder. We were able to determine the electrical conductivity, the thermoelectric power and the thermal conductivity, which play a role in the soldering process.

4.2 Why lead is prohibited

4.2.1 Lead’s history

Lead was the main component in the soldering of electronic circuits. Electronic appliances containing lead solders are often deposited in land-fills. Released into nature, the solder is dissolved more or less quickly by acids contained in the ground and can lead to ground water pollution. Lead dissolution in subsoil water can affect the food chain.

Two possible mechanisms have been published: \( Pb + \frac{1}{2}O_2 + H_2O \Rightarrow Pb(OH)_2 \) or: \( Pb + \frac{1}{2}O_2 + H_2O + CO_2 \Rightarrow Pb(HCO_3)_2 \).

4.2.2 Lead’s medical risks

Lead and lead-based alloys are among the 17 chemicals that are considered harmful for the health (affects the nervous and renal systems, among others) and the environment. Lead strongly binds onto proteins. Lead poisoning has harmful effects on health: weaken,
4.3 The choice of alternatives to lead

The removal of lead from the electronic circuit industry presents a challenge for manufacturers. The replacement of lead in soldering alloys by other elements such as silver, copper and bismuth creates various problems:

1. The temperature of solders is higher. It is necessary to increase the welding temperature from 20 to 40 degrees for the substitution alloys. Lead-free solders melt at a higher temperature than traditional tin-lead alloys (a (60%)tin-(40%)lead alloy melts at around 180°C, whereas the 99C alloy (99.7%tin-0.3%copper) becomes liquid at around 227°C). Consequently, it is necessary to increase the temperature of the welding device. The electronic components and the printed circuits have to resist these higher temperatures, which in turn, increases flux evaporation. It is necessary to choose better adapted fluxes.

2. Risk confusion: A very broad range of new alloys are available on the market with a diversity of surface compatibilities, completions and soldering temperatures.

3. Inspection: The tips of lead-free solders are very different in appearance compared to traditional tips of tin-lead solders. The tips are usually rather dull and the scattering is less important. The contact angles are rather narrow at the perimeter of the solder joint, where the solder meets the substrate. This does not mean that the tips are defective. Some studies have already proved that, in spite of their different aspects, the tips of lead-free solders are even more reliable than the equivalent tips in the tin-lead version.

4. Repairs: It is essential that all repairs are also carried out by using (the same) LFS. Before carrying out repairs, it is necessary to know the type of the solder used before. The nature of the solder alloy used is usually shown on the module or the printed circuits. Alloys used for the LFS can vary according to their use. However to carry...
out a repair of a solder manually, in the interest of compatibility, it is advisable to use the 99C alloy. In general, a small quantity of silver is added to the LFS alloy in order to sustain the humidification and the formation of the solder’s tip during the assembly phase. Electronic specialists have a significant number of solutions to replace lead solders. However, the only tree alternative to lead (Pb) is tin (Sn). In general, the new alloys consist of tin and other materials similar to lead. The problem of our solder is that the percentage of lead permitted by the RoHS directive is well below the brazing point.

4.4 Why choose SAC (SnAgCu)?

More than 100 possible alloys for making solders were proposed and evaluated, but none were optimum. Most current lead-free alloys melt at temperatures approximately 40°C higher than lead-tin alloys. The most widespread alloys, called "SAC alloys", are tin, silver and copper based alloys. They do not show a major loss in performance and resist thermal fatigue well. However, other available alloys have other specific advantages. The key differences between a SAC alloy and a tin-lead solder are:

- Higher melting point
- Decreased wetting
- Harder joint formation.
- A matte appearance (can resemble a poor joint of tin-lead solder).
- Can require a different more active flux.

4.5 Physical properties of LFS alloys

The physical and mechanical properties of substitution alloys have to be known in order to improve them. These alloys must be good conductors of electricity to avoid Joule heating. Thermal conductivity also plays an importance role in the soldering process. The replacement of traditional tin-lead alloys by lead-free solders (Sn-Ag, Sn-Cu, Sn-Sb, and SnAgCu) decreases the electrical resistance of the circuits and consequently the Joule heating. The resistivity of lead-free alloys must also be known in the solid state. In
some "poor quality" devices, it is necessary to know at least the thermoelectric effects and reduce them. The thermoelectric power of copper is positive while that of tin-lead alloy is negative. The difference in the thermoelectric powers can be reduced by using tin-metal-noble solders. We measured the resistivity and the thermoelectric power in the liquid and the solid states for several lead-free alloys and deduced their corresponding thermal conductivity in regards to temperature by using relations between the electronic transport coefficients. One of the essential properties of solders is their wetting and spreading ability over a copper substrate or a substrate covered with a thin layer of Ni, Pd and Au. The physical properties corresponding to this phenomenon are the surface and interfacial tensions. We studied this in collaboration with the University of Chemnitz in Germany. The objective of this work was to improve the properties of solders, specifically by using additives and by controlling the thermal process better.

To make solders, it is important to better understand their surface tension, wetting and viscosity. These are complementary to electronic transport properties, and have already been studied in Metz. It is also useful to examine solder quality by microscopy techniques (optical microscopy, scanning electron microscopy). The aim of this research work was both fundamental and industrial. The solder alloys used in this work were made from pure compounds as well as purchased industrial-ready samples at the companies "Stoop" and "wrought white metals". Our objective was to enhance solder properties by adding nanoparticle additives or transition metals. The first part of this work is devoted (chapter 4) to the study of the electronic properties of lead-free and tin-lead solders. Solder wetting (or contact angle) and surface tension are described in chapter 5. The viscosity of the solder alloys is briefly presented in the last chapter (chapter 6).

### 4.6 Objectives

Elements taken into account by industrialists in the choice of their new solders are:

#### 4.6.1 Appropriate properties in manufacturing

- Melting point (as low as possible).
- Environmental protection.
- Wettability of the printed circuits.
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- Ease of recycling.
- Aptitude for being used in industrial processes.
- Low cost.

4.6.2 Appropriate properties in achieving reliability

- Electrical conductivity must be as high as possible.
- Thermal conductivity must be as high as possible.
- Formation of inter-metallic bonding compounds between the solder and the circuit should support the connection.
- Expansion coefficients must be near that of the substrate.
- Solders must resist fatigue.
- Solders must wet the substrate and wires properly.
- A low viscosity supports the solder’s spreading; however, small pasty solders are preferable in some industrial processes.
Chapter 5

Electronic transport properties of lead-free solders in liquid and solid states

5.1 Introduction

The electronic transport properties (electrical conductivity, thermal conductivity and thermopower) of some industrial Sn-based alloys are particularly interesting to observe in the solid and liquid states. The direct determination of the thermal conductivity of alloys at high temperatures is difficult due to convection movements [49, 50, 51]. However, it is possible to get the thermal conductivity indirectly from electrical conductivity and from thermopower measurements using a relation between the electronic transport coefficients. The Wiedemann-Franz (W F) law is a simplified version of this relation when thermopower is neglected. In this chapter, experimental electrical conductivity and the Seebeck coefficient (absolute thermoelectric power: ATP) of solders are presented. The thermal conductivity is deduced thereafter from these two properties measured in a liquid and solid state. Comparisons are made of the results of lead-free and tin-lead solders. These three properties will be discussed and compared to theoretical calculations particularly for binary alloys. The theoretical interpretation of ternaries is more complex.
Chapter 5. Electronic transport properties of lead-free solders in liquid and solid states

5.2 Experimental details

So as to replicate a real situation in industry, we used the following industrial alloys: $Sn_{96.5}Ag_{3.5}$, $Sn_{97}Cu_3$, $Sn_{95}Sb_0.5$ and $Sn_{96}Ag_4$ from the companies "Stoop member of Fenix Metals" $Sn_{95.5}Ag_{3.8}Cu_0.7$ and $Sn_{99.3}Cu_0.7$ from "Métaux blancs ouvrés". The Sn60Pb40 is the commercial alloy. We also used a laboratory-made alloy $Sn_{96.75}Ag_{1.25}Cu_{2.00}$ prepared from pure tin (99.999%), silver (99.9999%) and copper (99.9999%). To carry out the measurements, a traditional fused silica cell was used for each composition. The tungsten and tungsten-26wt% rhenium electrodes were used for measuring the temperature and voltage between both sides of the sample. To check the accuracy of the temperature measured by this non-standard thermocouple (W/W-Re26), the temperature was measured simultaneously outside of the cell using a K-type thermocouple. The alloys analysed were first cleaned mechanically to eliminate the oxide coating, then by alcohol. The measurements were conducted under applied pressure (1 bar) of pure argon. To avoid breaking the cell during solidification, we always started the solidification process from the bottom of the cell. This allows the fluid to expand; however, it also creates a difference in temperature between the small and the large tanks, which does not allow for TEP measurements near the liquidus temperature.

5.3 Experimental results

5.3.1 Electrical resistivity

The electrical resistivity of six lead-free solder alloys (SAC, Sn-Ag, Sn-Cu and Sn-Sb) as well as the traditional solder $Sn_{60}Pb_{40}$, was measured during the heating and cooling phases from the melting point to 1000°C. Once the measurements in the liquid state were done, we solidify the alloy carefully and the measurements were then made in the solid state until room temperature. During the solidification phase the temperature at which the solidification occurs was noted to highlight the undercooling phenomenon. Figure 5.3.1 shows the results obtained in the liquid and solid states while figure 5.3.2 presents only the results in the solid state. These results show that the resistivity of all lead-free solders alloys is lower than that of the traditional solder (which favours lead-free solders). In the solid state, the electrical conductivity ($\sigma = 1/\rho$) of various lead-free solder alloys is higher than that of the traditional solder, except the alloy $Sn_{95}Sb_{0.5}$, which has an
5.3 Experimental results

Figure 5.3.1: Electrical resistivity of lead-free solders and of the classical tin-lead solder in the liquid and solid state

Figure 5.3.2: Electrical resistivity of lead-free solders and of the classical tin-lead solder in the solid state
### Liquid state

<table>
<thead>
<tr>
<th>Composition</th>
<th>A</th>
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<th>$B_2$</th>
<th>$B_3$</th>
<th>$B_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$_{95.3}$Ag$<em>4$Cu$</em>{0.7}$</td>
<td>43.53022</td>
<td>0.03199</td>
<td>-7.58183E-6</td>
<td>-2.37318E-9</td>
<td>6.08879E-12</td>
</tr>
<tr>
<td>Sn$_{99}$Cu$_1$</td>
<td>41.69948</td>
<td>0.02584</td>
<td>9.33628E-6</td>
<td>-2.1434E-8</td>
<td>1.34791E-11</td>
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<tr>
<td>Sn$_{96}$Ag$_4$</td>
<td>41.91105</td>
<td>0.03436</td>
<td>-1.63847E-5</td>
<td>1.28317E-8</td>
<td>-3.03722E-12</td>
</tr>
<tr>
<td>Sn$<em>{96.75}$Ag$</em>{1.25}$Cu$_2$</td>
<td>33.94772</td>
<td>0.08969</td>
<td>-1.54651E-4</td>
<td>1.59444E-7</td>
<td>-5.95739E-11</td>
</tr>
<tr>
<td>Sn$_{95}$Sb$_5$</td>
<td>42.23019</td>
<td>0.04494</td>
<td>-4.07069E-5</td>
<td>3.56373E-8</td>
<td>-1.06886E-11</td>
</tr>
<tr>
<td>Sn$<em>{70}$Pb$</em>{30}$</td>
<td>50.98566</td>
<td>0.03877</td>
<td>-1.86572E-5</td>
<td>1.67055E-8</td>
<td>-5.40563E-12</td>
</tr>
<tr>
<td>Sn$_{97}$Cu$_3$</td>
<td>42.05739</td>
<td>0.03018</td>
<td>-4.35325E-6</td>
<td>4.06962E-9</td>
<td>4.84186E-12</td>
</tr>
</tbody>
</table>

### Solid state

<table>
<thead>
<tr>
<th>Composition</th>
<th>A</th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$B_3$</th>
<th>$B_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$_{95.3}$Ag$<em>4$Cu$</em>{0.7}$</td>
<td>13.82162</td>
<td>-0.10794</td>
<td>0.00224</td>
<td>-1.36789E-5</td>
<td>3.03277E-8</td>
</tr>
<tr>
<td>Sn$_{99}$Cu$_1$</td>
<td>10.09766</td>
<td>0.03722</td>
<td>2.44294E-5</td>
<td>2.16994E-7</td>
<td>-5.12662E-10</td>
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<tr>
<td>Sn$_{96}$Ag$_4$</td>
<td>11.14907</td>
<td>0.03494</td>
<td>9.48365E-5</td>
<td>-1.16633E-7</td>
<td>0</td>
</tr>
<tr>
<td>Sn$<em>{96.75}$Ag$</em>{1.25}$Cu$_2$</td>
<td>10.82345</td>
<td>0.036</td>
<td>5.71106E-5</td>
<td>5.9624E-8</td>
<td>-1.24038E-10</td>
</tr>
<tr>
<td>Sn$_{95}$Sb$_5$</td>
<td>15.92636</td>
<td>0.04707</td>
<td>4.20394E-7</td>
<td>2.23468E-7</td>
<td>-3.74611E-10</td>
</tr>
<tr>
<td>Sn$<em>{60}$Pb$</em>{40}$</td>
<td>13.19958</td>
<td>0.06995</td>
<td>-4.27672E-4</td>
<td>4.07098E-6</td>
<td>-1.01061E-8</td>
</tr>
<tr>
<td>Sn$_{97}$Cu$_3$</td>
<td>12.17825</td>
<td>-0.03224</td>
<td>0.00117</td>
<td>-7.42971E-6</td>
<td>1.72435E-8</td>
</tr>
</tbody>
</table>

Table 5.1: Coefficient of the polynomials adjusted on the experimental resistivity of different LFS compositions in the liquid state (from 250°C to 1000°C), with $\rho = A + B_1.T_C + B_2.T_C^2 + B_3.T_C^3 + B_4.T_C^4(\mu\Omega.cm)$

Table 5.2: Coefficient of the polynomials adjusted on the experimental resistivities of different LFS compositions in the solid state (from room temperature to the melting point), with $\rho = A + B_1.T_C + B_2.T_C^2 + B_3.T_C^3 + B_4.T_C^4(\mu\Omega.cm)$
5.3 Experimental results

electrical conductivity lower than that of $Sn_{60}Pb_{40}$ alloy. We note that the solidification shows some anomalies (see figure 5.3.1) which are not physical. These anomalies are the result of the important temperature gradient that we introduced to avoid breaking the cell during the solidification process. The curves of resistivity versus temperature are approximated by a polynomial interpolation in the liquid and solid states. The polynomial coefficients are presented in table 5.1 for the liquid state, and are valid between 250°C and 1000°C. In table 5.2, the polynomial coefficients for the solid state are shown, which are valid from room temperature to the melting point.

5.3.2 Absolute thermoelectric power (Seebeck coefficient)

<table>
<thead>
<tr>
<th>Liquid state</th>
<th>A</th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$B_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Sn_{95.3}Ag_4Cu_{0.7}$</td>
<td>0.1058</td>
<td>-0.00324</td>
<td>2.12757E-6</td>
<td>0</td>
</tr>
<tr>
<td>$Sn_{99}Cu_1$</td>
<td>2.59981</td>
<td>-0.01628</td>
<td>2.40769E-5</td>
<td>-1.17652E-8</td>
</tr>
<tr>
<td>$Sn_{96}Ag_4$</td>
<td>-0.03763</td>
<td>-0.00125</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$Sn_{96.75}Ag_{1.25}Cu_2$</td>
<td>0.37591</td>
<td>-0.00396</td>
<td>2.75039E-6</td>
<td>0</td>
</tr>
<tr>
<td>$Sn_{95}Sb_5$</td>
<td>0.94912</td>
<td>-0.00585</td>
<td>4.04138E-6</td>
<td>0</td>
</tr>
<tr>
<td>$Sn_{60}Pb_{40}$</td>
<td>-0.71085</td>
<td>-0.00151</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$Sn_{97}Cu_3$</td>
<td>1.54883</td>
<td>-0.01062</td>
<td>1.57566E-5</td>
<td>-8.00669E-9</td>
</tr>
</tbody>
</table>

Table 5.3: Polynomial coefficients adjusted on the experimental ATP’s of different LFS compositions in the liquid state, with $S = A + B_1.T_C + B_2.T_C^2 + B_3.T_C^3(\mu V/K)$

The absolute thermoelectric power of solder alloys (LFS and Sn-Pb) were measured simultaneously with electrical resistivity as a function of temperature. The results of these measurements while passing from the liquid state to the solid state are shown in figure 5.3.3. The curves of thermoelectric power versus temperature are approximated by a polynomial interpolation. The coefficients are reported in table 5.3 for the liquid state and in table 5.4 for the solid state. We note that the ATP of the $Sn_{60}Pb_{40}$ alloy is more negative than that of lead-free solder alloys in the liquid state; however, all values are comparable in the solid state.
Chapter 5. Electronic transport properties of lead-free solders in liquid and solid states

<table>
<thead>
<tr>
<th>Solid state</th>
<th>A</th>
<th>B₁</th>
<th>B₂</th>
<th>B₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn₉₅.₃Ag₄Cu₀.₇</td>
<td>-1.21912</td>
<td>0.00113</td>
<td>-1.22147E-5</td>
<td>0</td>
</tr>
<tr>
<td>Sn₉₉Cu₁</td>
<td>-1.12599</td>
<td>-0.00177</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sn₉₆Ag₁</td>
<td>-0.93375</td>
<td>-7.3919E-4</td>
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<td>0</td>
</tr>
<tr>
<td>Sn₉₆.₇₅Ag₁.₂₅Cu₂</td>
<td>-0.90475</td>
<td>-0.0022</td>
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<td>0</td>
</tr>
<tr>
<td>Sn₉₅Sb₅</td>
<td>-0.77495</td>
<td>-0.0051</td>
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<td>0</td>
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<tr>
<td>Sn₆₀Pb₄₀</td>
<td>-1.05439</td>
<td>-1.4195E-4</td>
<td>0</td>
<td>0</td>
</tr>
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<td>Sn₉₇Cu₃</td>
<td>-1.7197</td>
<td>0.01596</td>
<td>-1.42801E-4</td>
<td>3.55243E-7</td>
</tr>
</tbody>
</table>

Table 5.4: Polynomial coefficients adjusted on the experimental ATP’s of different LFS compositions in the solid state, with \( S = A + BₑT + B₂T^2 + B₃T^3 (\mu V/K) \)

Figure 5.3.3: ATP of lead-tin and of LFS’s in the liquid and solid states
5.3 Experimental results

Figure 5.3.4: Thermal conductivity of different liquid and solid lead-free solders

Figure 5.3.5: Thermal conductivity of different lead-free solders in the solid state
Chapter 5. Electronic transport properties of lead-free solders in liquid and solid states

### Table 5.5: Coefficients of polynomials adjusted on the thermal conductivity of solders in the solid state, with \( \lambda = p_1 + p_2 \sqrt{T} + p_3 T + p_4 T^2 + p_5 T^3 + p_6 T^4 \)

<table>
<thead>
<tr>
<th>Solid state</th>
<th>( p_1 )</th>
<th>( p_2 )</th>
<th>( p_3 )</th>
<th>( p_4 )</th>
<th>( p_5 )</th>
<th>( p_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Sn_{99}Cu_1 )</td>
<td>65.65225</td>
<td>0.27191</td>
<td>-0.029532</td>
<td>-0.1498E-3</td>
<td>2.5825E-7</td>
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<td>( Sn_{96}Ag_4 )</td>
<td>59.56277</td>
<td>0.52336</td>
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</tr>
<tr>
<td>( Sn_{60}Pb_40 )</td>
<td>48.40991</td>
<td>0.14599</td>
<td>0.010552</td>
<td>-0.4602E-3</td>
<td>9.1703E-7</td>
<td>0</td>
</tr>
<tr>
<td>( Sn_{95}Sb_5 )</td>
<td>40.44278</td>
<td>0.43676</td>
<td>-0.002786</td>
<td>-0.6041E-4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( Sn_{96.75}Ag_{1.25}Cu_2 )</td>
<td>61.51759</td>
<td>0.08271</td>
<td>0.016408</td>
<td>-0.4211E-3</td>
<td>1.0911E-6</td>
<td>-1.0852E-9</td>
</tr>
<tr>
<td>( Sn_{95.3}Ag_4Cu_{0.7} )</td>
<td>54.66221</td>
<td>0.05487</td>
<td>0.163378</td>
<td>-0.1349E-2</td>
<td>2.3368E-6</td>
<td>0</td>
</tr>
<tr>
<td>( Sn_{97}Cu_3 )</td>
<td>64.34624</td>
<td>-0.24284</td>
<td>-0.00403</td>
<td>0.00001</td>
<td>-5.7929E-7</td>
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</table>

### Table 5.6: Coefficients of polynomials adjusted on the thermal conductivity of solders in the liquid state, with \( \lambda = p_1 + p_2 \sqrt{T} + p_3 T + p_4 T^2 + p_5 T^3 \)

<table>
<thead>
<tr>
<th>Liquid state</th>
<th>( p_1 )</th>
<th>( p_2 )</th>
<th>( p_3 )</th>
<th>( p_4 )</th>
<th>( p_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Sn_{99}Cu_1 )</td>
<td>11.72815</td>
<td>0.64031</td>
<td>0.019881</td>
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<td>0</td>
</tr>
<tr>
<td>( Sn_{96}Ag_4 )</td>
<td>11.34472</td>
<td>0.65102</td>
<td>0.017784</td>
<td>-4.8270E-6</td>
<td>0</td>
</tr>
<tr>
<td>( Sn_{60}Pb_40 )</td>
<td>9.56235</td>
<td>0.51364</td>
<td>0.016063</td>
<td>-3.9743E-6</td>
<td>0</td>
</tr>
<tr>
<td>( Sn_{95}Sb_5 )</td>
<td>10.98689</td>
<td>0.59919</td>
<td>0.018789</td>
<td>-4.9764E-6</td>
<td>0</td>
</tr>
<tr>
<td>( Sn_{96.75}Ag_{1.25}Cu_2 )</td>
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<td>( Sn_{97}Cu_3 )</td>
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<td>0.12823</td>
<td>-0.00015</td>
<td>1.2154E-8</td>
</tr>
</tbody>
</table>

96
5.3 Experimental results

5.3.3 Thermal conductivity

The thermal conductivity was deduced from the resistivity and from the Absolute Thermoelectric Power (ATP) values. The formula used to get the thermal conductivity is: 
\[ \lambda = \frac{L_0 - S^2}{\rho} \cdot T \], where \( L_0 \) is the Sommerfeld value of the Lorentz number, \( T \) the temperature in Kelvin and \( S \) is the ATP. This formula is used only when experimental thermoelectric power is available (the thermoelectric power was measured in solid and liquid states, but not during solidification). During the solidification phase, we used the approximate Wiedemann-Franz law: 
\[ \lambda = \frac{L_0 \cdot T}{\rho} \] when the thermo-electric power data were not measured (there is very little difference with the full expression). Giordanengo et al. [52] discussed the accuracy of this method compared to the direct experimental determination of thermal conductivity. The inaccuracy of this formula is of the same magnitude as the inaccuracy of the direct experimental determination of the thermal conductivity, which is estimated at \( U(\lambda) / \lambda \approx 3\% \).

Figure 5.3.4 presents the thermal conductivity of the solders in the liquid and solid states, while figure 5.3.5 shows the thermal conductivity only in the solid state. Thermal conductivity increases in accordance with the temperature in the liquid state and likewise decreases in the solid state. It is important to note that the thermal conductivity of the various lead-free solders, "LFS", is higher than that of traditional solders in the liquid and solid states, with the exception of the Sn-Sb alloy, which has a lower conductivity than that of the Sn-Pb alloy in the solid state. The thermal conductivity of lead-free solders is about 20% to 30% higher than the Sn-Sb alloy in the liquid state. LFS are better heat conductors. The thermal conductivity as function of temperature is approximated by a polynomial interpolation. The polynomial approximation uses a square root as the first term in order to accurately represent the convexity of the experimental curve. The degree of the polynomial used is determined in order to obtain a correlation coefficient higher than 0.995 in the liquid state. Polynomial expansion parameters in the solid state are valid between 20°C and the melting point, with accuracy above 0.9%. These parameters are shown in table 5.5. In table 5.6, polynomial expansion parameters in the liquid state are presented; this polynomial is valid between the melting point and 1000°C.
5.4 Theoretical interpretation

Within the framework of the free electron theory, the resistivity and the thermopower of pure metals are given by the Ziman formula. The thermopower "S" is written as function of the thermoelectric parameter \( \chi \), where \( \chi = 3 - 2\alpha - \beta/2 \).

The term \( \beta \) expresses the energy dependence. Generally, this term is very difficult to calculate. In the Faber Ziman [49] formula (Ziman formula extended to alloys), we dealt with three partial structure factors characterising the relative position of ions, and two form factors characterising the interaction between electrons and ions screened by the free electron gas "in the alloy". The simplest form factor is that which can be calculated from the Ashcroft potential [48]. Parameter \( R_C \) is the "core radius". Ashcroft proposed to take

\[
\chi = 3 - 2\alpha - \frac{\beta}{2}
\]

<table>
<thead>
<tr>
<th>pure elements</th>
<th>( R_C \left( 10^{-10} \right) ) (m)</th>
<th>( \Gamma )</th>
<th>( R_C \left( 10^{-10} \right) ) (m)</th>
<th>( \Gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>0.66069</td>
<td>0.05411</td>
<td>0.67864</td>
<td>0.06815</td>
</tr>
<tr>
<td>Cu</td>
<td>0.46139</td>
<td>-0.83551</td>
<td>0.90674</td>
<td>0.17029</td>
</tr>
<tr>
<td>Ag</td>
<td>0.88314</td>
<td>-1.03260</td>
<td>0.92721</td>
<td>0.40586</td>
</tr>
<tr>
<td>Sb</td>
<td>0.73298</td>
<td>-0.01051</td>
<td>0.71819</td>
<td>-0.02705</td>
</tr>
<tr>
<td>Pb</td>
<td>0.76368</td>
<td>0.19407</td>
<td>0.53787</td>
<td>0.21135</td>
</tr>
</tbody>
</table>

Table 5.7: Ashcroft radius \( R_C \) and energy dependent parameter \( \Gamma \) adjusted to the experimental resistivity \( (R_C) \) and thermopower \( (\Gamma) \) of pure elements at 250°C and 800 °C

<table>
<thead>
<tr>
<th>Alloys</th>
<th>( \rho_{mesure} )</th>
<th>( \rho_{calcul} )</th>
<th>( \rho_{mesure} )</th>
<th>( \rho_{calcul} )</th>
<th>( S_{mesure} )</th>
<th>( S_{calcul} )</th>
<th>( S_{mesure} )</th>
<th>( S_{calcul} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn99Cu1</td>
<td>48.3626</td>
<td>50.4641</td>
<td>62.9291</td>
<td>65.0854</td>
<td>-0.3367</td>
<td>-0.2956</td>
<td>-0.9839</td>
<td>-0.8729</td>
</tr>
<tr>
<td>Sn97Cu3</td>
<td>48.1895</td>
<td>49.7520</td>
<td>63.36904</td>
<td>65.2175</td>
<td>-0.4795</td>
<td>-0.2982</td>
<td>-0.9622</td>
<td>-0.9568</td>
</tr>
<tr>
<td>Sn95Sb5</td>
<td>51.6912</td>
<td>52.3189</td>
<td>65.9275</td>
<td>65.5962</td>
<td>-0.3782</td>
<td>-0.1962</td>
<td>-1.1091</td>
<td>-0.6630</td>
</tr>
<tr>
<td>Sn60Pb40</td>
<td>59.9624</td>
<td>59.3613</td>
<td>76.2421</td>
<td>73.0983</td>
<td>-0.7533</td>
<td>-1.3310</td>
<td>-1.86436</td>
<td>-2.8286</td>
</tr>
<tr>
<td>Sn96Ag4</td>
<td>50.0101</td>
<td>50.1937</td>
<td>64.1578</td>
<td>64.4610</td>
<td>-0.1794</td>
<td>-0.2629</td>
<td>-1.0061</td>
<td>-1.1285</td>
</tr>
</tbody>
</table>

Table 5.8: Experimental and calculated resistivities and ATP’s at 250 and 800 °C
into account an energy dependence of the $R_C$ parameter through a parameter called $\Gamma$. This parameter allows the energy-dependent term $\beta$ to be calculated analytically. This calculation was described by Gasser [44] (chap2, page 65) and by Sar and Gasser [53] in the equation (16, 17). Parameter $R_C$ of each metal was chosen in order to fit the experimental resistivity of each pure element at the chosen temperature. Parameter $\Gamma$ was fitted on the experimental thermopower of each pure element with the same $R_C$ previously determined. As a result, the calculated values in alloys exactly fit the experimental resistivity and thermopower of pure metals. A difference can only occur at other concentrations. Partial structure factors were calculated from the hard sphere model. The packing faction $\eta$ was determined for pure metals by Waseda’s temperature dependent formula (3.1.1 page 59) [38] which was fitted on the structure factors at different temperatures. The atomic volume $\Omega_i$ is obtained from the experimental density of Crawley [37]. Pure metal "hard sphere diameters" $\sigma_i$ are deduced at each temperature from $\eta_i$ and $\sigma_0_i$ and are kept constant at a given temperature in regards to concentration. This method gives good results if the liquidus phase diagram shows small variations in concentration. This is not the case for Sn-noble metal alloys. For example, the melting temperature of copper is 1083°C, while that of tin is 230°C. In this case, the use of the method above leads to a non-physical partial packing fraction for the noble metal at 230°C. Therefore, we introduced a term that we called "the liquidus correction" which aims to keep $\sigma$ constant on the liquidus curve (and not at a constant temperature), or more generally, at a constant temperature distance from the liquidus curve.

During our project, we limited the number of the compositions to six industrial alloys. We did not study the entire system, we only selected the compositions likely to replace traditional solders. We determined parameters $R_C$ and $\Gamma$ of the pure metals of various components at 250°C and 800°C and compared both experimental and calculated data for the binary alloys.

5.5 Conclusion

- The lead-free solder alloys studied in this work show lower resistivity relative to the $Sn_{60}Pb_{40}$ alloy in the liquid and solid states, with the exception of the $Sn_{95}Sb_5$ alloy in the solid state. Lower resistivity favours the use of lead-free alloys in solders.
Among the alloys studied, the $Sn_{99}Cu_1$ alloy is the best conductor of electricity due to its low resistivity. The gain is 30%.

Concerning the theoretical interpretation of lead-free alloys, calculated results of the electronic transport properties were compared to the experimental data and were found to be coherent. The difference between the calculated and the experimental results is less than 5%; this difference is due to the liquidus correction. However, it must be noted that parameters $R_{ci}$ were adjusted to reproduce the resistivity of pure metals. The difference may be due to an incorrect description of the alloys’ atomic structure by using the hard sphere model or an incorrect extrapolation of the noble metal packing fraction at temperatures lower than their melting point.

The difference between the calculated and measured values of the thermoelectric power may be due to the same reasons as the values for resistivity. The thermal conductivity was deduced from our experimental data on the resistivity and the absolute thermoelectric power $ATP$. Lead-free solders are better thermal conductors than the Sn-Pb alloy, with the exception of the Sn-Sb alloy in the solid state. There is a noticeable increase in thermal conductivity (about 20% to 30%).
Chapter 6

Surface and interfacial tension; wetting and spreading ability

6.1 Introduction

The surface tension of metals and liquid alloys is a very important parameter in many industrial processes and material processing, particularly in the soldering of electronic components. It is a relevant property which indirectly plays a role in defining the wettability of liquids. It is essential to determine the surface tension, as this influences the phenomenon of wetting or "the aptitude of a liquid to wet the substrate surface". Wetting is an essential parameter in the assembly of solid parts through brazing. In addition, there are many processes related to soldering, in which a metal or an alloy is dispersed in the form of droplets, such as gas jet atomization, turning disc, and revolving consumable electrode, among others. Once formed, these droplets can either be solidified to obtain a powder, or projected on a surface to create a coating. The common point of these processes is the creation of a free surface quantity of the molten metal, and so the surface tension is, for this reason, a key factor in the formation and the distribution of drop size. The characteristics of liquid surfaces are fundamental physical properties. These can be classified under three headings: capillarity, wetting and adsorption.
6.2 Phenomenon of capillarity

The free surface of a liquid in contact with a partition is curved, which is due to capillary forces. These forces also explain the formation of the liquid free surface in a tube, its rise in a porous solid and the formation of the bubbles.

6.2.1 Surface tension

The origin of surface phenomena is due to molecular interaction. Indeed, inside a liquid, each molecule is subjected to the attraction of all the molecules which surround it, each one maintains the surrounding molecules by thermal agitation. On the whole, the interactions have no statistical effect on any of the directions (fig. 6.2.1). On the contrary, the molecules at the surface are subjected to an asymmetrical action (there is practically no attraction from the interface in contact with vapour); they tend to be attracted to the liquid medium. This is why a liquid always strives to achieve its lowest energy configuration by reducing its surface area. The molecules located at an interface such as those between the air and the liquid do not have the same environment as those "in a volume". Creating an interface results in a loss of surface energy, which is proportional to the surface area. To increase the surface by a quantity dS, energy should be provided: \( \delta W = \sigma dS \), where \( \sigma \) is called interfacial tension for a liquid-liquid or solid-liquid interface, or surface tension for a liquid-gas interface. Surface tension \( \sigma \, (N/m) \) can also be defined in terms of force per unit of length. To move the limit of a surface of a quantity dx, it is necessary to provide a force proportional to the length L of the displaced line, which is shown as:

Figure 6.2.1: Energy interaction between molecules in bulk and at the surface
6.3 Wetting

\[ \delta W = F \, dx = \sigma \cdot l \, dx. \] Measurement methods of \( \sigma \) are based on this second definition. The surface tension depends on the nature of the liquid and the thermodynamic conditions (temperature, pressure...).

6.2.2 Mechanical equilibrium condition of an interface: the Laplace equation

The interface formed between two liquid phases is described by the Laplace equation (exp. [54]) provided that the external field is a pure gravitation field, then the equation is written as:

\[ \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P = \Delta \rho g x + \Delta p, \] (6.2.1)

\( x \) is the co-ordinate parallel with the direction of the force of gravitation, while \( R_1 \) and \( R_2 \) are the principal curvature radii of a surface. The average curve by \( R \) is indicated as: \( 1/R = 1/R_1 + 1/R_2 \), while \( g \) is the acceleration of gravity.

The pressure on the concave side is greater than on the convex side of the liquid surface. This fundamental equation of capillarity is written when there is a spherical drop of radius \( R \): \( \Delta p = \frac{2\sigma}{R} \). The Laplace formula expresses the increase in the hydrostatic pressure \( \Delta p \), which occurs when the separation surface between the two fluids is crossed. It connects \( \Delta p \) and \( \sigma \) at a surface point. The formula is applicable only when the actual surface weight is neglected.

6.3 Wetting

Wetting is a drop of liquid’s capacity to be spread out perfectly smoothly and homogeneously over a flat solid substrate and characterized by the contact angle \( \theta \) formed with the triple line of the system made up of the liquid (L), the solid (S) and the vapour phase (V). Two thermodynamic states can exist:

**Total wetting**: liquids with low surface tension readily wet most solids, giving a contact angle of zero (6.3.1). The final state is a thin film which results from competing molecular and capillary forces [55].

**Partial wetting**: The drop refuses to be spread out (fig. 6.3.2), and at equilibrium, forms a portion of a sphere which is pressed onto the solid by forming a finite contact
angle $\theta$. The liquid is known as wetting if the contact angle is lower than 90° and non wetting if it is higher than 90°.

![Figure 6.3.1: Total wetting](image1)

![Figure 6.3.2: Partial wetting](image2)

### 6.3.1 Young’s Law

When a drop of liquid is put on a plane solid, it adopts a contact angle. As this configuration corresponds to a minimum of surface energy, an infinitesimal displacement of the contact system will not cause any variation in energy (work calculation method).

By moving the contact system of $dx$ (fig. 6.3.3), the work variation brought on by this displacement is given by:

$$\delta W = (\sigma_{SV} - \sigma_{SL})dx - \sigma \cos \theta . dx \quad (6.3.1)$$

In this equation $\sigma_{SL}$, $\sigma_{SV}$ and $\sigma$ indicate respectively the solid/liquid, solid/air and liquid/air interfacial tensions. It is this last quantity which is indicated by surface tension. At equilibrium this work is equal to zero, which leads to the most well-known Young equation 6.3.2 (the equilibrium of capillary forces). By balancing the capillary forces acting on the contact system (triple line) per unit of length, forces (which are the interfacial tensions between the three phases S/L/V) are obtained. The projection of these three forces on the solid plane, gives us Young’s equation (1805).

$$\sigma \cos \theta = \sigma_{SV} - \sigma_{SL} \quad (6.3.2)$$

### 6.3.2 Adhesion and cohesion works

Wetting can be connected to the energies of interactions within the liquid and in the interface liquid-solid using the transformation described in figures 6.3.4 and 6.3.5. Here, let us consider a system made up of two phases: one liquid and the other solid.
6.3 Wetting

Figure 6.3.3: The contact angle at equilibrium (full line) and the work needed to move the interface

Figure 6.3.5 shows magnitude $W_a$, called "adhesion work", which directly reflects the intensity of the interactions between the atoms of the liquid and the solid through the common interface.

$$W_a = \sigma_{LV} + \sigma_{SV} - \sigma_{SL} \quad (6.3.3)$$

In the figure 6.3.4, the quantity $2\sigma_{LV}$ is cohesion work $W_c$, which takes into account the intensity of the interactions within the same liquid:

$$W_c = 2\sigma_{LV} \quad (6.3.4)$$

The fundamental Young-Dupré equation for wetting (eq. 6.3.5) is obtained from the adhesion work equation 6.3.3 and Young equation 6.3.2.

$$\cos \theta = \frac{W_a}{\sigma_{LV}} - 1 \quad (6.3.5)$$

This equation shows that wetting in a system (S/L/V) results from the competition between the adhesion forces between liquids and solids (which favours wetting) and the
cohesion forces between the molecules of the liquid (which, while trying to minimize liquid/vapour surface, impairs the formation of a common interface with the solid).

The thermodynamic adhesion work and interfacial energies $\sigma_{SL}$ and $\sigma_{SV}$ are not easily measurable. On the other hand, the contact angles and surface energies of the liquids can be obtained by different experimental methods. Sessile drop is among the methods used the most at high temperatures. A liquid will wet a solid easily, if the solid has a surface energy higher than that of the liquid. Indeed, the adhesion between a solid and a liquid is greater than the cohesion between the molecules of the liquid.

### 6.4 Capillary length

Capillary length corresponds to the length from which a liquid surface is not disturbed any more. It can be explained by the fact that beyond this length, gravity increases in comparison to surface tension. The capillary length, noted $\kappa^{-1}$, is defined as the boundary above which the effects related to surface tension become negligible. The equality of the Laplace pressure and hydrostatic pressure leads to the relation:

$$\kappa^{-1} = \sqrt{\frac{\sigma}{\Delta \rho \cdot g}} \quad (6.4.1)$$

where $\Delta \rho$ is the difference in density between the two fluids.
6.5 Meniscuses

A molten liquid is often contained in a solid container. Because of gravity, the surface of the liquid is horizontal, except near the container’s walls, where Young’s relation explains a deformation. For a fairly wetting liquid $\theta < 90^\circ$, the liquid will rise in the tube, whereas the liquid will go down if it is non-wetting $\theta > 90^\circ$. The zone where the surface is curved is called the meniscus.

The shape of the meniscus results from an equilibrium between the capillary forces responsible for its existence and the gravity which opposes its formation.
Principal of measurement
6.6 Principal methods of measuring surface properties

There are many methods to measure surface tension [56]. They can be classified according to various criteria, and the first subdivision can separate the dynamic from the static or quasi-static methods. For molten metals at high temperatures, in general, static processes are used over dynamic processes. In the dynamic process, the surface of the liquid is constantly renewed, not allowing time for the adsorption layer to be formed. As a result of this, this process is less sensitive to the presence of surface impurities. Dynamic processes are adapted to measuring the surface tension of aqueous solutions of organic substances at low temperatures.
There are indirect methods to measure the surface and interfacial tension, which are based on the experimental measurement of the force exerted on the rod immersed into liquid solder. Wilhelmy plate and Noüy rings are among the most well-known indirect methods of measurement. A new adapted immersion method was used in this research. The difference between the aforementioned methods and the method we used is in the type of immersion device (a cylindrical rod with a stamp) and in the analysis of the experimental results as well as ideal models used. This method is described in detail [57, 58]. Before presenting the analytical details of the experimental results as well as the necessary theoretical bases and models, the principle of measurement needs to be briefly explained so as to extract the surface and interfacial tension starting from a typical curve. We described the principles as well as the processes of measurement in detail [59]. (§ 6.7 to 6.12 of the French version of the thesis are not presented here).
Surface tension and density of binary lead and lead-free Sn-based solders

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Abstract

The surface tension and density of the liquid Sn60Pb40, Sn90Pb10, Sn96.5Ag3.5 and Sn97Cu3 solder alloys (wt%) have been determined experimentally over a wide temperature interval. It is established that the surface tension of liquid Sn90Pb10 is about 7% higher than that of a traditional Sn60Pb40 solder and that the surface tension of Sn96.5Ag3.5 and Sn97Cu3 alloys is about 12% higher than that of Sn60Pb40. The analytical expressions for the temperature dependences of the surface tension and density are given.

1. Introduction

In accordance with the Directives of the European Parliament and of the Council on ‘waste electrical and electronic equipment’ and on ‘restriction of use of certain hazardous substances’, lead will be banned from production of new electrical and electronic devices from 1 July 2006 [1]. The traditional lead–tin solders have to be replaced with new solders, free of lead. Other alloys with a melting temperature close to the commonly used Sn–Pb eutectic and having appropriate properties should be found. For industrial usage of a new soldering material its physical properties (electrical, chemical, thermal, mechanical etc) in the solid as well as in the liquid state should be well known. Therefore many potential candidates for lead-free solders are being intensively studied in various laboratories.

Among the most important physical properties and phenomena playing a crucial role in the soldering process are the surface tension and the wetting behaviour of the solder. In this work we study the surface tension of liquid Sn96.5Ag3.5, Sn97Cu3, Sn90Pb10 in comparison with the surface tension of the classical solder Sn60Pb40 (here and further all compositions are given in weight per cent). The densities of the alloys investigated are also reported.

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2. Measurement technique

2.1. Surface tension determination

The surface tension of liquid alloys was determined with a tensiometric method described in detail in \cite{2, 3}. The principles of the experimental set-up and measuring process are shown schematically in figures 1 and 2. The technique is based on the experimental measurement of the force exerted on the alumina stamp submerged below the level of the free liquid surface. It is noteworthy that in this method a complete set of experimental data (force as a function of the stamp height) are analysed, and not just a maximum force. The stamp’s form, as shown in figure 2, allows the investigation of meniscus formation and contraction up to the complete tearing of the stamp away from the surface. Thus, the force of interaction of the stamp with the liquid sample $F_{\text{exp}}$ is determined as a function of the stamp’s height $h$ with respect to the position of the crucible.

As an example, the experimental curve for liquid Sn$_{96.5}$Ag$_{3.5}$ at 550°C is shown in figure 2. The force $F_{\text{exp}}$ measured with the balance initially set to zero is the resultant of the Archimedes buoyancy force $F_A$ and the force caused by the meniscus $F_{\text{Men}}$:

$$F_{\text{exp}} = F_A + F_{\text{Men}}.$$  \hspace{1cm} (1)

The buoyancy force equals

$$F_A = \Delta \rho g V_A$$  \hspace{1cm} (2)

where $V_A$ is the volume of the stamp submerged into the melt, $g$ is the gravitational acceleration, $\Delta \rho = \rho - \rho_v$ is the density difference between the liquid phase ($\rho$) and the vapour phase ($\rho_v$).

The force caused by the meniscus can be expressed on the one hand through the contact angle $\Theta$ by the equation:

$$F_{\text{Men}} = \sigma 2\pi r_s \cos \Theta$$  \hspace{1cm} (3)
where $\sigma$ is the surface tension and $r_s$ is the radius of the stamp. On the other hand, the force on the part of surface acting on the stamp in the vertical direction is equal to the weight of the meniscus with volume $V_{\text{Men}}$:

$$F_{\text{Men}} = \Delta \rho g V_{\text{Men}}. \quad (4)$$

The relation between the shape of the meniscus and the force exerted by the meniscus on the stamp underlies the basis of the applied measurement technique.

Thus the volume of the meniscus can be calculated with equation (4) if the buoyancy and geometry of the crucible and of the stamp are taken into account. After transformation of coordinates, the volume of the meniscus $V_{\text{Men}}^{\text{exp}}$ is determined as a function of the height of the contact line $x_0$. This transformation is performed for the subsequent comparison of the experimental meniscus volume $V_{\text{Men}}^{\text{exp}}(x_0)$ with the modelled volumes $V_{\text{Men}}^{\text{model}}(x_0)$ in the same coordinates.

The meniscus is modelled by the numerical solution of the Laplace equation of capillarity, which describes the pressure difference $\Delta p$ across the curved liquid–vapour interface:

$$\sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta p = p_1 - p_2, \quad (5)$$

where $R_1$ and $R_2$ are the principal radii of curvature of the interface; $p_1$ and $p_2$ are, respectively, the pressure on the concave and the convex sides of the meniscus. Owing to the cylindrical
Figure 3. The experimental meniscus volume curve for the liquid Sn_{96.5}Ag_{3.5} at 550 °C compared to the volume curves modelled for various capillary constants.

form of the stamp, the solution of equation (5) is reduced to a one-dimensional problem, so the Laplace equation contains the curvature radii and a linear gravitation component:

\[ \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta \rho g x, \]  

where \( x \) is a coordinate in the direction of the gravitation force (i.e. along the axis of symmetry). Replacing the principal radii of curvature by the differential geometry expressions, one obtains the following equation [2–5]:

\[ \frac{x'}{r(1+x'^2)^{1/2}} + \frac{x''}{(1+x'^2)^{3/2}} = \frac{\Delta \rho g}{\sigma} x, \]  

where \( r \) is the radial distance in a horizontal plane from the axis of symmetry \( r^2 = y^2 + z^2 \), \( x' = dx/dr \), \( x'' = d^2x/dr^2 \).

The numerical solution of equation (7) allows modelling of the radial-symmetrical meniscus and calculation of the dependence of its volume on the height of the contact line \( x_0 = V_{\text{Men}}^{\text{model}}(x_0) \), for different radii of the contact line (i.e. for different stamps) and for various values of the capillary constant \( a \), which is defined as

\[ a = \frac{\sigma}{\Delta \rho g} \approx \frac{\sigma}{\rho g} \]  

since the vapour phase density can be neglected.

Comparison of the experimental volume curves \( V_{\text{Men}}^{\text{exp}}(x_0) \) with the volumes of menisci modelled for the size of the stamp used \( V_{\text{Men}}^{\text{model}}(x_0) \) results in the determination of the capillary constant for the liquid studied, as shown for example in figure 3. The surface tension can be calculated from the capillary constant \( a \) with equation (8) when the density of the liquid is known.

2.2. Density determination

It is an advantage of the measurement technique that the density of a liquid being studied can be found from the same experimental data as are used for the determination of the capillary
constant. It is assumed that the shape of the meniscus and the surface tension are constant when the liquid surface moves along the cylindrical stamp (stages (C)–(D) in figure 2). At this stage, only the buoyancy force exerted by the liquid on the stamp immersed into it changes. Thus, from the linear part of the experimental curve, the variation of the measured force $F_{\text{exp}}$ with the height $h$ can be determined. Then the density of the liquid can be calculated using the expression

$$\rho = \frac{dF_{\text{exp}}}{dh} \frac{1}{g\pi} \left( \frac{1}{r_s^2} - \frac{1}{R_t^2} \right)$$

where $R_t$ and $r_s$ are the radii of the crucible and stamp, respectively. The experimental density is represented in figure 4.

3. Experimental details

Industrial lead-free solders Sn$_{96.5}$Ag$_{3.5}$, Sn$_{90}$Cu$_{10}$, Sn$_{90}$Pb$_{10}$ (Stoop n.v., a member of Fenix Metals) and Sn$_{96}$Pb$_{4}$ alloy prepared from pure Sn (99.99%) and Pb (99.999%) were used for the investigations.

The measurements have been performed in the tensiometer shown schematically in figure 1. Before heating, the chamber was evacuated to better than 5 × 10$^{-5}$ mbar and then filled with a gas mixture of Ar–10% H$_2$ with a total pressure of ~1 bar. Additionally a niobium getter was used to reduce the amount of oxygen that gets into the chamber through leaks during measurements. The heating system consisted of a concentric Kanthal heater outside the chamber, a power supply and an electronic temperature control device. The graphite crucible (5 cm inner diameter, 4 cm height) was moved by an ultrahigh vacuum manipulating system. The diameter of the working part of the alumina stamp was 15 mm and its height was 3 mm. The force exerted on the stamp was measured by a balance with an accuracy of 1 mg. The experimental error did not exceed ±3% for the surface tension and ±1.5% for the density.
Figure 5. The temperature dependences of the surface tension for the liquid alloys studied. The dashed lines are the linear fits (see table 1 for details).

4. Results and discussion

Experimental curves similar to those shown in figure 2 have been obtained for all alloys investigated. It is noteworthy that the forward and backward curves were smooth and coincided. The meniscus volumes $V_{\text{Men}}(x_0)$ were calculated from the experimental data and compared with the respective simulated functions $V_{\text{model}}(x_0)$. From the comparison, the capillary constants were determined. Then the surface tension of the alloys studied was calculated with equation (8) using the capillary constants and experimentally determined densities.

Figures 4 and 5 show the temperature dependences of the density and surface tension for the alloys studied. As one can see, both the surface tension and density decrease with increasing temperature. Obviously one can accept linear temperature dependences in the temperature intervals investigated. Therefore, for convenience of practical use the experimental values of $\sigma$ and $\rho$ were fitted with the linear functions $\sigma(T) = \sigma_0 - \frac{d\sigma}{dT}T$ and $\rho(T) = \rho_0 - \frac{d\rho}{dT}T$ ($T$ is the absolute temperature). The parameters $\sigma_0$ and $\rho_0$, the temperature coefficients $d\sigma/dT$ and $d\rho/dT$, and the errors of the fits are given in table 1. For comparison, the respective data for liquid Sn taken from [6] are presented in table 1.

The experimental results show that the surface tension of liquid Sn$_{96.5}$Ag$_{3.5}$, Sn$_{97}$Cu$_3$ and Sn$_{90}$Pb$_{10}$ is higher than that of a traditional Sn$_{60}$Pb$_{40}$ solder. For example, at 250 °C $\sigma$ (Sn$_{96.5}$Pb$_{35}$) = 477 mN m$^{-1}$, $\sigma$ (Sn$_{90}$Pb$_{10}$) = 508 mN m$^{-1}$, $\sigma$ (Sn$_{96.5}$Ag$_{3.5}$) = 532 mN m$^{-1}$, and at 350 °C $\sigma$ (Sn$_{97}$Cu$_3$) = 521 mN m$^{-1}$.

The very good agreement between the absolute values of the density for liquid Sn$_{98.5}$Ag$_{3.5}$ and Sn$_{90}$Pb$_{10}$ obtained in the present work and the published data [7, 8] confirms the reliability of the method applied for density determination (see figure 4). The reliability of the surface tension measurements is proven by a coincidence within 1% of our results for liquid Sn$_{98.5}$Ag$_{3.5}$ and the recent data [8] (see figure 5). The surface tension of liquid Sn$_{90}$Pb$_{10}$ measured by us (480 mN m$^{-1}$ at 200 °C) lies in a middle of the values from other works [9–12]. For example, $\sigma$ (Sn$_{60}$Pb$_{40}$) $\approx$ 507 mN m$^{-1}$ has been obtained at 215 °C [11] and $\sigma$ (Sn$_{65}$Pb$_{35}$) $\approx$ 461 mN m$^{-1}$ at 200 °C [12]).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{The temperature dependences of the surface tension for the liquid alloys studied. The dashed lines are the linear fits (see table 1 for details).}
\end{figure}
Table 1. The temperature dependences of the surface tension $\sigma(T)$ and the density $\rho(T)$ for the liquid alloys studied: the linear fits to the experimental data. The data for pure Sn are taken from [6].

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma_0$ (mN m$^{-1}$)</th>
<th>$d\sigma/dT$ ($10^{-2}$ mN m$^{-1}$ K$^{-1}$)</th>
<th>$\rho_0$ (g cm$^{-3}$)</th>
<th>$d\rho/dT$ ($10^{-4}$ g cm$^{-3}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>572 ± 3</td>
<td>7.6 ± 0.3</td>
<td>7.37 ± 0.06</td>
<td>8.2 ± 0.8</td>
</tr>
<tr>
<td>Sn0.5Ag3.5</td>
<td>580 ± 7</td>
<td>8.7 ± 0.9</td>
<td>7.48 ± 0.05</td>
<td>7.2 ± 0.8</td>
</tr>
<tr>
<td>Sn0.7Cu3</td>
<td>569 ± 8</td>
<td>7.6 ± 1.0</td>
<td>7.15 ± 0.07</td>
<td>4.0 ± 0.9</td>
</tr>
<tr>
<td>Sn0.5Pb10</td>
<td>543 ± 4</td>
<td>6.6 ± 0.5</td>
<td>7.54 ± 0.04</td>
<td>7.2 ± 0.6</td>
</tr>
<tr>
<td>Sn60Pb40</td>
<td>514 ± 2</td>
<td>7.1 ± 0.3</td>
<td>8.45 ± 0.02</td>
<td>7.6 ± 0.2</td>
</tr>
</tbody>
</table>

5. Summary

The surface tension and density of the liquid Sn$_{60}$Pb$_{40}$, Sn$_{90}$Pb$_{10}$, Sn$_{96.5}$Ag$_{3.5}$ and Sn$_{97}$Cu$_{3}$ solder alloys were determined over a wide temperature interval. The surface tension and the density of the alloys studied decrease with increasing temperature. The temperature dependences $\sigma(T)$ and $\rho(T)$ in the ranges investigated can be well approximated by linear functions. Comparison of the experimental data for the alloys studied shows that the reduction of the Pb content in the Sn–Pb soldering materials and, moreover, the change from Pb to Ag or Cu significantly increase the surface tension in the liquid state.

Acknowledgment

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References


6.7 Other experimental results

The experimental results of the surface tension (fig. 6.7.1) and density (fig. 6.7.2) of various binary alloys relative/related to the lead-free or tin-lead solder are presented [59]. In this section, this research is briefly supplemented with the yet-to-be-published results of the industrial ternary solder $Sn_{95.5}Ag_{3.8}Cu_{0.7}$ and a pure metal alloy $S\,Sn_{99.3}Cu_{0.7}$ [60] (measured by S. Grüner for pure metals). Details on the measurements are the same as for the other compositions of lead-free solders [59]. Generally, the surface tension of all lead-free solders is higher than that of the tin-lead solder, and the replacement of lead by copper or silver in tin-based solders results in an increase in the surface tension. Surface tension and density decrease according to the temperature. The surface tension values of all lead-free solders are close to each other (fig. 6.7.1).

![Figure 6.7.1: The surface tension of different lead-free solders](image)

Figure 6.7.1: The surface tension of different lead-free solders
Figure 6.7.2: The density of different lead-free solders
Contact angle and wetting
6.8 Measurements of wettability and their limitations

There are various experimental techniques to measure wettability. Only the most published methods are mentioned here. These methods fall into two categories: dynamic (Wilhelmy, Noüy, etc.) and static (sessile drop, bodies of immersion, maximum pressure of bubble, wrenching, capillary rise, etc.). In this work, we used the sessile drop method to measure the contact angle directly. The details of this method will be discussed in the following paragraphs.

6.8.1 Contact angle: the sessile drop method

This method is among those usually used for molten metals. It consists of using a CCD camera equipped with an enlargement optical device connected to a computer to follow the evolution of the profile of a drop deposited on a flat and horizontal substrate. If the interactions at solid/liquid interface do not cause an evolution of the contact angle with time, sessile drop technique constitutes a static measurement method of the contact angle. The measured angle $\theta$ evolves according to time until a certain value. It is correlated with both the reduction in height and the increase in the radius of the drop according to the time.

6.8.2 Drop Size

A liquid drop resting on a horizontal plane of substrate together form a contact angle $\theta$ determined by Young’s law (eq. 6.3.2). The shape of the drop will pass from a portion of a sphere to a more or less flattened form according to the dimension of its radius compared to the capillary length $\kappa^{-1}$.

1. **Small drops**: For small drops, the deformation under the effect of gravity is weak; only the capillary forces participate (gravity is negligible). This condition is checked when the height of the drop is lower than the capillary length $\kappa^{-1}$. Small drops have a low mass (not exceeding a few milligrams of metal), and their internal pressure is constant. According to the Laplace equation (eq. ??), the profile of the drop is also constant: a drop placed on a horizontal surface has a portion shape of a sphere.

2. **Large drops**: Gravitational forces dominate and consequently, the radius of the drop is greater than the capillary length. At equilibrium, the drop forms a liquid
wafer with a thickness $e$ (the drop is flat on top). The assessment of the acting forces consisted of the surface forces and the force $P$ due to the hydrostatic pressure integrated throughout the entire thickness of the liquid ($P = \frac{1}{2} \rho gc^2$). This kind of drop is better adapted for measuring surface tension than for the contact angle.

### 6.9 Method of measurement

In practice, the sessile drop method in its traditional version consists of placing a small piece of the solid solder onto a horizontal nickel or copper substrate, then heating it to above the melting point. So as to be able to negate the effects of gravity effects on drop shape, the choice of the solder’s mass is influenced by capillary considerations. It is also necessary to take into account the dimensions of the substrates which do not exceed 14 mm by 10 mm. Other difficulties were encountered during this phase of research, such as the heating time, the atmospheric conditions, oxides, and flux choice. Throughout these measurements, we studied the effects of the temperature, substrates and flux either in laboratory conditions (very clean solder under controlled atmospheric conditions), or in industrial conditions (on air with flux). The use of flux is among the essential conditions for industry.

### 6.10 Experimental equipment of Chemnitz

#### 6.10.1 The system

The principle consists of recording the profile of the liquid drop placed on a horizontal substrate at a given temperature. The equipment used for this measurement consisted of the following elements:

- An adjustable, horizontal furnace (on the three axes).

- A light source (a lamp) placed opposite the furnace.

- Along the optical axis at the other end of the furnace, a photographic lens attached to a CCD "camera" is installed.

- A vacuum/pressure chamber was connected to a quartz tube. This tube contained a cut ceramic tube. This part of the tube supported the solid substrate and the
6.11 Preparation of the samples

The solders were first cleaned mechanically, then with ethanol. The nickel and copper substrates were placed horizontally so as to not influence the wetting. They were cleaned with a mixture of \( HCl \) and \( HNO_3 \) then rinsed with methanol. Once the sample was placed in the suitable device and before moving the furnace towards the sample to heat it, we...
applied vacuum in the measuring chamber greater than $5 \times 10^{-5}$ mbar. As a precaution, a niobium getter was used to absorb the maximum oxygen remaining in the vessel as a result of micro-leaks or outgassing during measurements. Once an optimum vacuum was obtained, the heating phase began at a slope in increments of $5^\circ$C/min, then of $1^\circ$C/min $10^\circ$C below 250°C or 270°C to stabilize the drop profile. Then, at a given temperature, an image was taken every 2 to 5 minutes in order to check the influence that time has on the drop profile and on the contact angle.

6.12 Experimental results

The sessile drop experiments were carried out with two types of substrates (copper and nickel). We specifically chose these two substrates because they are usually used in the assembly of electronic printed circuits.

The melting point of the new lead-free solder is higher than that of the traditional solder (melting point between 207°C and 230°C, whereas that of the Sn$_{60}$Pb$_{40}$ solder is 186°C). We fixed these two working temperatures at 250°C and 270°C (more than 30°C to 50°C at the melting point) because they are those used in industry.

6.12.1 Contact angle under vacuum and without flux

The study of solder wetting under laboratory conditions (in vacuum and without flux) consists of measuring the contact angle of the deposited solder on a flat and horizontal substrate, and slowly heating it under vacuum conditions. Unfortunately, we were unable to have good wetting in a vacuum because of the limited temperature and the presence of oxides. That is why the measurements took longer under vacuum conditions. Figures 6.12.1 to 6.12.1 show the measurements of a lead-free solder ($Sn_{95.5}Ag_{3.8}Cu_{0.7}$) at various temperatures and at various moments. Figures SACtemps1, SACtemps2 and SACtemps6 show the profiles respectively at 200°C (solid), 250°C and 350°C in equilibrium. Figures SACtemps3 to SACtemps6 show the drop profile’s evolution over time. In laboratory conditions, more time was needed to stabilize the drop. The temperature where the drop is spread out is too high for industrial conditions (risk of burning the electronic cards) and the spreading time is too long. Table 6.1 shows the variation of the wetting contact angle versus time at 350°C. We noted that in laboratory conditions, it is necessary to wait
between 5 and 10 minutes in order to have contact angle stability. At a given temperature, the contact angle varied approximately 20 degrees throughout the 5 minute period. The fact that it remains at a high temperature for a long time can induce the dissolution of the substrates in the alloy and create inter-metallic compounds. In table 6.2, we summarize our results for the three alloys Sn$_{97}$Cu$_3$, Sn$_{95.5}$Ag$_{3.8}$Cu$_{0.7}$ and Sn$_{60}$Pb$_{40}$ studied under vacuum conditions. Two cases are worth noting:

For nickel substrates, the wetting of the two alloys (Sn$_{97}$Cu$_3$ et Sn$_{95.5}$Ag$_{3.8}$Cu$_{0.7}$), is

<table>
<thead>
<tr>
<th>time $t_i$</th>
<th>$\theta_{left}$</th>
<th>$\theta_{right}$</th>
<th>$\theta_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_1 = 0$</td>
<td>53.32 ± 2</td>
<td>49.86 ± 2</td>
<td>51.59 ± 2</td>
</tr>
<tr>
<td>$t_2 = 1$ min</td>
<td>43.32 ± 2</td>
<td>41.84 ± 2</td>
<td>42.58 ± 2</td>
</tr>
<tr>
<td>$t_3 = 2$ min</td>
<td>31.85 ± 2</td>
<td>33.24 ± 2</td>
<td>32.54 ± 2</td>
</tr>
<tr>
<td>$t_4 = 4$ min</td>
<td>30.53 ± 2</td>
<td>29.79 ± 2</td>
<td>30.16 ± 2</td>
</tr>
<tr>
<td>$t_5 = 5$ min</td>
<td>30 ± 2</td>
<td>29.95 ± 2</td>
<td>29.97 ± 2</td>
</tr>
</tbody>
</table>

Table 6.1: The effect of time on the wetting angle of Sn$_{95.5}$Ag$_{3.8}$Cu$_{0.7}$ on a copper substrate in a vacuum at 350°C
Chapter 6. Surface and interfacial tension; wetting and spreading ability

<table>
<thead>
<tr>
<th>Substrates/vacuum</th>
<th>$Sn_{60}Pb_{40}$</th>
<th>$Sn_{97}Cu_{3}$</th>
<th>$Sn_{95.5}Ag_{3.8}Cu_{0.7}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle/T(°C)</td>
<td>$\theta_{moy}/copper$</td>
<td>$\theta_{moy}/copper$</td>
<td>$\theta_{moy}/Nickel$</td>
</tr>
<tr>
<td>250</td>
<td>135.42 ± 6</td>
<td>–</td>
<td>127.84 ± 6</td>
</tr>
<tr>
<td>270</td>
<td>–</td>
<td>46.57 ± 6</td>
<td>–</td>
</tr>
<tr>
<td>350</td>
<td>134.81 ± 6</td>
<td>35.94 ± 6</td>
<td>104.23 ± 6</td>
</tr>
<tr>
<td>370</td>
<td>–</td>
<td>30.34 ± 6</td>
<td>–</td>
</tr>
<tr>
<td>400</td>
<td>52.57 ± 6</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>470</td>
<td>–</td>
<td>–</td>
<td>42.37 ± 6</td>
</tr>
</tbody>
</table>

Table 6.2: The wetting angle on copper and nickel substrates under vacuum conditions

very poor and remains "not-wetting" up to 400°C. Wetting took place at 470°C. It can be concluded that there is no wetting below 470°C under these conditions.

For copper substrates, wetting of the $Sn_{97}Cu_{3}$ alloy is good even at low temperatures (from 270°C until 370°C), which improves with the temperature. For the $Sn_{95.5}Ag_{3.8}Cu_{0.7}$ alloy, there is almost no wetting below 350°C (see table 6.2). The traditional solder $Sn_{60}Pb_{40}$ is a very poor wetter (almost no wetting below 400°C). This can be explained by the presence of an oxide layer on the solder or on the substrate. The improved spreading out at higher temperatures may be explained by the possibility that the oxide layers were reduced either by thermal decomposition or by dissolution in the solder.

Our results reveal that there is almost no wetting on either the copper or nickel substrates. The wetting on the copper substrate was nevertheless somewhat better than on nickel. It can also be concluded that the solder under vacuum conditions "without flux" is almost impossible on electronic circuits, whose temperature should not pass 270°C. The exception is tin-copper solder on copper substrate. There is no published explanation for this phenomenon.

This phenomenon is probably due to the fact that the existing amount of copper in the alloy $Sn_{97}Cu_{3}$ (3% in mass) is considerable compared to that of $Sn_{95.5}Ag_{3.8}Cu_{0.7}$ (0.5 à 0.7%). Indeed, copper reduces the brazing melting point and improves wettability. It also reduces the velocity of dissolution of the copper substrates in the solder alloy. The
presence of flux as well as the speed of measurement is of primary importance in producing a good solder.

6.12.2 Contact angle on air and with flux

The use of flux when measuring the contact angle under industrial conditions is of primary importance. It occurs in three ways:

- It eliminates the traces of oxide which obstruct the adhesion of the solder.
- It facilitates "wetting" i.e. the spreading out of the solder on the metal substrate.
- It protects the substrate and the solder from oxidation during the heating process.

We used a flux from the GLT Gesellechaft für Löttechnik mbH company (flux for soldering for electronic connections). The solder’s heating process covered by flux on the solid substrate was carried out quickly (a few tenths of second). Prolonged heating involved reactions between the substrate and the solder, and wetting did not take place. Measurements with flux follow the procedure described afterwards. First, the furnace was heated 20°C above the work temperature. Moreover, the sample was placed on the sessile drop measurement device of the sessile drop. Once the temperature was reached, the furnace was moved towards the device where the sample is. Generally, 10 to 20 seconds is enough for the solder to wet the substrate completely. Thereafter, the solder as well as the substrate were quickly cooled. The flux did not evaporate quickly and remained in liquid form. The sample was then cleaned with ethanol before taking images and determining the contact angle of the solidified solder. Measurements in the liquid state were not possible in the presence of flux. Table 6.3 presents the wetting angle of the various solders on air and with flux for a process which barely exceeded 10 to 20 s. Contrary to what was previously noticed under vacuum conditions with flux and on air, the $Sn_{95.5}Ag_{3.8}Cu_{0.7}$ solder wets the copper substrate better than $Sn_{97}Cu_{3}$ solder. We can postulate that when measurements are carried out under vacuum conditions over a certain amount of time, the copper of the substrate is dissolved in the solder, even more when the alloy is poor in copper. A two-part analysis of the experimental results will study the effects of temperature and substrates in industrial conditions. Table 6.3 gathers all of the results.
Chapter 6. Surface and interfacial tension; wetting and spreading ability

<table>
<thead>
<tr>
<th>Flux/Air</th>
<th>250°C</th>
<th>270°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle/Substrate (°C)</td>
<td>(\theta_{moy}/\text{Copper} )</td>
<td>(\theta_{moy}/\text{Nickel} )</td>
</tr>
<tr>
<td>(Sn_{\text{pur}})</td>
<td>38.37 ± 2</td>
<td>32.39 ± 2</td>
</tr>
<tr>
<td>(Sn_{60}\text{Pb}_{40})</td>
<td>17.37 ± 2</td>
<td>33.76 ± 2</td>
</tr>
<tr>
<td>(Sn_{97}\text{Cu}_{3})</td>
<td>33.88 ± 2</td>
<td>44.91 ± 2</td>
</tr>
<tr>
<td>(Sn_{99.3}\text{Cu}_{0.7})</td>
<td>31.53 ± 2</td>
<td>30.15 ± 2</td>
</tr>
<tr>
<td>(Sn_{96.5}\text{Ag}_{3.5})</td>
<td>28.42 ± 2</td>
<td>34.72 ± 2</td>
</tr>
<tr>
<td>(Sn\text{AgCu})</td>
<td>29.27 ± 2</td>
<td>30.98 ± 2</td>
</tr>
<tr>
<td>Brazing paste</td>
<td>20.46 ± 2</td>
<td>18.1 ± 2</td>
</tr>
</tbody>
</table>

Table 6.3: The wetting angle on copper and nickel substrates of the solidified solder after heating at 250°C and at 270°C under flux and in air.

obtained by this measurement technique (T = 250°C and 270°C, with flux and on air). It is essential to note that, contrary to soldering under vacuum in liquid and solidified states, the solders with flux and on air wet the nickel and copper substrates very well. The flux ensures a rapid and better quality wetting. The second observation that can be made from this experiment is the effect of substrate and temperature.

In general, wetting is better with copper substrates than with nickel substrates. The images in fig. 6.12.7, and 6.12.8 show a melted drop of \(Sn_{60}\text{Pb}_{40}\) at 200°C on nickel substrate and on copper substrate, respectively. The drop was spread out almost completely and covered the copper substrate while forming a portion of a sphere with contact angle \(\theta\) on the nickel substrate. Copper has more affinity with the solders than nickel. The wetting angle of the solidified solder is also influenced by the treatment temperature. The wetting angle decreases with the treatment temperature, and consequently, wettability increases with the temperature (tab. 6.3). \(Sn_{60}\text{Pb}_{40}\) solder always has a better wettability than lead-free solders. However, the solder obtained from the brazing paste possess properties close to the traditional solder \(Sn_{60}\text{Pb}_{40}\). Adhesion work values \(W_a\) (see table 6.4) were calculated from the equation 6.3.5 according to the surface tension and to the contact angle. The margin of error for \(W_a\) was estimated by allowing a margin of 2° for the measured contact angles, as well as the uncertainty of the measured surface tension.
6.13 Conclusions

[59]. It can be noted that if the contact angles are high (for example, measurements in a vacuum), a small uncertainty on $\theta$ led to a strong uncertainty on the adhesion work value.

<table>
<thead>
<tr>
<th>Substrat</th>
<th>Cuivre</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$_{pur}$</td>
<td>$\theta$ = 38.37 ± 2</td>
<td>$W_a$ (mJ.m$^{-2}$) = 948 ± 6</td>
</tr>
<tr>
<td>Sn$<em>{60}$Pb$</em>{40}$</td>
<td>$\theta$ = 17.37 ± 2</td>
<td>$W_a$ (mJ.m$^{-2}$) = 932 ± 6</td>
</tr>
<tr>
<td>Sn$<em>{97}$Cu$</em>{3}$</td>
<td>$\theta$ = 33.88 ± 2</td>
<td>$W_a$ (mJ.m$^{-2}$) = 968 ± 6</td>
</tr>
<tr>
<td>Sn$<em>{96.5}$Ag$</em>{3.5}$</td>
<td>$\theta$ = 28.42 ± 2</td>
<td>$W_a$ (mJ.m$^{-2}$) = 1000 ± 6</td>
</tr>
<tr>
<td>SnAgCu</td>
<td>$\theta$ = 29.27 ± 2</td>
<td>$W_a$ (mJ.m$^{-2}$) = 998 ± 6</td>
</tr>
</tbody>
</table>

Table 6.4: Contact angle and adhesion work obtained for the solders on the two kinds of substrates (copper and nickel) at 250°C

6.13 Conclusions

The study of surface tension is a necessary parameter in characterizing wettability. Liquids with low surface tensions favour wetting. Measuring the surface tension is essential to determine the interfacial tension. Indeed, this is difficult to determine directly. From the surface tension (liquid/vapour), contact angle (liquid/solid) and surface tension of the solid (solid/vapour) known as interfacial tension can be reached. In this chapter, we determined the adhesion energy, the surface tension, the contact angle and the density, but not the interfacial tension. During our measurements, we were able to conclude that the lead-free solders wet copper and nickel substrates better. Surface tension decreases with the lead composition of the liquid alloy. The addition of copper or silver results in an increase in surface tension.
The contact angle was determined by the traditional sessile drop method. Spreading out is influenced by several parameters (atmosphere, flux, mass, temperature and nature of the substrates...), but the effect of flux is predominant. According to adhesion work values, it can be noted that, with the exception of pure tin, solders have more affinity with copper than with nickel. Thus the interfacial tension $\sigma_{SL}$ between solders and copper substrate is lower than that between solders and nickel substrate with or without flux. The lead-free ternary with flux has a better wettability than the binary solders (Sn-Ag, Sn-Cu.). The treatment temperature notably improves the spreadability of a solidified solder, because with an increase of 20°C, the contact angle decreases about 10°. To conclude, lead-free solders with flux wet the substrates (Cu; Ni) less than the Sn-Pb solder. Nevertheless, wettability can be regarded as satisfactory, because their contact angles lie between 11° and 39°. In general, we have a good wetting when the contact angle is lower than 90°.

From this study, the three alloys esteemed to best replace lead-tin solder $Sn_{60}Pb_{40}$ are in the following order: the brazing paste $Sn_{96.5}Ag_{3}Cu_{0.5}$ (a mixture of 20 µm solder particles and additives from the Avantec company), ingot-formed $Sn_{95.5}Ag_{3.8}Cu_{0.7}$ alloys, and $Sn_{97.3}Cu_{0.7}$ with flux.
Chapter 7

Influence of additives on viscosity

7.1 Introduction

Metallurgists have shown an interest in the viscosity of metals and liquid alloys because of the influence this property has on the spreadability of a liquid onto a solid. The viscosity of liquid alloys is sensitive to the existence of atomic clusters within the liquid. Hence, viscosity is an important macroscopic parameter in analysing order effects. Solder fluidity influences its wetting capacity; thus it is important to understand viscosity. More recently, the removal of lead from solders in electronic assemblies has required a good knowledge of the viscosity of new solders. Measurements of viscosity or fluidity were done in regards to temperature (from the melting point until about 950°C) using an oscillating crucible viscometer at Chemnitz. We studied the effect of copper and silver on this property. The influence of nickel on the physical properties of solder was also studied, because nickel is an element which can be used to improve the technological and operational performance of tin-based solders. Guo et al. [63] proved that Sn-Ag-Cu alloys with trace additives of nickel show better creep resistance.

7.2 Definition

Viscosity is the property of a fluid that resists the force tending to cause the fluid to flow. Indeed, the movement of the fluid can be regarded as resulting from the slip of the fluid layers onto one another. The velocity \( v(z) \) of each layer is a function of distance \( z \) from a fixed plan. Let us consider two contiguous layers separated by \( dz \). The force of friction
F exerted on the separation surface of these two layers keeps one layer from slipping onto the other (fig. 7.2.1). It is proportional to the difference in velocity of layers, \( dv \), and is inversely proportional to their thickness \( dz \). The factor of proportionality \( \eta \) is the viscosity coefficient of the fluid.

\[
F = -\eta S \frac{dv}{dz}
\]  

(7.2.1)

The viscosity coefficient of a Newtonian fluid is defined as the ratio between the forces exerted on a unit plane surface and the velocity gradient obtained by the action of this force within the liquid.

A unit of viscosity is \( \text{Pa.s} \) or Poiseuille (Pl): 1 Pl = 1 kg/m.s.

Viscosity is a combination of two different mechanisms: the movement of individual molecules and an interaction between fluid molecules through intermolecular forces. For low-density fluids such as gases, the first mechanism prevails, while the second mechanism dominates for dense fluids like molten metals.

Viscosity depends on the interactions between the molecules of the liquid; therefore it depends on the chemical nature of the liquid. In the case of liquid metals and alloys, any inter-atomic arrangement must be reflected in their physical or physico-chemical properties and particularly on their viscosity. Temperature has a great influence on viscosity because it changes the intensity of attraction forces within the liquid. These forces become relatively weaker when the temperature rises, which leads to a reduction in viscosity. Highly viscous liquids are particularly sensitive to temperature.
7.3 Variations of viscosity with temperature

7.3.1 Background

In a microscopic context, viscosity is due to the thermal movement of fluid molecules. The velocity of the fluid particles has two parts: a disordered thermal part and a macroscopic part related to the overall movement of the fluid. When a particle passes from one layer to a slower adjacent one, it carries with it the overall velocity of its original layer. The velocity difference of the particles leads to a transfer of the exceeding momentum of the new particle to adjacent layer’s particles. Taking into account the chaotic dynamics of particles, this transfer is irreversible. By averaging this transfer of momentum between adjacent layers, we get the macroscopic effect.

On the other hand, each molecule (or atom) is surrounded by "neighbours", at an average distance "a" between molecules, characteristic of the density. The displacement of a molecule also requires the motion of its closest molecules; this effect could be described by the existence of an energy barrier of height "b" and length "L" ("L" is smaller than "a" but is of the same order of magnitude). The physical model is as follows: once we apply shear stress in the liquid, we favour the displacement of molecules in the direction of the applied force, because the work of this force decreases the barrier height in the force direction (driving work); while in the opposite direction (resistant work) the barrier is increased.

7.3.2 Models of viscosity

Many theories were proposed to describe viscosity as a function of temperature. A first class of phenomenological models was developed and improved upon many years ago. A summary of these models can be found in a paper by Brooks et al. [64]. Quantum mechanics models (pseudo potential and effective potential), with statistical physics and numerical simulation allow for ab-initio calculations of viscosity [65] (chapter 6). Andrade theory’s serves as the initial basis of phenomenological theories. According to this author, for a transfer of momentum to take place, it is necessary that the molecules in question have a potential energy $E$. The variation of the viscosity as a function of temperature is controlled by the fraction of molecules having this energy with its maximum amplitude. According to the Boltzmann law of distribution, the ratio of the number of molecules
Chapter 7. Influence of additives on viscosity

having this energy $E$ at temperature $T$ to the number of molecules having this energy at temperature "$T'$" is:

$$\exp \frac{E}{k} \left( \frac{1}{T} - \frac{1}{T'} \right)$$

(7.3.1)

$$\frac{\eta_T}{\eta_{T'}} = \exp \frac{-E}{kT'} \exp \frac{E}{kT}$$

(7.3.2)

$$\eta_T = A \exp \frac{E}{kT}$$

(7.3.3)

This equation 7.3.3 is often called Andrade's first law.

### 7.3.3 Arrhenius' law

The main temperature-dependent viscosity laws are Arrhenius' law and Andrade's law. Arrhenius' law [66] is based on the theory of a particle’s jump through a potential barrier of activation energy $E_a$. A description Arrhenius viscosity is given by equation:

$$\eta(T) = \eta_0 \exp \left( \frac{E_a}{RT} \right)$$

(7.3.4)

Here, the constants $E_a$ and $\eta_0$ are respectively the activation energy of the viscous fluid and the pre-exponential factor.

### 7.4 Choice of the viscometer method

Viscosity measurements generally require measuring a force either directly or indirectly by the use of an easier measurement parameter such as: the flow of a liquid, the velocity limit of the fall of a solid body, or the logarithmic decrement of oscillations. The choice of methods to determine the viscosity of liquid metals and alloys is relatively limited because of the technological problems relating to high temperature and of the low viscosity of molten metals.

The oscillatory method is very well adapted to molten metals. This method consists of measuring time intervals between successive oscillations of the crucible containing the liquid at a fixed position. There are exact mathematical theories for two simple geometrical crucible forms: spherical and cylindrical. This method allows for an absolute measurement of the viscosity coefficient. In our research, this method was used with a cylindrical
7.5 Method and principle of measurement

The method of measurement is based on the damping study of the crucible oscillations containing the liquid. The experiment consists of placing the liquid to be studied inside a closed cylindrical crucible and then oscillating it (fig. 7.5.1). Knowing the logarithmic decrement and the oscillation period allows the viscosity to be determined.

We will briefly recall the calculation to determine viscosity from the measurement of the period and the logarithmic decrement of the oscillating crucible. Then, we will give the expression used during the measurements of viscosity \( \eta \). The relative movement of the liquid layers produces oscillation damping. It is a measurement of viscosity flow. The differential equation for the movement of the torsion pendulum is given as:

\[
I \frac{d^2 \varphi}{dt^2} + L \frac{d\varphi}{dt} + f \varphi = 0 \tag{7.5.1}
\]

The solution for equation 7.5.1 is:

\[
\varphi(t) = \varphi_{\text{max}} \exp(-\delta t/T) \sin(2\pi t/T + \alpha) \tag{7.5.2}
\]

Figure 7.5.1: Scheme of the oscillating crucible viscometer
Chapter 7. Influence of additives on viscosity

T is the period, δ is the logarithmic decrement and α is the initial phase.
The logarithmic decrement δ and the period T are related to the viscosity of the fluid.
The proposed method is based on measuring the intervals of time between two consecutive passages of the oscillating crucible. The values of (δ, T) and (δ₀, T₀), for the full and empty crucible were determined. The viscosity of the liquid can be deduced by using the relations proposed by Roscoe [67].

7.5.1 Period and logarithmic decrement

The period and the logarithmic decrement of the oscillations were obtained by using an optical system. A laser beam was directed on the mirror (fig. 7.5.2) (mounted on the viscometer suspension wire) and reflected onto a photodiode located away at an angle φ. For each oscillation, the reflected beam passed twice in front of a fixed photodiode. The intervals of time between these passages decreased when the oscillations were damped. Impulses were transmitted to an electronic device which measured the intervals between successive passages of the light beam. Corresponding times (t₁, t₂, t₃, t₄, t₅ ...) were measured and recorded (fig. 7.5.3). The period and the logarithmic decrement of the oscillations were obtained by an optimization process, described in detail in [68, 69].

φ₀ < φₘₐₓ is the angle which measures the position of the detector from the equilibrium.

Figure 7.5.2: Principle of measurement

Figure 7.5.3: A harmonic damped function used to adjust the time points for deriving the logarithmic decrement
position at an arbitrary time \( t=0 \). Starting from this arbitrary origin, we measured the time values \( t_k(k = 1, 2, \ldots N) \) in which the laser beam induced an impulse in the photodiode until the angular displacement of the crucible reached a fixed value \( \varphi_0 \) (fig. 7.5.3). Using \( \sin \alpha = \frac{\varphi_0}{\varphi_{\text{max}}} \), the equation 7.5.2 becomes:

\[
\sin\alpha = \exp(-\delta t_k/T) \sin(2\pi t_k/T + \alpha) \quad (7.5.3)
\]

Practically equation 7.5.3 is an approached equation, which can be written as:

\[
\phi_k = \exp(-\delta t_k/T) \sin(2\pi t_k/T + \alpha) - \sin\alpha \quad (7.5.4)
\]

The best values of the parameters \( (\delta, T, \alpha) \) can be determined by minimizing the function \( F \) using the least square method.

\[
F(\delta, T, \alpha) = \sum_{k=0}^{N} (\phi_k)^2 = \text{min} \quad (7.5.5)
\]

The details of this calculation have been published [68, 69, 70]. We will give the three relations which allow for the deduction of the three unknown parameters \( (\delta, T, \alpha) \).

\[
\phi_k(p) \approx \phi_k(p_0) + \sum_{j=1}^{3} \left( \frac{\partial \phi_k}{\partial p_j} \right)_0 \Delta p_j \quad (7.5.6)
\]

where \( p = p_0 + \Delta p \). The necessary condition for the existence of a minimum of the function \( F(\delta, T, \alpha) \) is given by:

\[
\frac{\partial F(\delta, T, \alpha)}{\partial \delta} = \frac{\partial F(\delta, T, \alpha)}{\partial T} = \frac{\partial F(\delta, T, \alpha)}{\partial \alpha} = 0 \quad (7.5.7)
\]
These two equations 7.5.6 and 7.5.7 (approximation of first order of Taylor, and the linearity of the equations) lead to a system of three equations:

\[
0 = \sum_{k=0}^{N} \phi(\delta, T, \alpha) + \left( \frac{\partial \phi}{\partial \delta} \right)_{\delta_0, T_0, \alpha_0} \delta_0, T_0, \alpha_0 \\
0 = \sum_{k=0}^{N} \phi(\delta, T, \alpha) + \left( \frac{\partial \phi}{\partial T} \right)_{\delta_0, T_0, \alpha_0} \delta_0, T_0, \alpha_0 \\
0 = \sum_{k=0}^{N} \phi(\delta, T, \alpha) + \left( \frac{\partial \phi}{\partial \alpha} \right)_{\delta_0, T_0, \alpha_0} \delta_0, T_0, \alpha_0
\]

This system of linear relations is solved iteratively using the Gauss algorithm. The program stops automatically, if the reduction of the percentage of F is lower than a given value on two or three successive iterations, or when the number of iterations exceeds the entry value.

### 7.5.2 Determination of dynamic viscosity

Once logarithmic decrement \( \delta \) and period \( T \) have been determined, the viscosity can be finally given by using the modified Roscoe equation [67] for a cylinder of radius \( R \) and height \( H \):

\[
\eta = \left( \frac{I \delta}{\pi R^3 H Z} \right)^2 \times \frac{1}{\pi \rho T} \tag{7.5.8}
\]

with

\[
Z = \left( 1 + \frac{R}{4H} \right) a_0 - \left( \frac{3}{2} + \frac{4R}{\pi H} \right) \frac{1}{p} + \left( \frac{3}{8} + \frac{9R}{4H} \right) \frac{a_2}{2p^2} \tag{7.5.9}
\]

\[
p = \left( \frac{\pi \rho}{\eta T} \right)^{1/2} \frac{R}{a_0} = 1 - \frac{3}{2} \Delta - \frac{3}{8} \Delta^2 \\
a_0 = 1 + \frac{1}{2} \Delta + \frac{1}{8} \Delta^2 \\
a_2 = 1 + \frac{1}{2} \Delta + \frac{1}{8} \Delta^2 \\
\Delta = \frac{\delta}{2\pi}
\]

The logarithmic decrement noted above is the difference between the values obtained for the two crucibles, one containing the liquid and one empty.
7.6 Experimental results

7.6.1 Preparation of samples and experimental procedure

Viscosity measurements were carried out using an automated viscometer with an oscillating crucible. A detailed description of the experimental device was published by Volmann et al. [69] and Herwig et al. [68] using the modified Roscoe equation. Viscosity is calculated from the logarithmic decrement and the period of the oscillations [69]. The solders studied in this work are industrial solders. They were cleaned mechanically then with methanol in order to eliminate the maximum amount of oxides. The sample was placed in a boron nitride crucible, put in a cylindrical graphite crucible and suspended on a torsion wire with a ceramic rod. Viscosity measurements were carried out in a vacuum of about $10^{-5}$ mbar at a broad range of temperature (from the melting point until 900°C). The temperature was measured with a Pt/PtRh thermocouple placed just below the graphite crucible. The viscosity was measured during the cooling phase when the alloy was homogeneous. Each sample was weighed before and after measurements, with no loss of mass to be noted. Data on viscosity were obtained with a margin of error of ± 5% [71].

To check the reliability of industrial solders, we compared their measured viscosities to that of a laboratory-produced sample made of pure metals of the same nominal concentration as found in industrial solders ($Sn_{96.5}Ag_{3.5}$ and $Sn_{95.5}Ag_{3.8}Cu_{0.7}$). As previously mentioned, the viscosity of these solders with 1% nickel additive was also measured.

7.6.2 Results and discussion

Determining the dynamic viscosity of lead-free solders alloys is the subject of a great number of studies. The viscosity of eight alloys including six alloys of different compositions was measured. In two cases, we compared "industrial" solders to our laboratory reference solder, which enabled us to check the effects of impurities on viscosity. Figure
Figure 7.6.1: The viscosity of different tin-based alloys as function of temperature. The curves from the work of Plevachuk et al. are indicated by the full lines.

7.6.1 shows the results of viscosity in regards to temperature. Viscosity decreases with increasing temperature because the thermal movement becomes higher than the attraction forces at short distance. The viscosity of liquids varies exponentially with temperature. This behaviour can be described by Arrhenius’ law: $\eta(T) = \eta_0 \exp \left( \frac{E_a}{RT} \right)$, where $\eta_0$ is a pre-exponential constant (mPa.s), R is the gas constant ($J/mol^{-1}K^{-1}$) and $E_a$ is the activation energy ($J/mol^{-1}$). A higher concentration of silver or copper increases the viscosity of the solder, which results in the reduction of the wetting velocity. It was noted that viscosity increases with the concentration of lead in tin-based solders. The viscosity of various lead-free solders is lower than that of the traditional solder ($Sn_{60}Pb_{40}$). We presented the viscosity obtained by Plevachuk et al. [71] together with our results in figure 7.6.1. The nominal concentration reported by them is the same as ours, but the units are not the same: Plevachuk’s concentration is expressed as a percentage of the atomic mass...
7.6 Experimental results

\[ \eta = \eta_0 \exp \left( \frac{E_a}{RT} \right) \]

<table>
<thead>
<tr>
<th>industrial alloys</th>
<th>( \eta_0 , /, mPa.s )</th>
<th>( E_a , /, KJ.mol^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Sn_{60}Pb_{40} )</td>
<td>0.4791 ± 0.0084</td>
<td>6.688 ± 0.120</td>
</tr>
<tr>
<td>( SnAgCu )</td>
<td>0.4689 ± 0.0078</td>
<td>6.027 ± 0.079</td>
</tr>
<tr>
<td>( Sn_{97}Cu_3 )</td>
<td>0.4295 ± 0.0062</td>
<td>6.881 ± 0.088</td>
</tr>
<tr>
<td>( Sn_{98}Pb_{10} )</td>
<td>0.4772 ± 0.0066</td>
<td>5.839 ± 0.067</td>
</tr>
<tr>
<td>( Sn_{96.5}Ag_{3.5} )</td>
<td>0.3795 ± 0.0217</td>
<td>7.406 ± 0.369</td>
</tr>
<tr>
<td>( Sn_{99.3}Cu_{0.7} )</td>
<td>0.4371 ± 0.0098</td>
<td>6.379 ± 0.155</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pure alloys</th>
<th>( \eta_0 , /, mPa.s )</th>
<th>( E_a , /, KJ.mol^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Sn_{96.5}Ag_{3.5} )</td>
<td>0.4631 ± 0.0135</td>
<td>5.965 ± 0.129</td>
</tr>
<tr>
<td>( Sn_{96}Ag )</td>
<td>0.4649 ± 0.0063</td>
<td>5.808 ± 0.062</td>
</tr>
<tr>
<td>( Sn_{100} ) ([71])</td>
<td>0.42</td>
<td>6.56</td>
</tr>
<tr>
<td>( Sn_{98.7}Cu_{1.3} ) (%at [71])</td>
<td>0.51</td>
<td>5.84</td>
</tr>
<tr>
<td>( Sn_{94.9}Ag_{3.3}Cu_{1.3} ) (%at [71])</td>
<td>0.48</td>
<td>6.26</td>
</tr>
</tbody>
</table>

Table 7.1: Determination of the \( \eta_0 \) and \( E_a \) parameters of different solders

while ours is a percentage of the mass, according to industrial criteria. The viscosities obtained by Plevachuk are slightly higher than ours. The viscosity of liquid alloys appears to be strongly dependent on their purity. The majority of our alloys are industrial whereas those of Plevachuk are prepared from pure metals. Inclusions such as oxide particles considerably increase the viscosity of alloys. Our measurements were conducted in a vacuum, whereas those of Plevachuk et al. were conducted under controlled atmospheric conditions \( Ar - 10\%H_2 \). L.D. Lucas indicates that in the case of the molten metals, the dispersion of the measured viscosity by different authors could reach 20% because of the difficulties in measuring very weak forces (about \( 10^{-7} N \)). The viscosities of all liquids greatly depend on the temperature. Consequently, the temperature must correspond to the time when viscosity is measured. Our viscosity measurements were conducted at stabilized temperatures, in increments of 50°C. Once the temperature was reached, several viscosity measurements were taken at this temperature for 1 hour, going on to the following temperature afterwards. The measurements were done during the cooling phase.
within a temperature range of a few hundred degrees. These results were fitted to the Arrhenius equation, whose parameters are reported in table 7.1. We studied the influence nickel (as an impurity) has on the viscosity of the solder. The addition of 1% of nickel to the solders increases the viscosity by approximately 8.5%. Once the temperature reaches 400°C during the cooling period, the solder’s viscosity is almost multiplied by five (pasty fusion) (fig. 7.6.2). This corresponds to the crystallization of nickel in suspension in the solder. Towards 200°C, the apparent viscosity approaches zero at the same temperature where the tin-silver alloy solidifies (in this device, the temperatures are less accurate at low temperatures than the ones at higher temperatures).
7.7 Conclusion

The study of the physical properties of lead-free solders, which are a possible substitute to traditional solders, piqued our interest in certain thermodynamic properties such as the viscosity of these alloys and the effect of the additives like nickel. Viscosity measurements carried out on lead-free solders allowed us to see the influence of silver or copper additives on tin viscosity. A small amount of silver or copper added to the tin-based solder led to an increase in viscosity (as was with the addition of lead). The presence of copper or silver in tin-based solders improves their electrical and thermal conductivity (see chap. 6), but decreases the wetting velocity. The concentration of copper, silver or both in the tin-based solder must be maintained in small quantities (less than 3\%) in order to have a reasonable melting point. We note that our experimental values are consistent with previously published values. Some anomalies are observed at low temperature (350 °C) for Sn$_{60}$Pb$_{40}$ and Sn$_{96}$Ag$_{4}$ alloys, which might be due to the influence of metal impurities and/or to the presence of non-soluble oxide particles found in industrial solders. The addition of 1\% of nickel to these solders induced a "jump" in the viscosity, which was due in particular to the crystallization of nickel below 400°C. To have a good solder, the concentration of nickel must be maintained below 1\%. The experimental study of the dynamic viscosity of tin-based alloys showed that this property is very sensitive to small quantities of Ag, Cu or Ni.
General conclusions
This work is an experimental contribution to the study of the electronic transport properties, the surface tension, the density, the wettability and the viscosity of binary and ternary liquid alloys with and without additives. These results contribute to solving certain technological problems mainly in the field of lead-free solders. In the following discussion, we will summarize our results and highlight their industrial and fundamental interest.

First, we studied the influence of cyclic thermal treatment on the physical properties of liquid metals. The solidification of liquid alloys depends on the history of the molten metal and the presence of solid or liquid impurities. Resistivity measurement is an appropriate way to study material properties. In fact, the resistivity measurement of $Cd_{60}Sb_{40}$ alloy under cyclic thermal treatment with increasing amplitude pointed out an effect of hysteresis similar to the one observed by M.P.K. The origin of this effect can also be interpreted as being due to the incomplete melting of antimony.

Our study of Cd-Sb resistivity throughout the whole phase diagram at a large temperature range extends and completes previous work done by Gasser [1]. A temperature-dependent resistivity maximum was observed. A first maximum appeared at low temperature at $Cd_{52}Sb_{48}$ composition which is not far from the one observed by Gasser for the $Cd_{50}Sb_{50}$ composition. At high temperatures, the maximum shifts to the $Cd_{60}Sb_{40}$ composition. The Cd-Sb alloys in the liquid state show a metallic behaviour at high temperatures (increasing resistivity with temperature). At low temperatures, the liquid exhibits weak semiconductor characteristics, remnants from the solid state. In an equiatomic composition, this transition occurs at a temperature of about 760°C. We also studied the metal/semi-metal transition in Cd-Sb alloys in regards to concentration. We observed three behaviours. A metallic behaviour for cadmium rich alloys ($Cd_{93}Sb_{7}, Cd_{90}Sb_{10}$ and $Cd_{80}Sb_{20}$) is observed. Adding antimony to these compositions produces an important change of the temperature coefficient and of its sign. Intermediate compositions ($Cd_{70}Sb_{30}, Cd_{60}Sb_{40}, Cd_{52}Sb_{48}, Cd_{50}Sb_{50}, Cd_{48}Sb_{52}, Cd_{43}Sb_{57}$ and $Cd_{40}Sb_{60}$) have a behaviour similar to that of semiconductors with a negative temperature coefficient largely higher than those usually observed for metals.

As far as we know, this is the first time the resistivity and thermo-power of pure antimony has been quantitatively interpreted by correcting the Ziman formula by the factor due to Mott. For antimony-rich alloys, we once again observed a purely metallic behaviour. Re-
General conclusions

Sistivity in regards to concentration is interpreted by the Faber-Ziman theory, using local pseudo potentials and hard sphere structure factors. The predicted results underestimate the experimental resistivity by 35%. We explained this difference by the appearance of a pseudo gap in the middle of the phase diagram which disappears with temperature.

In the third part of this work, we compared the physical properties of traditional solders (tin-lead) with industrial lead-free solders (tin-based, with silver and copper). The electrical and the thermal conductivities as well as the Seebeck coefficient of these alloys (solders) in the liquid and solid states were measured at the LPMD laboratory (Metz). We showed that the electrical and thermal characteristics of lead-free solders are better than those of the lead-tin solders in both the liquid and solid states, except for Sn$_{95}$Sb$_5$ in the solid state. Lead-free solders are thus better conductors of electricity and heat, which is an important improvement from an industrial point of view.

To make a high-quality solder, liquid alloys must have low viscosity and high wettability. We measured the surface tension and the contact angle which characterize wettability using two different methods. The first one is based on the measure of applied forces on an immersed stamp, and the second one is carried out by the sessile drop method. Finally, we studied the effects of incorporating nickel on solder viscosity. Surface tension and density decrease with temperature. Throughout our measurements, we showed that the surface tension of the traditional solder is lower than that of lead-free solders and increases with the silver or the copper concentration which is not conducive to proper wetting. We have noted the crucial influence of oxides on the wettability of solders. In fact, the experiments made in a vacuum and without flux show that there is almost no wetting. To have a better wetting, it is essential to work under industrial conditions: in air and using flux. The use of flux when measuring the contact angle is of primary importance, because it eliminates the oxide traces which keep the solder from adhering properly. The flux also facilitates the spreading of the liquefied solder onto the solid base metal and protects it against oxidation during the heating process. Solders have more affinity with copper than with nickel substrate, which explains the lower interfacial tension $\sigma_{SL}$ between the solders and the copper substrate than that between the solders and nickel substrates. Hence, the choice of the substrates significantly influences solder wetting. The temperature also has an important effect on the kinetics of solder spreading; we noted an improvement of the wettability at higher temperatures. Lead-free solders wet less substrates of Cu or Ni than
the traditional solder (Sn-Pb), which still has good wetting properties because their contact angles are usually between 11° and 39° ($\theta < \frac{\pi}{2}$, for proper wetting). One can deduce that the three best alloys replacing lead-tin solder $Sn_{60}Pb_{40}$ are: $Sn_{96.5}Ag_{3.5}Cu_{0.5}$ (brazing paste), $Sn_{95.5}Ag_{3.8}Cu_{0.7}$ and $Sn_{97.3}Cu_{0.7}$ (eutectic).

The last part of this work was devoted to the study of solder viscosity with and without nickel. The low contact angles and viscosities contribute to a high degree of wettability. Indeed, an increase in viscosity reduces the spreading rate, which leads to poor wetting. We observed that viscosity is very sensitive when there are impurities or additives, even at low concentrations. The addition of copper or silver results in an increase in the viscosity. Our viscosity measurements are coherent with the few values previously published. The addition of 1% of nickel to the solders resulted in a sharp rise in viscosity, particularly at temperatures between 400°C and the melting point (pasty fusion). This phenomenon considerably slows down the spreading rate. To avoid this, the concentration of nickel should be maintained below 1%; even if nickel improves the solder’s mechanical properties, in particular for "creep". Our experimental study of tin-based alloys proved that viscosity is very sensitive to small quantities of nickel or copper or silver.

Analyses by Scattering Electron microscopy (SEM) and by optical microscopy were carried out at the Jussieu School of Chemistry and at the LPMD laboratory in Metz. They are presented in the appendix. These measurements consist of analyzing the influence and the distribution of alumina nanograins in lead-free solders. It appears qualitatively that solders containing nanograins crystallize differently from those without nanoparticles. The Chemnitz laboratory in Germany has a device for measuring the surface tension and density of liquid metals and alloys with an immersion alumina body. It would be worthwhile to replace it with a copper or nickel element to be able to study the contact angle using the same equipment used for surface tension and density. This would make it possible to carry out simultaneous measurements so as to avoid the experimental errors related to the change of the immersion body or method of measurement.

It would have also been interesting to study liquid LFS mixed with nanoparticles both for resistivity and for viscosity and surface tension. We did not succeed in mixing nanoparticles with ingots of LFS solders because of the great difference in density between the liquid solder and the nanoparticle powder.

We only succeeded in mixing nanoparticles with the brazing paste, which allowed us to
General conclusions

observe (with different microscopes, appendix A) the differences between solidified solders with and without nanoparticles. Due to the reaction of the flux included in the paste, we could not measure properties like resistivity, which require long measurement times in hours and days.

We observed that only LFS (brazing paste) exhibited an important undercooling effect (appendix B). It seems to us that it is very difficult to be sure that the nanoparticles are kept in the solder when the experiment takes too long time, but a more rapid experiment may produce interesting effects.
appendix A

Observation of solders by optical and electron microscopy

A.1 Optical microscopy

Figure A.1.1: Brazing paste with and without alumina (Al$_2$O$_3$) heated at 260$^\circ$C for 10 min.

Brazing paste without alumina nanoparticles

Brazing paste with 0.1% alumina nanoparticles

Brazing paste with 0.3% alumina nanoparticles
Figure A.2.1: Brazing paste without alumina ($Al_2O_3$) heated at 260°C for 10 min

Figure A.2.2: Brazing paste mixed with 1/1000 of $Al_2O_3$ heated at 260°C for 10 min
Figure A.2.3: Brazing paste mixed with 3/1000 of Al$_2$O$_3$ heated at 260°C for 10 min
Measurements with Scattering Electron microscopy (SEM) and with optical microscopy consist of analyzing the influence of the alumina nanograins in lead-free solders. Qualitatively speaking, solders containing nanograins seem to crystallize differently from those without nanoparticles. To interpret our results, a closer cooperation with the laboratory in Jussieu should be considered.
appendix B

Undercooling observed by resistivity measurement

Resistivity measurements during solidification make it possible to highlight the phenomenon of undercooling. On figure B.0.1 we presented this phenomenon which we obtained with the lead-free solder $Sn_{96.5}Ag_3Cu_{0.5}$. Undercooling was observed with the brazing paste made by Avantec company (ref.: ECOREL FREE 305-6). In our two measurements, we observed an undercooling phenomenon respectively of 16°C and 10°C. We did not observe this phenomenon with the other lead-free solders samples.
Figure B.0.1: Undercooling of the brazing paste $Sn_{96.5}Ag_3Cu_{0.5}$
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