On the thermopower of liquid antimony

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Abstract. The resistivity and the thermopower of pure antimony have been measured. The electronic transport properties of antimony can be calculated using the extended Ziman formalism. In this formalism the absolute thermoelectric power is negative, while we found that the experimental one is positive.

Antimony is a semi-metal. Hafner et al. [J. Hafner and W. Jank. Phys. Rev. B45 6 2739 (1992)] calculated its density of states and showed that it splits into an s and a p band very far from the picture of a free electron band. Taking into account the real density of states, we proposed, for the first time to our knowledge, a "modified extended Ziman formula" which is able to explain the positive thermopower of antimony and its order of magnitude.

1. Introduction

Most of liquid non-transition metals behave as nearly free electron conductors, and their electronic properties can be well described by the theory which has been originally developed by Ziman [1] for pure normal metals and has been “extended” by Evans et al. [2] to apply to liquid noble and transition metals. The weak ion pseudo potential in the Ziman theory [1] was simply replaced by the t-matrix determined using the muffin-tin approximation expressed in terms of phase shifts. Within the “extended Ziman formalism”, two approaches have been developed. The first one has been initiated by Dreirach et al. [3] and the second one by Esposito et al. [4].

The main difference lies in the fact that the former includes only s and p electrons to form the free electron conduction band whereas the latter takes also into account the d electrons. The electronic transport properties of liquid metals are based on the scattering of nearly free electrons by potentials. We used the approach called "method of the neutral pseudoatoms" introduced by Ziman [5]. It consists to start with the muffin-tin potential of an atom and to take into account the exchange contribution through a Slater [6] (or Kohn and Sham [7]) formula. We used a description of the exchange and correlation effects [8] by employing the Local Density Approximation (L.D.A.) [9] approach. It is clear that the position of the Fermi energy, with respect to the scattering muffin-tin potential, plays an essential role in the electronic transport properties (Figure 1). Its position depends on the location of the conduction band bottom relative to the muffin-tin zero and on the shape of the density of states. Dreirach et al. [3] assumed a free electron density of states band whose bottom is shifted by $E_B$ from the muffin-tin zero (Figure 1a). The $E_B$ value is calculated following an expression due to Ziman [5] and discussed explicitly by Ballentine et al. [10]. Esposito et al. [4] postulate that the bottom of the
free electron band is located at the muffin-tin zero (Figure 1b). But they take into account the real shape of the conduction band by using Lloyd’s formula [11] to calculate the integrated density of states. Ben Abdellah et al. [12] made a synthesis of the two approaches (Figure 1c), and took into account the fact that, according to the experimental total density of states [13,14], the liquid heavy polyvalent DOS is split into two bands separated by a gap.

In §2 we recall shortly the theoretical formula of the resistivity and the calculation of bottom of the free electron band. We describe the experimental method in §3. Our experimental results are presented in §4 and are discussed semi-quantitatively.

2. Extended Ziman theory

2.1. Expression of the resistivity

We express the electrical resistivity of a normal metal as a function of both the energy $E$ and the wave vector $k$ following a scheme described by Makradi et al. [8] using the Ziman [1] formula. The resistivity $\rho$ can be written as function of energy:

$$\rho(E) = \frac{3\pi}{4e^2h^2k^6} \int_0^{2k} a(q) |t(q, E)|^2 q^3 dq$$

where $\Omega_0$ is the atomic volume, $q$ is the transfer wave vector, $a(q)$ is the structure factor, $t(q, E)$ is the $t$ matrix expressed in term of energy dependent phase shifts by Dreirach et al. [3] and by Delley et al. [15]

$$t(q, E) = -\frac{2\pi \hbar^3}{m^2E \Omega_0} \sum_r (2l+1) \sin \eta_r(E) \exp(i \eta_r(E)) \mathcal{P}_l(\cos \theta)$$

where $\mathcal{P}_l(\cos \theta)$ are the Legendre polynomials, $\theta$ is the angle between the incident and the scattered wave vector. The phase shifts $\eta_r(E)$ are calculated from muffin-tin potentials constructed following Mukhopadhyay et al. [16] method. The same formalism has also been applied to transition metals by Zrouiri et al. [17] taking into account explicitly the fact that electrons with spin up and electrons with
spin down do not feel the same potential. To compare with the experimental resistivity, the formula (1) has to be taken at the Fermi energy \( E = E_F \) and at the Fermi wave vector \( k = k_F \). This approach gives an energy dependent resistivity and permits the calculation of the thermopower as follows:

\[
S(E) = -\frac{\pi^2 k_B^2 T_K}{3|e|E} \chi \quad \text{with} \quad \chi = \left[ \frac{\partial \ln \rho(E)}{\partial \ln E} \right]
\]

where \( k_B \) is the Boltzmann constant, \( T_K \) the absolute temperature in Kelvin and \( \chi \) the dimensionless thermoelectric parameter. To compare to the experiment it is necessary for the resistivity, the thermopower and the thermoelectric parameter to take their values at \( E_F \). The thermoelectric parameter can also be written: \( \chi = 3 - 2\alpha - \beta/2 \), where the expressions of \( \alpha \) and \( \beta \) can be found in the paper of Vinckel et al [18].

The wave vector is written:

\[
k = \left( \frac{3\pi^2 N_c(E)}{\Omega_0} \right)^{1/3}
\]

\( k \) and \( E \) are related by \( E = \frac{\hbar^2 k^2}{2m_e} + E_B \) (\( E_B \) is the bottom of free electron band).

2.2. Muffin-Tin potentials and phase-shifts
The construction of the liquid antimony muffin tin potential is based on the superposition of neutral atomic charge. The phase-shifts entering in the expression of the electronic properties are calculated from a muffin-tin potential using the L.D.A. approximation.

2.3. Fermi energy determination
Three approaches have been described for the determination of the Fermi energy by Ben Abdellah et al. [12] and are summarised in Figure 1. We used approach 1.c taking \( E_B = 0 \).

3. Experimental design
Resistivity and Absolute Thermoelectric Power (ATP) measurements were performed by using the four-probe method described by Vinckel et al. [18] with a quartz cell (Figure 2) fitted with two tungsten and two tungsten-rhenium electrodes.

4. Results and discussion
For the theoretical interpretation of our experimental results, we used the Ziman extended formula expressed in terms of the phase shifts. We have calculated the phase shifts as a function of the energy for electrons scattered by a muffin-tin potential as described by Makradi et al. [8].

4.1. Electrical resistivity of antimony
The resistivity and the absolute thermoelectric power of antimony were measured simultaneously from 650 to 1020°C. These measurements are carried out in a fused silica cell (Figure 2). On Figure 3 the results of electrical resistivity like those of some other authors have been represented. Our measurements are in very good agreement with those obtained by Gasser [19]. With regard to the results of Benazzi [20] and Roll and Motz [21], our curve of resistivity is located below their measurements between 700 and 850 °C, but the difference decreases above 850°C. However, the
variation does not exceed 2%. Electrical resistivity of pure antimony shows a nearly parabolic behaviour without any minimum. The values of resistivity have been fitted by a second order polynomial:

$$\rho_{SS}(T) = 122.91524 - 0.04152 \cdot T + 4.25612 \cdot T^2$$  \hspace{1cm} (5)$$

4.2. Thermoelectric power of antimony

The experimental value of thermoelectric power of pure antimony is slightly positive whereas the free electrons theory gives a negative value. We deferred on Figure 4 results of our ATP measurements on
liquid antimony compared with those obtained by Benazzi [20] and Bath [22]. Our values frame those of Benazzi and Bath. Under the conditions of measurement (K2000 Voltmeter of resolution 0.1 µV) the accuracy obtained is estimated at ± 0.5 µV.K⁻¹ for the systematic error (calibration of the couple) and at 0.2 µV. K⁻¹ (accidental error: dispersion of the results).

4.3. Theoretical interpretation

To understand the sign of the thermopower of liquid metals we will use an approximation that we progressively correct to take into account its inaccuracy. In a first crude evaluation we can approximate the product a(q) t(q)² by a constant (see Figure 5).

The Ziman equation can then be integrated analytically and gives a resistivity inversely proportional to the energy (ρ~1/E) which always gives a negative Absolute Thermoelectric Power (ATP) since the ATP is the derivative of the logarithm of the resistivity to regard to the logarithm of the energy. This 1/E curve can first be corrected by introducing the first peak of the structure factor schematically drawn on Figure 5 which can explain the positive thermopower of noble and divalent metals like cadmium [23] since the limit of integration k_F is in the increasing part of the ρ(E) function. In our calculation, we used the program developed by Makradi [14] (LDA) at the laboratory which is based on the extended Ziman formula in term of phase shifts. These results include the energy dependence term which was absent in pseudopotential calculations. The position of the Fermi energy compared to the muffin-tin zero potential plays a very important role in the electronic transport properties.

On Figure 6 we represent the resistivity of liquid antimony as a function of energy. At the Fermi energy obtained with a five electron free electron band we obtain a resistivity of 61.68 µΩcm and a thermopower of -5.19 µV/K with Z=Ne=5 (free electron band) and E_F = 0 at a Fermi energy of 0.783 Ry. The resistivity is the half of the experimental one (117 µΩcm) and the thermopower is negative (-5.19 µV/K) when the experimental ATP is positive (+0.5 µV/K). If we consider a three electron free electron band (Figure 6) we obtain a resistivity of 134.34 µΩcm (near the experimental value) but a
thermopower of -8.76 μV/K with \( Z=\text{Ne}=3 \) (free electron band) and \( E_B = 0 \) at a Fermi energy of 0.557 Ry. The ATP remains negative and is very far from the experimental ATP. If we examine the density of states calculated by Hafner [24] we observe a gap between the two s and p bands but also a higher (than free electron) DOS at low energies and a dip in the higher energy part of the p band DOS (Figure 7). It is consequently necessary to introduce a second correction in our \( 1/E \) resistivity curve. We propose to use the \( g \) factor introduced by Mott [25] in order to explain the semi-metals and the bad semiconductors properties. Mott proposes to correct the resistivity expressions by a \( g^2 \) coefficient in the mean free path which lower value is limited by the interatomic distance. This was precised by Faber in his book [26] using a different approach from the calculation of electrical conductivity in traditional way. He establishes a formula [formula 5.42 of his book, [26]] which expresses conductivity as a function of the square of the density of states. This is coherent with the term \( g \) introduced by Mott and Davis (page 80 [25]) who write the mean free path by dividing that of Ziman by \( g^2 \). The Faber approach is more rigorous and does not require the arbitrary introduction of the substitution of the mean free path by the interatomic distance. After some very simple calculations we deduce that the resistivity can be simply written in the following form:

\[
\rho(E) = \frac{\rho_{\text{Ziman}}(E)}{g^2(E)}
\]  \hspace{1cm} (6)

where \( \rho_{\text{Ziman}}(E) \) is the Ziman resistivity calculated in the free electron density of states approach while \( g \) is the ratio of the real density of states to the free electron density of states. We corrected the Ziman formula by the factor \( g^2 \) and the derivative as regard to energy will consequently change drastically. To correct resistivity it is necessary to know the real and free electrons densities of states at Fermi energy \( E_F \). The correction of the ATP is more complex because it is necessary to know the dependence in energy of \( g \). This led us to record the density of states calculated by Hafner as function of energy (Figure 7) and to deduce \( g \) (E) according to energy (Figure 8). In this last calculation we determine the

![Figure 6. Resistivity of liquid antimony as a function of energy calculated with Esposito’s approach of the extended Ziman formula. The two arrows indicate the results with respectively 3 and 5 free electrons.](image-url)
ratio $g$ by using a free electron density of states having the same origin as the real density of states of the $p$ band. Taking into account Hafner’s DOS we used 3 electrons in the conduction band. It is also necessary to observe that Hafner’s DOS is well above the free electron one, thus the $p$ band is more rapidly filled by the $Z=3$ electrons. This lowers considerably the Fermi energy (from .56 to .40 Ry) and shifts the Fermi energy into the structure factor peak. We represented on Figure 9 the resistivity calculated in the Ziman approach compared with that corrected according to our model and in Figure 10 the corresponding ATP. With $Z=3$ one obtains a corrected resistivity of 150 μΩcm and a positive ATP of +1.66 μV/K. Our calculation makes it possible to be near the experimental resistivity and thermopower and to find the good sign for the ATP. One can consider that this last approach is very satisfactory in comparison with the approximations made.

Figure 7. Comparison of the free electron $p$ DOS and of Hafner’s $p$ DOS (in the hypothesis of 3 valence electrons).

Figure 8. Corrective Mott factor $g$ as a function of energy. The Fermi energy is lowered to .403 Ry for $Z=3$.

Figure 9. Comparison of the resistivity as a function of energy within the “modified (by $g^2$) extended Ziman formula” to the free electron “extended Ziman formula”.

Figure 10. Corrective Mott factor $g$ as a function of energy $E$ (for $Z=3$).

$g(E) = 1$

$E_F = 0.4035$ Ryd

$E_{F-free electrons} = 0.5569$ Ry
Figure 10. Comparison of the ATP as a function of energy within the “modified (by $g^2$) extended Ziman formula” to the free electron “extended Ziman formula”.

5. Conclusion
The classical extended Ziman approach underestimates the resistivity and gives a false sign for ATP. If we take into account 3 electrons of conduction as suggested by Hafner’s density of states and if we correct the free electron density of states through a $g^2(E)$ term, it is possible to approach considerably resistivity and thermopower and to explain the positive sign of the ATP. The “extended –Ziman formula” is valid thanks to Mott–Faber correction through the $g^2$ term in a “modified extended Ziman formula”.

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