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# EXPERIMENTAL DENSITY OF STATES FOR CALCULATION OF EFFECTIVE MASSES AND RESISTIVITIES OF TRIVALENT LIQUID METALS

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Experimental density of electronic states (DOS) data are used to evaluate the DOS effective mass. It is compared with the DOS effective masses calculated within the pseudopotential formalism by several authors and by ourselves. When they are introduced in a calculation of electrical resistivity of trivalent simple metals (Al, Ga and In), experimental effective masses lead to improvement on the calculated resistivity. Discrepancies between calculated and experimental DOS effective masses are discussed.

KEY WORDS: Ziman Theory, density of states, effective masses, pseudopotential.

## 1 INTRODUCTION

Ziman's formula (Ziman 1961) has been widely used for the calculations of the electrical resistivity of metals and metallic alloys in the liquid state. It is based on the ideal model of the nearly free electrons. This restricts its applicability to metals whose electronic structure is near from this ideal model and explains why many attempts to improve the results obtained using this formula have been reported. The aim of these corrections was to take into account the fact that real metals deviate from this ideal model. The density of electronic states (DOS)  $N(E)$  is certainly one of the physical properties that contains the best indications to know how near from the ideal behaviour a metal is. Consequently, it is not surprising that some earlier corrections can be linked to the DOS. Some authors have proposed expressions that allow numerical estimations of these corrections which can be inserted in calculations of the resistivity. On the other hand, increasing reliability of XPS and UPS measurements enables us to obtain experimental values of  $N(E)$  and so, an experimental estimation of these corrections. Our aim in this paper is to introduce these experimental corrections in calculations of resistivity and to compare them with those calculated using pseudopotential theory by

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some other authors and by ourself. In a first part, we will report on corrections that we have found in literature and we will explain their relations with  $N(E)$ . In a second part, we will present our calculations of resistivity and how we did correct them. Finally, in a third one, we will discuss our results and present our conclusions and remarks.

## 2 EARLIER CORRECTIONS

Ziman's formula for the resistivity

$$\rho_z = \frac{3\pi}{4e^2 \hbar k_F^4 (v_F^{\text{free}})^2} \frac{V}{N} \int_0^{2k_F} a(q) |W_{\vec{k}}^0(\vec{q})|^2 q^3 dq$$

ensues from the nearly free electrons model. Assuming that the diffusing potential is a weak and local one (Ziman 1967, Wang and So 1977) allows us at the first order to write the Fermi velocity  $v_F = v_F^{\text{free}} = \hbar k_F/m$  and to replace the wave function of an electron by a plane wave. This is of course an ideal model and it is not surprising that many authors have developed corrections whose aim was to bring the ideal model closer to the reality that is:

- a wave function different from a plane wave
- an energy  $E_{\vec{k}}$  different from  $(\hbar^2 k^2)/(2m)$  and consequently a Fermi velocity  $v_F$  different from  $\hbar k_F/m$ .

Analytically, these adaptations were made within the scope of the perturbation theory (Shaw and Smith 1969, So *et al.* 1977, Shaw 1969). It allows to get the pseudo-wave function  $\chi_{\vec{k}}$  and to replace

$$W_{\vec{k}}^0(\vec{q}) = \langle \vec{k} | W | \vec{k} + \vec{q} \rangle$$

by

$$W_{\vec{k}}(\vec{q}) = \langle \chi_{\vec{k}} | W | \chi_{\vec{k} + \vec{q}} \rangle.$$

We can get too the expression of  $E_{\vec{k}}$  and thus, we are allowed to replace

$$v_F^{\text{free}} = \frac{\hbar k_F}{m}$$

by

$$v_{\vec{k}} = \frac{dE_{\vec{k}}}{\hbar dk} = \frac{\hbar k}{m^*}$$

introducing the density of state effective mass in a liquid that is an isotropic medium (the Fermi surface being spherical)

$$m^*(k) = \frac{\hbar^2 k}{\frac{dE}{dk}}.$$

The resort to an effective mass became early widespread (Ashcroft 1964, Weaire 1967, 1968, Faber 1972) and we can now write:

$$\rho = \frac{3\pi}{4e^2 \hbar k_F^4 (v_F^{\text{free}})^2} \frac{V m^{*2}}{N m^2} \int_0^{2k_F} a(q) |W_{\vec{k}}(\vec{q})|^2 q^3 dq$$

introducing two corrections, the first one about the form factor and the second one about the Fermi velocity. This conclusion ties up with the one of Wang and So (1977) or of Akinlade *et al.* (1992) who wrote  $\rho = (m^*/mm_E)^2 \rho_Z$  where  $m^*$  is the DOS effective mass at the Fermi energy and  $m_E$  is introduced by the renormalisation of the wave function in the expression of the form factor. This can be tied up too with Shaw's conclusions (Shaw 1969 p. 2365). He recommended the introduction of a correction factor  $1/m_E^2$  coming from the modifications in the form factor.

Both corrections can be expressed analytically for each model or pseudopotential and it can be done to different orders in the perturbation development. For local potentials, they only appear at the second order. This supports the idea that the initial formulation of the resistivity is suitable to local and weak potentials. The pseudo-wavefunction  $\chi_{\vec{k}}$  being directly depending on the potential used,  $m_E$  is analytical in essence and thus, must be calculated analytically. On the other hand, it is not the case for  $m^*$  that can be formulated using  $N(E)$ :

$$\begin{aligned} N(E) &= \frac{2V}{8\pi^3} \int_{s(E)} \frac{dS_{\vec{k}}}{|\nabla_{\vec{k}} E_{\vec{k}}|} \\ &= \frac{V k^2}{\pi^2 \frac{dE}{dk}} \quad \text{for an isotropic medium.} \end{aligned}$$

So

$$g = \frac{N(E)}{N_{FE}(E)} = \frac{\hbar^2 k}{m \frac{dE}{dk}} = \frac{m^*}{m}.$$

This expression explains why  $m^*$  is called the ‘‘DOS effective mass’’. Faber (1972 p. 52) deplored that it was experimentally unworkable to measure  $m^*$ . But increasing reliability of DOS measurements using XPS and UPS (Indlekofer 1987) allows us now to fill this deficiency. So, having measurements of  $N(E)/N_{FE}(E)$  at our disposal, we can get  $m^*/m$ . It allows us to compare the calculated corrections with the ones obtained experimentally and to use these latter in the calculations of electrical transport properties.

### 3 INTRODUCTION OF EXPERIMENTAL CORRECTIONS

We have chosen to apply our approach to trivalent metals (Al, Ga and In) for the following reasons:

- availability of experimental data
- it enables us to draw trends through the series

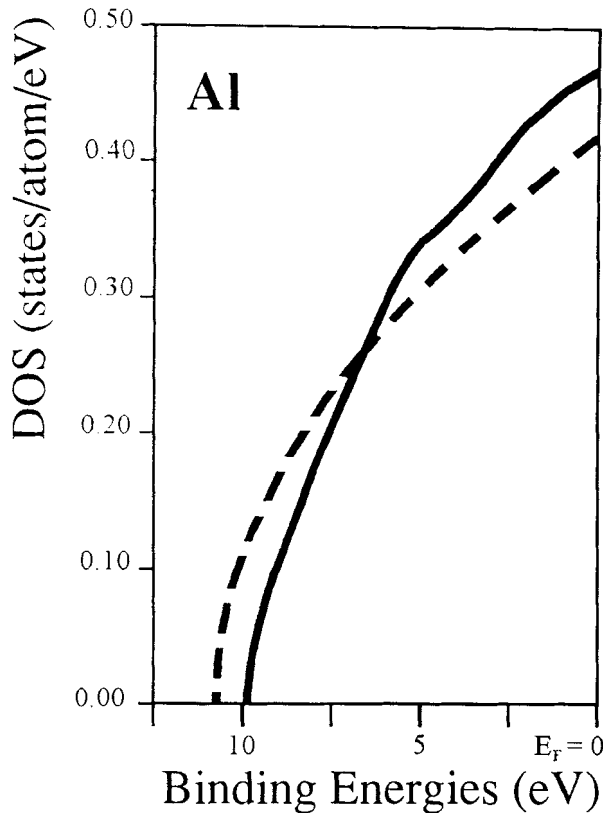
- these metals are quite of nearly free kind according to their DOS curve (see Figures 1, 2 and 3) at least the two first.

This last point will be discussed in the third paragraph. The next step was to develop a calculation of the resistivity in which we could insert the correction of density of states. We used Shaw's optimized model of potential:

$$\omega_0 = -\frac{Z}{r} - \sum_{l=0}^{l_0} \theta(R_l(E) - r) \left[ A_l(E) - \frac{Z}{r} \right] P_l$$

for the following reasons:

- it is a first principle one

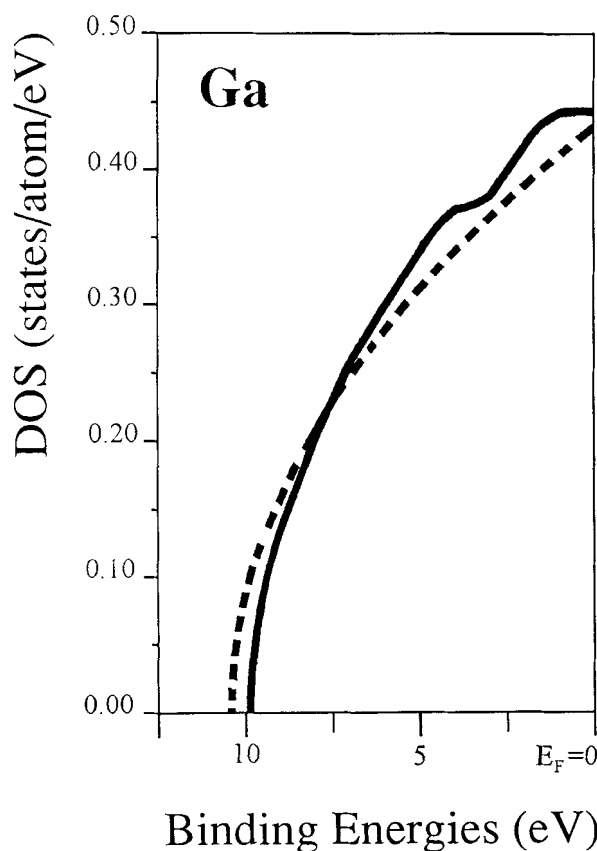


**Figure 1** DOS curves for aluminum:

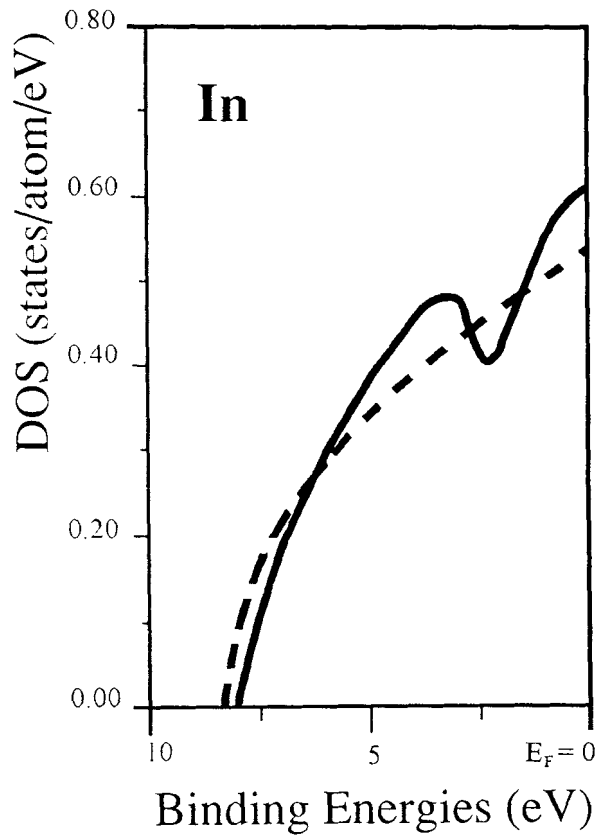
- full line: experimental data from Indlekofer (1987).
- dashed line: free electrons model at the same temperature.

– analytical corrections such as  $m_E$  and  $m^*$  had already been developed. We recall that Shaw (1969) introduced three effective masses ( $m^*$ , the density of states effective mass,  $m_E$  and  $m_k$  to deal with the renormalisation of the wave function) to improve the efficiency of the perturbation development on his model potential (Shaw 1968). Interested reader will find helpful formulae in Shaw (1969).

Thus, following Shaw's prescriptions, we calculated the parameters  $A_i(E) = Z/A_i(E)$  starting from the spectral terms of each ion. We used Ballentine and Gupta's (1970) formulation of the core-shift to extrapolate them at the Fermi energy of the liquid metal. Dielectric screening was accounted for with the exchange-correlation function of Ichimaru and Utsumi (1981). So, we were able to calculate the form factors, resorting or not to the introduction of  $m_k$ ,  $m_E$  and  $m^*$ . Our calculated values of  $m^*$  are presented in Table 1 together with those we've found in the literature and those experimental coming from Indlekofer (1987). With the help of Waseda's experimental structure factors (1980), we calculated the resistivities incorporating the different kinds of corrections. These results, compared with experimental values, are presented in



**Figure 2** DOS curves for gallium. For explanations, see Figure 1.



**Figure 3** DOS curves for indium. For explanations, see Figure 1.

**Table 1** Values of  $m^*/m$ .

Element	$(m^*/m)^a$	$(m^*/m)^b$	$(m^*/m)^c$	$(m^*/m)^d$	$(m^*/m)_{\text{exp}} = (N(E_F)/N_{f_e}(E_F))^e$
Al	1.016	1.04	1.045	1.032	1.119
Ga	0.938	—	—	0.981	1.047
In	0.865	0.89	0.933	0.935	1.129

<sup>a</sup> Wang *et al.* (1977)

<sup>b</sup> Shaw and Smith (1969)

<sup>c</sup> Shaw (1969)

<sup>d</sup> our results with Shaw's potential

<sup>e</sup> Indlekofer (1987)

Table 2. Notations are explained in the caption. We would like to point out more specially that the corrections of the form factors were made using Shaw's expressions of  $m_k$  and  $m_E$  and that the DOS corrections were done using only Indlekofer's experimental data for  $N(E_F)$ .

**Table 2** Calculated resistivities (in  $\mu\Omega\cdot\text{cm}$ ) with different corrections:  $\rho_Z$  is calculated using pure Ziman's formula;  $\rho_E$  is obtained by correcting the form factor from renormalization of the pseudo-wavefunction;  $\rho^*$  means that the experimental DOS correction has been applied.  $\rho_{\text{exp}}$  are experimental values.

Element	$\rho_Z$	$\rho_E$	$(m^*/m)^2$	$\rho^*_Z$	$\rho^*_E$	$\rho_{\text{exp}}$
Al(670°C)	16.02	14.95	1.252	20.05	18.71	24.50 <sup>a</sup>
Ga(35°C)	19.89	18.10	1.097	21.82	19.85	25.98 <sup>b</sup>
In(200°C)	22.39	20.11	1.276	28.57	25.66	33.45 <sup>c</sup>

<sup>a</sup> M. Mayoufi (1985)

<sup>b</sup> L. Anno (1985)

<sup>c</sup> J. G. Gasser (1982)

#### 4 DISCUSSION AND CONCLUSION

Our approach is original in that sense that experimental data are used to estimate a correction factor applied to a calculated resistivity but the form of this factor is not new. By the way, there has been controversy about corrections of that kind. So, we'll begin this discussion by justifying our approach. We would first like to point out the difference that exists between normal liquid metals and compounds characterized by localized electronic states (this explanation was suggested by Mott (1966) to explain properties of liquid mercury). For this latter case it is commonly accepted that  $\rho \propto 1/g^2$ . On the other hand a quarrel did divide for a long time people as Faber and Ziman (1965) who believed that  $\rho \propto g^2$  and people pretending that DOS effects on resistivity did cancel for weak scattering systems. A clarification has been brought about this problem by Van Oosten and Geertsma (1985). Their calculations have shown that in the case of metals not presenting localization phenomena ( $g \in [0.7; 1.35]$ ) and as typically of nearly free kind as sodium we can write

$$\rho_{KG} = g^2 \times \rho_Z$$

where  $\rho_{KG}$  means the resistivity calculated using Kubo's (1956) and Greenwood's (1958) formula. They did not apply their calculations to metals we are concerned by.

This clarification being brought, let's now have a look at our results. We can first notice that correcting the calculated resistivities for renormalization yields results that are worse. We recall that this correction is analytical in essence and we will return to that point a few lines later. Secondly, it can be noticed (see Table 1) that the calculated values of  $m^*/m$  and experimental ones disagree. We would have liked to know the uncertainties on the DOS measurements but they were not published. Whatever they are, we point out that experimental corrections always improve the results. So we can question about the validity of calculated  $m^*$ . It could be argued that this is because of the choice of the potential, but then we would have to recall that the values of Wang *et al.* (1977) were obtained with a different kind of potential (EIMP) and that they are not exceptions to the rule. It should be thought too that it is because of Ziman's formula, but this would be as reversing the problem: aren't they the corrections that are



supposed to improve the deficiencies of the formula and not the opposite? So, it might rather be the resort to the perturbation theory that is not quite legitimate. Indeed the more the experimental DOS curve deviates from the free electrons one (see Figures 1, 2 and 3), the bigger are the deviations between calculated and experimental  $m^*$ :

- in Al case both are greater than one but calculated values are not large enough.
- in Ga case whose DOS curve deviates a bit more, calculated values are lower than one, while experimental one is larger but the absolute difference remains small.
- in In case whose DOS curve presents a singular kink, conclusions are the same as for Ga but absolute differences become important.

This statement would have to be explored farther in the light of other facts but we close the discussion here.

Whatever are the reasons, our calculations confirm Van Oosten's and Geertsma's conclusions by improving the resistivity calculations. Experimental measurements of  $N(E)$  allow an estimation of DOS corrections. These are not the only one that are reported in the literature. According to Leavens *et al.* (1981), they can for instance be mixed with the finite mean free path correction introduced by Ferraz and March (1979).

To conclude, we would like to point out that experimentally estimating  $m^*$  leads to good results improving the calculated resistivities for trivalent metals. It seems to be applicable to more numerous metals than classical analytical estimations whose applications field seems to be restricted to authentic nearly free electrons like metals. Our approach might be extended to the calculation of other properties such as magnetic susceptibility within which the DOS partially enters.

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