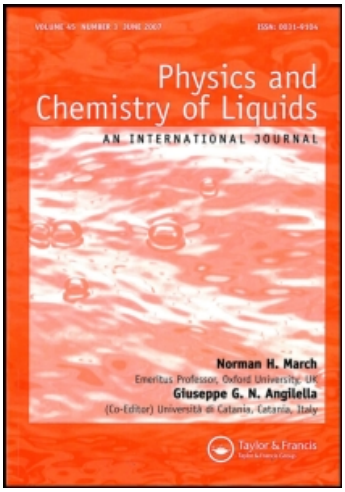

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The Temperature Dependence of the Resistivity of Liquid Silver

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The Temperature Dependence of the Resistivity of Liquid Silver

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The resistivity of pure liquid silver is not well known. Important differences exist between the scarce old data. In this paper we present new accurate measurements and discuss the temperature dependence of the resistivity in the framework of Ziman formalism in terms of structure factor and form factor.

We used both experimental and calculated (following a hard sphere description) structure factors. The form factor has been deduced from model pseudopotentials which take into account the *d* band like the Moriarty (1972) potential; or from the *t* matrix expressed in terms of phase shifts. The different calculations are in fairly good agreement.

Key Words: Model potentials, phase shifts, liquid metal, resistivity, silver.

1 INTRODUCTION

It is largely agreed that electrical transport in simple liquid metals has been well resolved from a theoretical point of view. The transport properties are described by the nearly free electron theory with Ziman's formula.[1] However the model potential formalism developed before 1970 was not suitable to describe noble or transition metals. Two approaches have been developed; the first includes *d* electron effects in the pseudopotential through an hybridization of the *d* band with the free electron conduction band[2,3]; the second replaces, in Ziman formula, the pseudopotential form factor by a *t* matrix expressed in term of phase shifts.[4]

After recalling the basic formula in § 2 and the experimental method in § 3, we present our measurements in § 4. The experimental and theoretical results are discussed in § 5.

2 THEORY

For simple liquid metals the nearly-free-electron (N.F.E.) model appears to be reasonably well based and the well-known Born approximation formula proposed by Ziman is given by:

$$\rho = 3 \cdot \pi \cdot m^2 \cdot \Omega_0 / (4 \cdot \hbar^3 \cdot e^2 \cdot k_f^6) \int_0^{2 \cdot k_f} a(q) \cdot w(q)^2 \cdot q^3 \cdot dq \qquad (1)$$

where Ω_0 is the atomic volume, $a(q)$ the structure factor, $w(q)$ the model potential form factor, and k_f the value of the Fermi wavevector defined by the equation:

$$k_f^3 = 3 \cdot \pi^2 \cdot Z / \Omega_0 \qquad (2)$$

m, e, $\hbar$, and π are the usual constants and Z is the valence. In order to compute the resistivity, we must choose an appropriate model potential and structure factor. We also use the t matrix form factor $t(q)$ instead of $w(q)$.

Structure Factors

Our calculations have been performed with hard sphere structure factors.[5] At each temperature the hard sphere diameter is deduced from the experimental density of the pure metal compiled by Crawley[6] and from its packing fraction given by the Waseda[7] empirical law:

$$\eta(T) = A \exp(-B \cdot T) \qquad (3)$$

The parameters A and B have been taken from Waseda's book.[7] The hard sphere diameter is given by:

$$\sigma^3(T) = [\sigma \cdot \eta(T) \cdot \Omega_0(T) / \pi] \qquad (4)$$

The experimental structure factors have been taken from Waseda's book.[8]

Form Factors

Difficulties arise when the pseudopotential theory is used for noble and transition metals because of the hybridization of d states with the free electron conduction band. Harrison[2] has generalized the pseudopotential theory to include the d band metals. Moriarty,[9] using Harrison's generalized formalism, calculated the silver form factor at both liquid and solid densities. Two years later, Moriarty[3] completed his earlier calculations using d exchange potential in a manner suggested by Lindgreen.

On the other hand, Animalu[10] has used the concept of quantum defect in setting up a model potential for transition metal ions. The resistivity of liquid silver has been calculated with Moriarty's[3] tabulated form factor, which was renormalized in order to take into account the true atomic volume of the liquid at the considered temperature, following the procedure discussed by Ziman.[11] The Animalu[10] transition metal model potential (T.M.M.P.) given in an analytical form has also been used together with the Vashishta-Singwi[12] screening function.

An alternative solution to model potential treatment has been proposed by Evans *et al.*[4] for pure metals, and by Dreirach *et al.*[13] for alloys. The model potential form factor is simply replaced by a t matrix form factor in Ziman's formula. It can be expressed in term of phase shifts who are computed from a muffin-tin potential constructed either by the method of Dreirach *et al.*[13] or by that described by Mukhopadhyaya *et al.*[14] In this paper we used the phase-shifts of Dreirach[13] obtained in the framework of the quasi-crystalline approximation, and those of Waseda[15] constructed following the Mukhopadhyaya method.[14]

3 EXPERIMENTAL METHOD

Resistivity measurements were performed by the four probe method using a quartz cell fitted with tungsten electrodes. The accuracy of the resistivity is estimated to be 0.4% and that of the temperature 0.4%. The geometrical constant of the cell was calibrated by measuring the resistivity of triple distilled mercury. Full experimental details have been described by Gasser.[16]

4 EXPERIMENTAL RESULTS

Our experimental results (curve 1), together with other experimental one's have been plotted on Figure 1. The electrical resistivity of liquid silver has been measured by Uemura and Ikeda[17] (symbol: $\times$) by Soifer *et al.*[18] (symbol: $+$), by Matuyama[19] (symbol: Δ) by Ozelton *et al.*[20] (symbol: $\square$) and in our laboratory by Mayoufi[21] (curve 2). The results obtained by Uemura are near our values at the melting point but their temperature coefficient is 4 times smaller than ours. Soifer *et al.*[18]

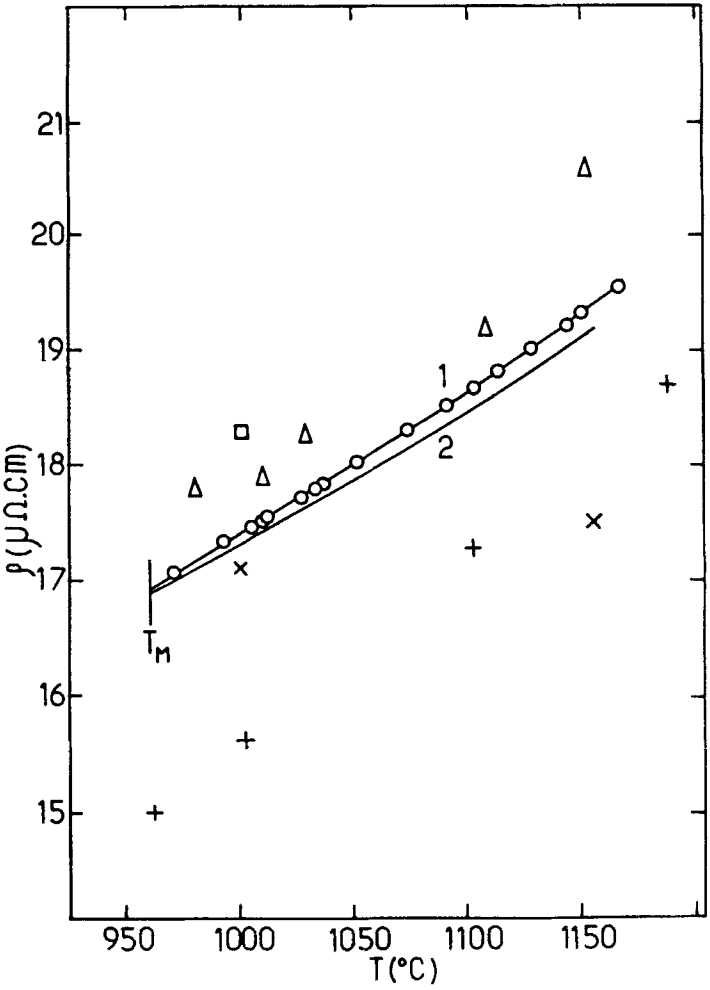

Figure 1 Electrical resistivity of liquid silver between the melting point and 1160°C. Comparison with earlier measurements. Curve 1, our measurements; curve 2 Mayoufi[21] values; × Uemura *et al.*[17]; + Soifer *et al.*[18]; △ Matuyama[19]; □ Ozelton *et al.*[20]

results are 11% smaller than ours at the melting point and their temperature coefficient is 30% greater than ours. The old values of Matuyama are near our values (3% higher) but are more scattered. The value of Ozelton lies 5% higher than ours at 1000 Celsius, while our older values (curve 2) are at less than 1% from our last one's at 1100 Celsius.

5 DISCUSSION

The electrical resistivity of silver has been calculated at 1000 and 1150°C with the pseudopotentials of Moriarty[3] and Animalu[10] and with the t matrix using the phase shifts of Waseda[15] and Dreirach[13] both with experimental and hard sphere structure factors. Some of these values are shown in Table 1. The resistivity curves calculated with hard spheres and the points obtained with Waseda's[8] experimental structure factors are reported on Figure 2.

At 1000 and 1150°C, the results obtained with Waseda's[8] structure factors are always higher than those calculated with hard spheres for all form factors used. However the difference is less pronounced with Moriarty potential (13 and 9% at 1000 and 1150°C respectively) than with the T.M.M.P. (26 and 17%) or with the two sets of phase shifts (31% and 24% for both phase shifts). The best results compared to our measurements are obtained with Dreirach phase shifts (curve 2) and Moriarty pseudopotential (curve 4). With Dreirach *et al.* phase shifts and with hard spheres we obtain at respectively 1000 and 1150°C a value 14 and 10% (curve 2) greater than our experimental one (but 50 and 36% with experimental structure factors (points "2"). With Moriarty pseudopotentials the results are respectively 33 and 20% greater with hard spheres (curve 4) and 50 and 43 with experimental structure

Table 1 Electrical resistivity of liquid silver (in $\mu\Omega \cdot$ cm) and its temperature coefficient (in $n\Omega \cdot cm \cdot K^{-1}$) computed with experimental and hard sphere structure factors and different form factors.

Structure factors \ Form factor		Phase shifts		Pseudopotentials		Experimental resistivity
		Waseda	Dreirach	Moriarty	Animalu	
Waseda[8]	1000°C	31.35	26.22	26.20	54.50	17.40
Hard spheres	1000°C	23.89	19.99	23.17	44.00	
Waseda[8]	1150°C	30.84	25.79	24.90	52.96	18.96
Hard spheres	1150°C	24.90	20.88	22.90	45.41	
$d\rho/dT$ between 1000 and 1150°C						
Waseda[8]		−3.4	−2.9	−8.7	−10.3	10.4
Hard spheres		6.7	5.9	−1.8	9.4	

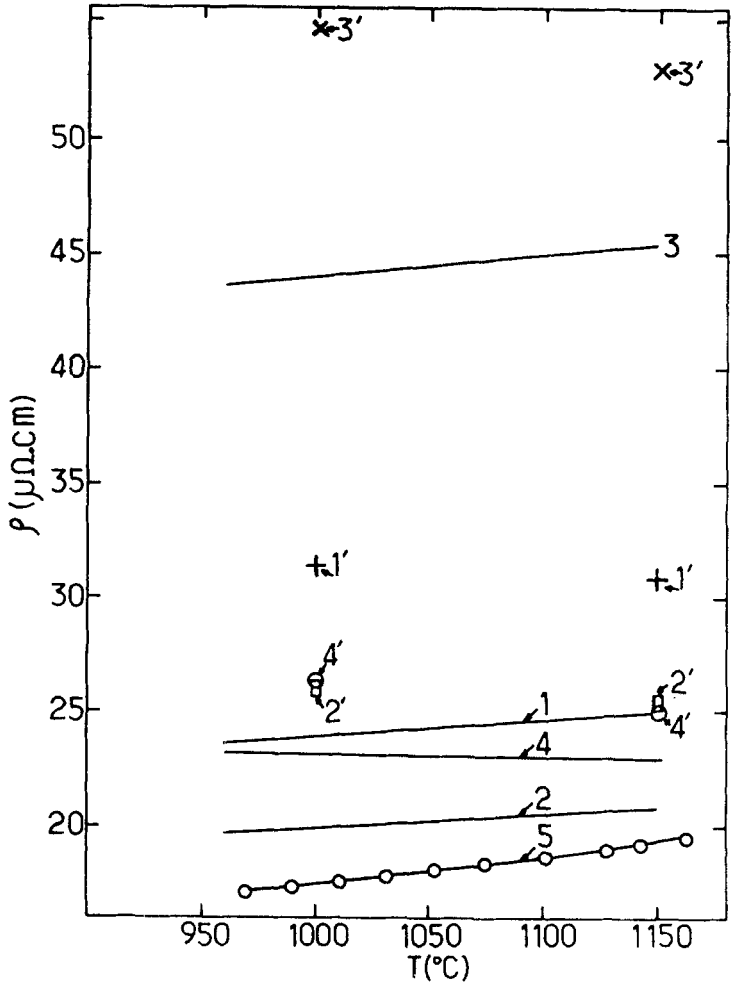

Figure 2 Electrical resistivity of liquid silver between the melting point and 1160°C. CURVE 1 Computed with hard sphere structure factors and Waseda[7] phase shifts. CURVE 2 Computed with hard sphere structure factors and Dreirach *et al.*[12] phase shifts. CURVE 3 Computed with hard sphere structure factors and Animalu[9] transition metal model potential (T.M.M.P.). CURVE 4 Computed with hard sphere structure factors and Moriarty[3] hybridized model potential. CURVE 5 Experimental resistivity. Experimental points 1'; 2'; 3'; 4' correspond to the same form factors and to the Waseda[8] experimental structure factor at 1150°C.

factors (points "4"). The Waseda phase shifts overestimate the resistivity of 37 and 31% with hard spheres (curve 1) and 80 and 62% with experimental structure factors (points "1"), while the T.M.M.P. completely fails by overestimating it of about 3 times (curve 3 and points

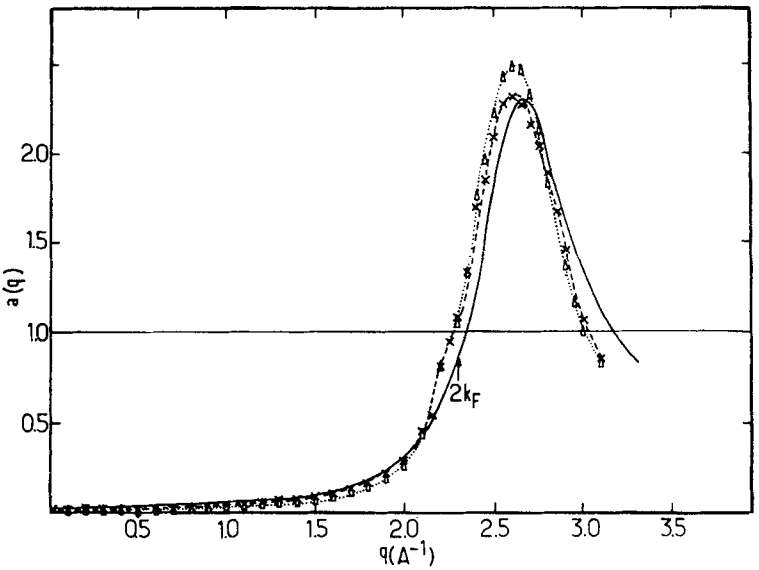

Figure 3 Experimental (Waseda)[8] and hard sphere structure factors (packing fraction: $\eta = 0.4322$). The arrow indicates the position of $2k_f$. △: 1000°C; ×: 1150°C.

"3"). These results cannot be considered as good if one uses the experimental structure factors. However with the hard sphere structure factors, the calculated resistivities can be considered as acceptable. Noble metals resistivities are very sensitive to accurate structure factors near $2k_f$. The attentive examination of Waseda's structure factors shows a shoulder in this q region and explains the important difference with the hard sphere structure factors. This shoulder must be confirmed experimentally before definitive conclusions can be drawn.

In order to compare more precisely this result and to analyse from where the difference comes from, we have plotted in Figure 3 the experimental and calculated structure factors, in Figure 4 the square of the form factors obtained with the different model potentials and phase shifts and in Figure 5 the integrand of the resistivity for the same potentials.

We observe on Figure 3 that the shapes of the structure factors are different above 1.5 $Å^{-1}$. The effect of the difference is minimized near 1.5 $Å^{-1}$ because the nodes of the form factors lie in this region, but the shoulder of the structure factor near 2.2 $Å^{-1}$ has an important effect on the resistivity. In all cases, the most important contribution comes from the region near the backward scattering, as can be seen on Figure 5. The

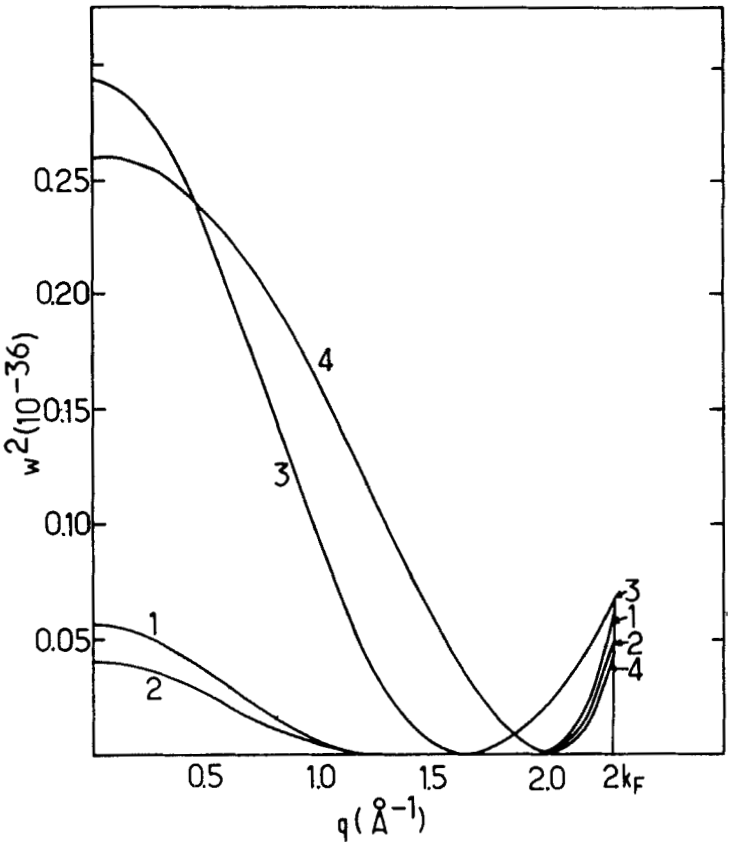

Figure 4 Square of the form factor (in S.I. units) obtained with: 1) Waseda[15] phase shifts. 2) Dreirach *et al.*[13] phase shifts. 3) Animalu[10] T.M.M.P. 4) Moriarty[3] form factor.

very important resistivity obtained with the T.M.M.P. comes from the fact (Figure 4) that the T.M.M.P. node is located at smaller q values than other form factors. We also remark on Figure 4 that the $q = 0$ limit of the pseudopotential form factors are not the same; the low q limit of the Moriarty potential is different from $-2/3$ Ef because of the hybridization term as can be seen in Moriarty's[3] paper on his Figure 4. The difference with the phase shift form factors is much more important, but the contribution to the resistivity of the q domain below 1.5 Å^{-1} is negligible.

Concerning the temperature coefficient of the resistivity, (Table 1) the hard sphere structure factors give a coefficient of about 60% of the experimental one for the phase shifts, about 90% of it for the T.M.M.P.

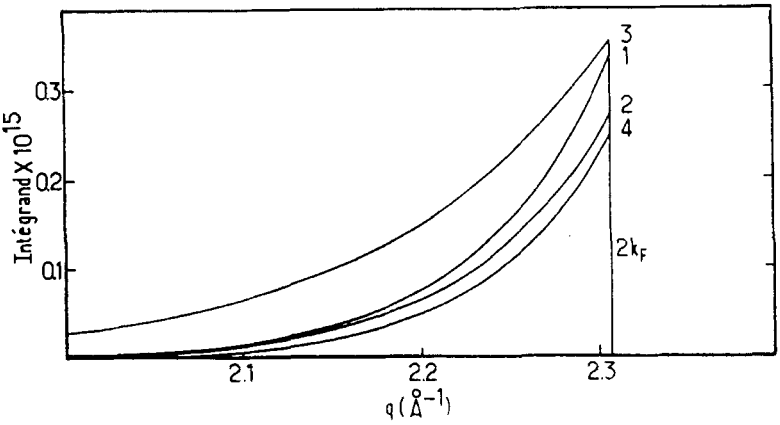

Figure 5 Integrands of the resistivity (in S.I. units) between 2 $Å^{-1}$ and $2k_f$ obtained with the hard sphere structure factor at 1000°C and with: 1) Waseda[15] phase shifts. 2) Dreirach *et al.*[13] phase shifts. 3) Animalu[10] T.M.M.P. 4) Moriarty[3] form factor.

pseudopotential (but with absolute values of resistivity very different) and a negative value with the Moriarty potential. This result is, a priori, surprising since negative temperature coefficients have only been explained by the decrease of the first peak of the structure factor. In the case of silver, the limit $2k_f$ lies at the left of the main peak and is smaller than 1. This feature can be explained by the decrease of the limit of integration with temperature. In certain cases, this negative contribution to the temperature coefficient is greater than the positive contribution resulting from the increase of the structure factor when it is smaller than 1.

The use of the experimental structure factors gives in all cases a negative temperature coefficient. The explanation of this must probably be found in the too important uncertainty in the measurement of a structure factor at high temperatures.

6 CONCLUSION

We have in this paper presented new accurate measurements on the resistivity of liquid silver. Surprisingly, they rather confirm very old (and dispersed) measurements of Matuyama.

The theoretical interpretation shows that the use of the experimental structure factor does not improve the calculated values nor the temper-

ature dependence. Both phase shifts and model potentials have been used. The quasi-crystalline approximation phase shifts of Dreirach give better results than the Mukhopadhyaya method. Harrison's generalised pseudopotential theory used by Moriarty leads also to good results.

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