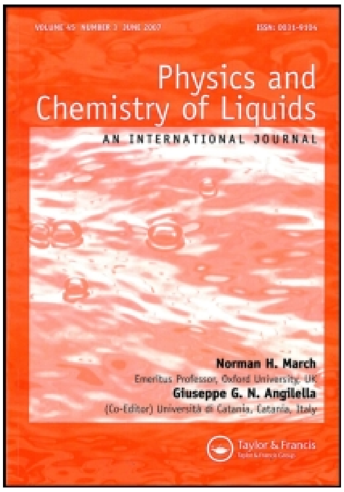

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The Temperature Dependence of the Resistivity and Thermopower in Some Polyvalent Liquid Metals

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Abstract—Calculations of the temperature dependence of the resistivity and thermopower of liquid indium, cadmium, thallium, lead and mercury are presented. The values of the thermopower are in better agreement with experiment than the results of previous calculations. The success and validity of the Ziman nearly-free-electron theory is discussed in connection with the results for the resistivity.

1. Introduction

The Ziman nearly-free-electron model (Ziman,(1) Bradley *et al.*(2)) has been fairly successful in describing the qualitative behaviour of the electrical resistivity in many liquid metals. One expects the model to be good for the alkalis because in these metals the mean free path λ is about one hundred times the interatomic distance d and the weak scattering picture should be valid. In some of the heavier polyvalent metals such as lead, thallium and mercury $\lambda \sim 2d$ and it is not obvious that a simple nearly-free-electron approach is correct. Previous calculations, using the Ziman theory, for polyvalent metals have given values of the resistivity ρ and the thermopower S which differ considerably, the latter sometimes in sign as well as magnitude, from the experimental results.

The purpose of the present work is to recalculate the resistivity and thermopower, using new model potentials to describe the scattering, for several polyvalent metals and ask whether the Ziman theory is successful in these cases. It is well known (e.g. Wiser(3)) that the Ziman formula for the resistivity is very sensitive to small changes in the positions of the zero of the angular scattering cross-section and the peak of the liquid structure factor. Consequently, it is more realistic to consider the temperature variation of the resistivity when comparing theory and experiment. Here results for the temperature variation of the resistivity and thermopower in liquid indium, cadmium, thallium, lead and mercury are presented. These calculations explicitly evaluate the change of the scattering cross-section with temperature and include the energy dependence of the scattering. Previous work on the polyvalent metals omitted the latter and the present results indicate that the thermopower depends strongly on this energy dependent contribution.

It should be noted that there has been a good deal of controversy concerning the success and validity of the Ziman theory even for the alkali metals (Greenfield,(4) Greenfield and Wiser,(5) Adams and Ashcroft(6) and Ziman(7)). Recently Greenfield and Wiser(8) have argued that the nearly-free-electron model is not reliable in zinc and cadmium but base their conclusion on a single result for the resistivity and thermopower.

2. Details of Calculation

The calculations of the resistivity and thermopower were carried out essentially as described by Evans.(9) The resistivity ρ can be written in the usual way as:

$$\rho = \frac{3\pi \Omega_0}{e^2 \hbar V_F^2} \langle a(q) \, |W(K, q)|^2 \rangle \tag{1}$$

where Ω_0 is the atomic volume, V_F is the Fermi velocity, $a(q)$ is the structure factor and $W(K, q)$ is the model potential matrix element describing scattering from a free electron state K to another state $K+q$ on the Fermi sphere of radius K_F. The brackets indicate an average of the kind:

$$\langle f(q) \rangle = \int_0^1 d\left(\frac{q}{2K_F}\right) 4 f(q) \left(\frac{q}{2K_F}\right)^3 \tag{2}$$

The thermopower S, at temperature T, can be expressed as:

$$S = \frac{-\pi^2 K_B^2 T}{3\,|e|\,E_F} X \tag{3}$$

where K_B is Boltzmann's constant, E_F is the free electron Fermi energy and X is given by:

$$X = -\left.\frac{\partial \ln \rho(E)}{\partial \ln E}\right|_{E=E_F} \tag{4}$$

Equation (4) can be rewritten, using (1) and (2) as:

$$X = 3 - 2q' - \frac{r}{2}$$

with

$$q' = \frac{|W(K_F, 2K_F)|^2 a(2K_F)}{\langle a(q)\,|W(K_F, q)|^2\rangle}$$

$$r = \frac{K_F \langle a(q)\,(\partial/\partial K)\,|W(K, q)|^2\rangle}{\langle a(q)\,|W(K_F, q)|^2\rangle} \tag{5}$$

The screened model potentials $W(K, q)$ are modified versions of the Animalu–Heine⁽¹⁰⁾ type. The bare model potential parameters of Animalu were revaluated using more accurate interpolation techniques based on the quantum defect method and taking into account the effects of high lying atomic core states, Evans.⁽⁹⁾ The screening calculation retains the non-locality of the model potential and the resultant energy dependence of the screened model potential gives rise to the term r of Eq. (5). This term can represent a large contribution to the thermopower parameter X. In mercury, for example, $r \sim -12$. Previous calculations omitted the term r as they either used a local model potential or were unable to do the relevant differentiation.

The matrix elements $W(K, q)$ can differ considerably from those of Animalu and Heine⁽¹⁰⁾ in the region around backscattering $q \sim 2K_F$. The major contribution to the resistivity comes from this region of q so small changes in the form factor are important.

The resistivity and thermopower parameter were calculated at those temperatures for which experimental structure factors were available. Percus–Yevick hard sphere approximations are not very reliable for polyvalent liquid metals. The screened model potential depends upon the density of the liquid metal since the Fermi wave number is given by:

$$K_F^3 = 3\pi^2 Z/\Omega_0 \tag{6}$$

where Z is the valence and Ω_0 is the atomic volume at the relevant temperature. It was assumed that the *bare* potential of the ion does not change with density so that all the volume dependence of the model potential arises from the change of the screening electron density, Ziman.⁽⁷⁾ In other words, a new scattering cross-section was evaluated at each temperature but using the same bare model potential parameters A_l etc. as given by Evans.(9)

3. Results

The results for the five metals considered are shown in Figures 1 to 10 where they are compared with experiment, and where appropriate, previous calculations. For all these metals the thermopower parameter X has been plotted as a function of temperature rather than the thermopower itself. Since the latter contains a factor T, see Eq. (3), it is a much more sensitive test of the theory to predict the correct behaviour of $X(T)$. The experimental values of X were all taken from Marwaha(11) and he estimated the accuracy of X to be ± 0.2. It is difficult to estimate the accuracy of the present calculations. There are many approximations and assumptions in the construction of the model potential but the numerics used to evaluate it are very accurate. For a *given* model potential the uncertainties in the experimental structure factors are still large enough to influence both the resistivity and the thermopower. An estimate of the resultant error in the resistivity has been calculated by North *et al.*(12) for lead and North and Wagner(13) for cadmium. In each case the error is about 2% and in the present work this accuracy has also been assumed.

INDIUM

The ratio of mean free path to interatomic distance, λ/d, is about 5 for indium. The structure factor has been measured by Ocken and Wagner(14) at five different temperatures and they have used their results along with the Animalu–Heine model potential corrected for volume changes to calculate the values of ρ and X given in Figs. 1 and 2. Although the present results for the resistivity are numerically closer to experiment than the previous they do not give the observed temperature dependence. The experimental points are due to Roll and Motz.(15) In Fig. 2 it can be seen that the predicted thermopower X is quite close to experimental value and has the correct temperature variation. Ocken and Wagner's values for X were negative. The energy dependent term r of Eq. (5) is important here and is sufficiently negative to give X the correct sign.

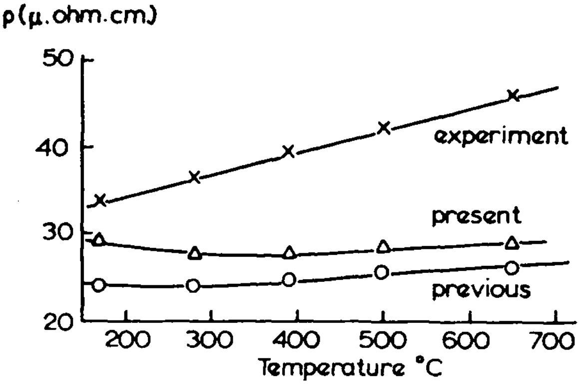

Figure 1. Resistivity ρ of liquid indium.

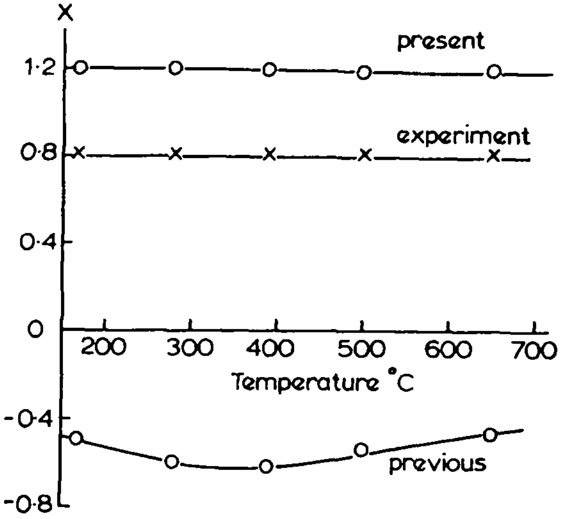

Figure 2. Thermopower X of liquid indium.

CADMIUM

In this metal λ is about 6.7 d, North and Wagner⁽¹³⁾ have measured the structure factors of cadmium and calculated the resistivity and thermopower using the Animalu–Heine model potential. These results are shown in Figs. 3 and 4. The experimental values of the resistivity are due to Roll and Motz.⁽¹⁵⁾ The temperature coefficient $(\partial\rho/\partial T)$ is very small in cadmium and the calculated results also predict a small coefficient but the numerical results are much smaller than the experimental ones. Since the Animalu–Heine form factor is larger than the present one near $q = 2K_F$ the results of North and Wagner are somewhat closer to experiment than the present. The thermopower does not agree with experiment. As already stated the model potential is not strong enough near backscattering to give good value for the resistivity and, consequently, the coefficient q' of Eq. (5) which is proportional to $|W(K_F, 2K_F)|^2$ is small and X is dominated by the positive free electron term. Thermopower results are not very meaningful unless there is reasonable numerical agreement between theory and experiment for the resistivity.

It is interesting that the model potential fitted to the Fermi surface of solid cadmium by Stark and Falicov⁽¹⁶⁾ is much steeper and larger than both the present model potential and that of Animalu and Heine in the region $q \sim 2K_F$. The calculations of Greenfield and Wiser⁽⁸⁾ using the Stark and Falicov potential gave a value of ρ which was 3.6 times larger than experiment and their result for X was about -13. Their calculations on zinc using another Stark and Falicov potential gave results which were also significantly different from experiment. On the basis of these results Greenfield and Wiser concluded that the Ziman theory was incorrect. The present work on cadmium and previous work on zinc (Evans⁽⁹⁾) indicate that model potentials intermediate between the present ones and those of Stark and Falicov should give values of both ρ and X which would be close to experiment in both zinc and cadmium. It may well be that the Stark and Falicov model potentials are not suitable for describing the scattering properties of ions in the liquid metal. Some non-local model potentials which are fitted to band structure data are susceptible to the truncation of the appropriate secular determinant and are subsequently strongly dependent on crystal structure (see

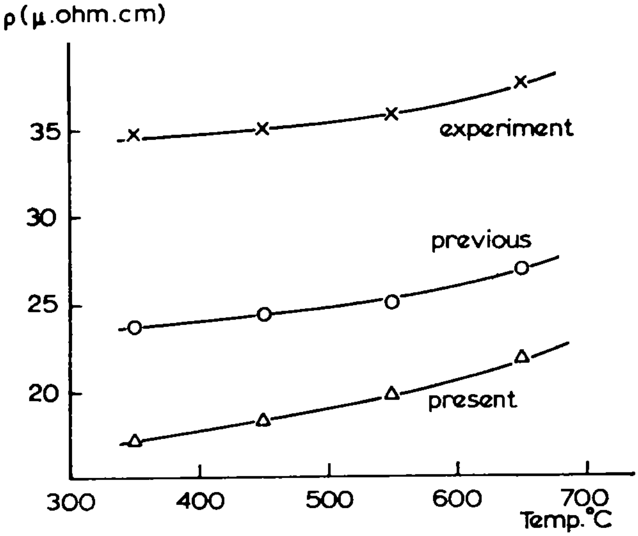

Figure 3. Resistivity ρ of liquid cadmium.

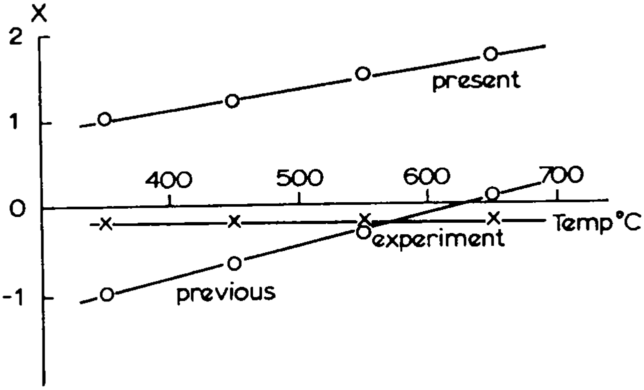

Figure 4. Thermopower X of liquid cadmium.

for example Cohen and Heine(17)). Such model potentials may not be at all related to those of the screened ion type which are used here.

THALLIUM

The ratio λ/d in thallium is about 2.5. Halder and Wagner(18) measured the structure factors and used the Animalu–Heine model potential to calculate the results shown in Figs. 5 and 6 where they are compared with the present results. The experimental values of the resistivity are due to Roll and Motz.(15) Reasonable numerical agreement with experiment is obtained for the absolute value of the resistivity at any one temperature and the calculated value of $(\partial\rho/\partial T)$ agrees with experiment to within the accuracy of the measured structure factors. The absolute values of the thermopower parameter are closer to experiment than the previous ones but are still too large. The temperature variation $X(T)$ agrees well with experiment and the calculations predict the observed fall off of $(\partial X/\partial T)$ with increasing temperature T.

LEAD

Here the ratio λ/d is about 1.6. The structure factors in lead have been measured over a wide range of temperature by North *et al.*(12) This makes lead a suitable metal to study. Although the calculated value of ρ at 340 °C is quite close to the experimental value the predicted temperature variation of the resistivity is much weaker than that observed (Davies and Leach(19)) and is much weaker than that calculated by North *et al.*(12) who used the Animalu–Heine model potentials (see Fig. 7). The coefficient

$$\frac{\rho_T - \rho_{340}}{\rho_{340}(T - 340)}$$

is 5.05×10^{-4}/deg.C from experiment, $(3.8 \pm 0.7) \times 10^{-4}$/deg.C. from the work of North *et al.* and $(1.75 \pm 0.6) \times 10^{-4}$/deg.C. from the present work and $T = 1100$ °C. The errors here refer to a 2% estimate made by North *et al.* to which reference has already been made. Even if one takes the maximum allowed error in the structure factor (as given by North *et al.*) the present value of the temperature coefficient is $(1.75 \pm 1.7) \times 10^{-4}$ deg.C. which is still well outside the observed value. It is difficult to understand why the present results

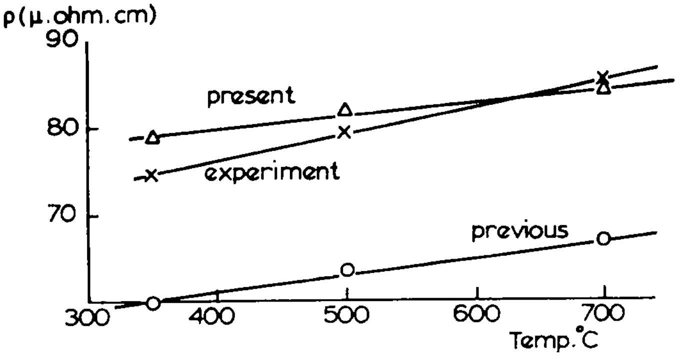

Figure 5. Resistivity ρ of liquid thallium.

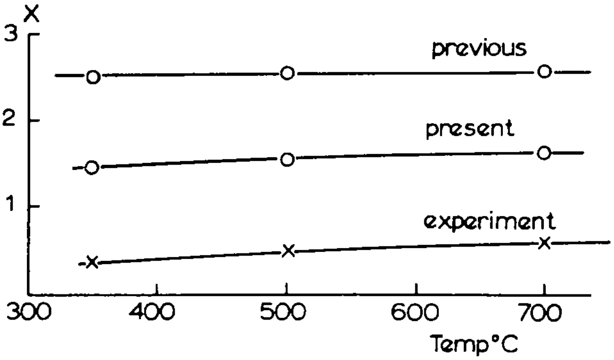

Figure 6. Thermopower X of liquid thallium.

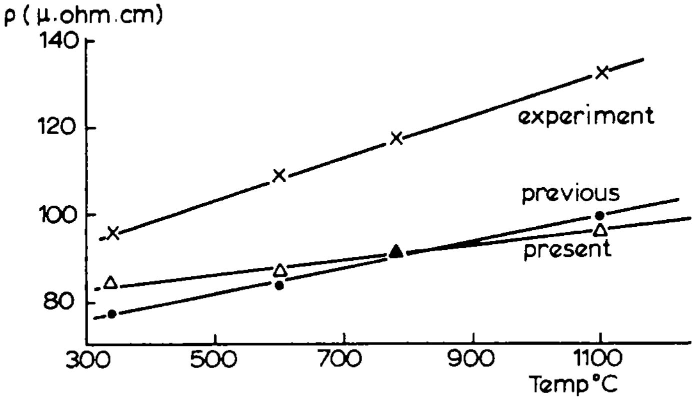

Figure 7. Resistivity ρ of liquid lead.

E

are so different from those of North *et al.* There are two possibilities: (a) North *et al.* used an approximation for the volume dependence of the model potential whereas in the present work the potential was evaluated at each density. (b) The resistivity is very sensitive to the integration mesh and this was probably different in each calculation. The calculated temperature dependence of the thermopower parameter, Fig. 8, is in good agreement with experiment and better than the previous results.

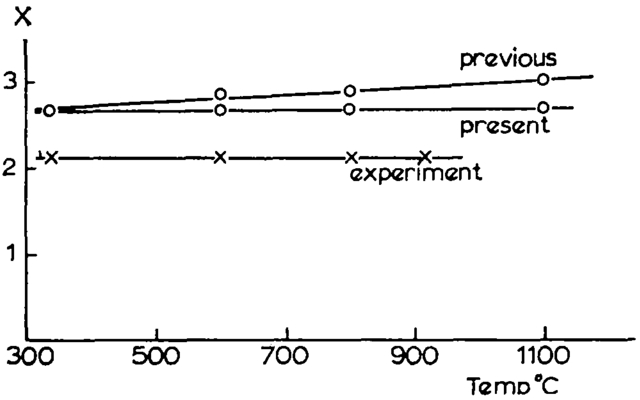

Figure 8. Thermopower X of liquid lead.

MERCURY

The ratio λ/d in mercury is approximately 2.3. Rivlin⁽²⁰⁾ *et al.* measured the structure factor at three different temperatures. The calculated temperature variation (see Fig. 9) of the resistivity is in reasonable agreement with experiment (Bradley⁽²¹⁾). The thermopower coefficient $(\partial X/\partial T)$ is positive but the results are available over too small a range of temperature to be very meaningful. These results are much better than previous calculations, see for example Evans.⁽⁹⁾

In each of these metals the volume dependence of the screened model potential is weak since K_F changes very little over the temperature ranges involved. The main contribution to the temperature coefficients $(\partial\rho/\partial T)$ and $(\partial X/\partial T)$ comes from the change in structure factor with temperature. In zinc $\partial\rho/\partial T$ is small and negative and

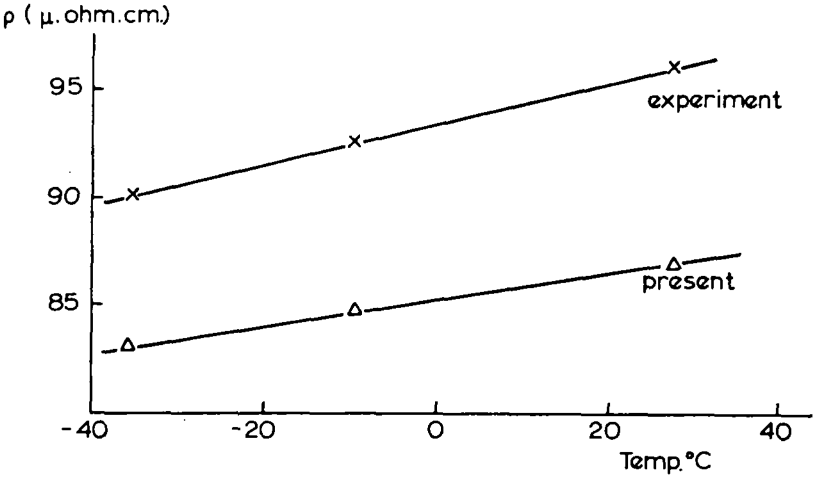

Figure 9. Resistivity ρ of liquid mercury.

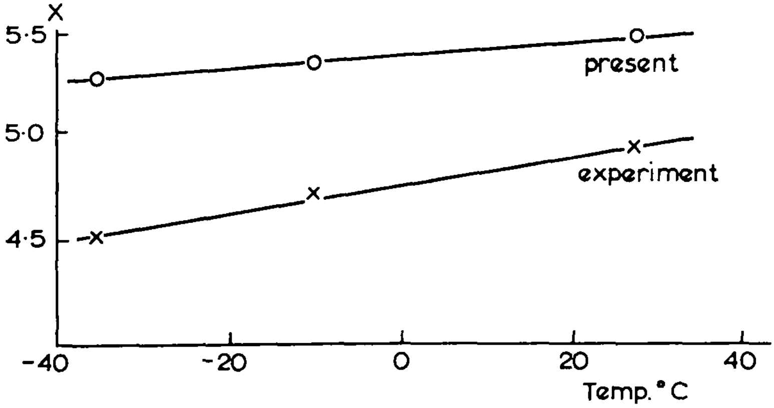

Figure 10. Thermopower X of liquid mercury.

this seems to be due to the fact that the structure factor does not change much with temperature for this metal (Wingfield and Enderby(22)).

4. Conclusions

It has been shown that inclusion of the energy dependent term in the thermopower leads to better agreement with experiment than the results of previous calculations for polyvalent liquid metals. In thallium, lead, indium and mercury the temperature dependence and the numerical values of the thermopower are now in reasonable agreement with experiment. Dickey *et al.*(23) Young *et al.*(24) and Thornton and Young(25) came to similar conclusions during their work on the alkali metals. Uncertainties about the absolute values of the model potentials and structure factors lead to considering the temperature dependence of the resistivity ρ rather than the absolute value at only one temperature. The behaviour of the model potential with temperature can be calculated straightforwardly but the structure factors have *random* errors and possible inaccuracies in the calculated values of say $1/\rho(\partial\rho/\partial T)$ can still be large. For thallium, mercury and cadmium the predicted values of this coefficient include the experimental results, but for lead the predicted value is only one-third of the measured value and for indium agreement is much worse. These results indicate that the Ziman nearly-free-electron model gives a reasonable qualitative account of the behaviour of $\rho(T)$ even for those metals where the mean free path is not much bigger than the interatomic distance.

Possible improvements on the Ziman model have been suggested by Faber(26) and more recently by Ashcroft and Shaich(27) and these suggest that the model potential matrix element should be replaced by an " effective potential " in the resistivity integrand of Eq. (1). This " effective potential " includes both the model potential and the structure factor because the actual scattering at any given ion depends upon the scattering due to its neighbours. Numerical calculations using this formalism have proved difficult (Shaich private communication) but it appears that, at least for sodium and aluminium, the " effective potential " is quite close in both shape and magnitude to the model potential. This may well be a further justification for the nearly-free-electron model. Ashcroft and Shaich's results are only valid in the weak scattering limit $\lambda \gg d$ and further analysis is required to see if a similar formalism can be derived for stronger scattering. The results of the present work in mercury, thallium and lead suggest that such analysis should lead to another nearly-free-electron like formula. One would then expect the " effective potential " to have the same magnitude as the model potential but to be more temperature dependent as it includes the structure factor.

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Note added in proof

Recently the structure factor of liquid indium has been measured at different temperatures by Ruppersberg, H. and Winterberg, K. H., *Phys. Letters* **34A,** 11 (1971). They find higher maxima in $a(q)$ than Ocken and Wagner and their calculations of the temperature dependence of the resistivity now agree well with the experiment.