

are additive, and that the same amount of Baber scattering present in pure Pd is also present in the alloys. The modifications appropriate for the case of the local-enhancement model are shown in Fig. 1, where the results of including various percentages of Baber scattering are indicated. A similar modification to the uniform-enhancement model is not shown, for it results in Lorenz numbers which fall off far too fast with increasing nickel concentration to represent the data in a reasonable fashion. Note in Fig. 1 that it is possible either to fit the data at one point (pure Pd), which gives $87\frac{1}{2}\%$ Baber scattering, or to project a Lorenz number which is truly independent of nickel concentration, which yields 75% Baber scattering. However, in view of the simplicity of the model, it is felt that such fits do not give a realistic estimate of the relative amounts of Baber and paramagnon scattering present in this system.

In the case of rhenium, the modification described above yields a Lorenz number $L_e = 1.108 \times 10^{-8} \text{V}^2 \text{K}^{-2}$. Although this is some 20% higher than the estimate presented in I, it still compares very favorably to the experimental value³ of $0.9 \times 10^{-8} \text{V}^2 \text{K}^{-2}$.

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¹J. T. Schriempf, A. I. Schindler, and D. L. Mills, *Phys. Rev.* **187**, 959 (1969).

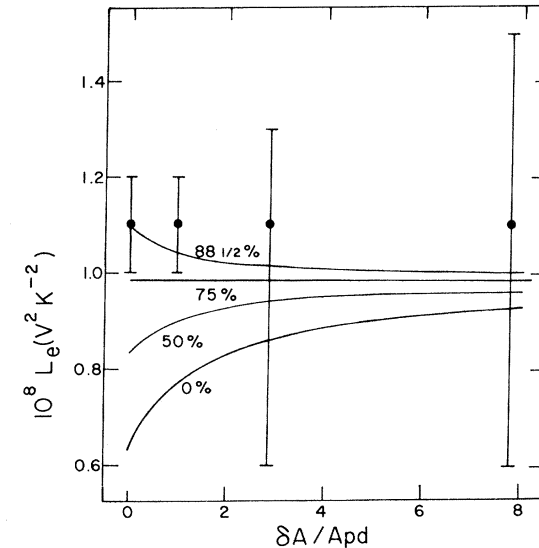


FIG. 1. Comparison of calculated and measured values of L_e for Pd and dilute Pd-Ni alloys. A is the coefficient of the T^2 term in the electrical resistivity, and $\delta A = A_{\text{alloy}} - A_{\text{Pd}}$. Solid dots and error bars represent values of L_e extracted from the data. The 0% curve is the result of a calculation with the local-enhancement model of paramagnon scattering with $\bar{I}_{\text{Pd}} = 0.9$, $k_s = 0.9125 \times 10^8 \text{cm}^{-1}$, and $k_d = 2k_s$. The other curves are the results of modifying the calculation by adding a concentration-independent amount of Baber scattering to the paramagnon scattering. The percentages indicate for each curve the amount of the total resistivity in pure Pd which is assumed to be Baber scattering.

²M. J. Rice (private communication).

³J. T. Schriempf, *Phys. Rev. Letters* **20**, 1034 (1968).

Electron-Electron Scattering in the High-Temperature Thermal Resistivity of the Noble Metals

M. J. Laubitz

Division of Physics, National Research Council, Ottawa, Canada

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Recently reported values for the Lorenz function of the noble metals show, at high temperatures, deviations from the expected standard value. These deviations can be satisfactorily explained, both in magnitude and temperature variation, in terms of normal electron-electron scattering.

The recently completed measurements of the high-temperature transport properties of the noble metals¹ show an interesting feature in that none of the electronic Lorenz functions L_e actually reach the standard Sommerfeld value $L_0 = \frac{1}{3}(\pi k/e)^2$ even at the highest temperatures investigated, contrary to theoretical expectations for electron-phonon

scattering.² This feature is shown in Fig. 1, where L_e is plotted versus a reduced temperature T/Θ_R . L_e has been calculated by subtracting the phonon contribution to the thermal conductivity, given by White,³ from the measured total conductivity; Θ_R is the Debye temperature obtained from electrical-resistivity data, and has been taken

from Gschneidner.⁴ The observed deviations in L_e are about twice as large as the estimated *maximum* experimental error,⁵ and the fact that they do not depend on the absolute temperature and the specimen conductivity, as would be the case with some unrecognized experimental error, lends support to their genuineness. Further confirmation in that direction, at the lower end of the temperatures investigated, is given by the close agreement of subsequent results obtained from completely different experimental systems.⁶ The purpose of this note is to point out that these deviations can be satisfactorily explained, both in magnitude and their temperature variation, by (normal) electron-electron scattering, which, because it contributes to the thermal but not electrical resistivity, depresses L_e below its expected value.

To evaluate the extra contribution to the electronic thermal resistivity W_e we proceeded as follows. One can show, quite generally,² that for electron-phonon interactions for $T > \Theta$,

$$(W_e - \rho/L_0 T) \propto T^{-2},$$

where ρ is the electrical resistivity. This depends neither upon the shape of the Fermi surface, lattice dynamics, interaction matrix, nor type of scattering, but only on the appropriateness of the trial functions used in the variational calculations of W and ρ , viz., $(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{F}}) \vec{k} \cdot \vec{u}$ and $\vec{k} \cdot \vec{u}$, respectively. As the left-hand side of this proportionality is essentially due to "vertical" processes, to which umklapp scattering does not contribute greatly (if at all), the pertinent Θ here is not Θ_R but Θ_L , the Debye temperature of the longitudinal phonons, which is of the order of $\frac{3}{2}\Theta_R$. We have therefore analyzed our experimental results for $T > \frac{3}{2}\Theta_R$ by fitting them to an equation of the form

$$W_e - \rho/(L_0 - S^2)T = A/T^2 + B_n T^n. \quad (1)$$

The inclusion⁷ of the absolute thermoelectric power S is a minor refinement to account partially for second-order effects in L . Three least-squares fits were performed for each metal to determine A and B_n , with $n=0, 1$, and 2 . The best fits in each case were obtained for $n=1$, and the resul-

TABLE I. Comparison of the experimental and theoretical coefficients of electron-electron thermal resistivity B in cm/MW. (dHvA stands for deHaas-van Alphen.)

	Cu	Ag	Au
Expt	4.4	4.2	7.3
Theor:			
V_F for free electrons	9.5	17.5	17.3
V_F from dHvA	15	8	24

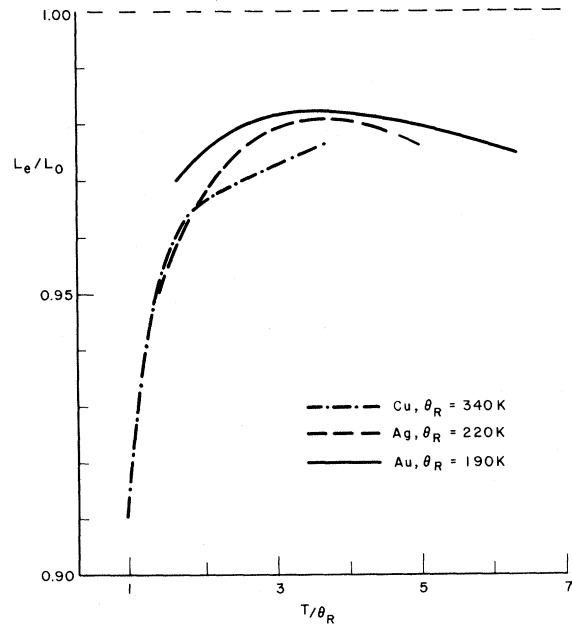


FIG. 1. Experimental values of the electronic Lorenz function L_e expressed as a ratio to its normal value L_0 as a function of the reduced temperature T/Θ_R .

tant values of B_1 are given in Table I; these values could be out by as much as 50%, and their probable error is of the order of 25%. For $n=0$, for which in any case there is no acceptable theory, no fit could be obtained within the estimated maximum error. For $n=2$, the rms deviations were roughly twice those for $n=1$; however, the fitted and experimental values still agreed within the maximum-error limits, and thus second-order effects in L , which lead to quadratic deviations,⁸ cannot be ruled out altogether as a possible explanation of the observed effects.

In deriving a theoretical expression for electron-electron scattering, we used the Fermi liquid theory, and, in particular, followed the development given by Baym and Ebener.⁹ Using the Born approximation for the electron-electron scattering matrix,¹⁰ we have arrived at the following formula¹¹:

$$\begin{aligned} W_{ee} &= 144\pi e^4 k_F T c / (5\hbar^3 v_F^4 q^4) = B T, \\ c &= b[b(1-b^2) \\ &\quad + (1+b^2)^2 \arcsin(1+b^2)^{-1/2}] / (1+b^2), \\ b &= q/2k_F, \end{aligned} \quad (2)$$

where q is the screening parameter, e is the electronic charge, and v_F and k_F the Fermi velocity and wave vector of the electron, respectively.

Taking

$$q^2 = 4\pi e^2 N(\epsilon_F),$$

$c \sim \frac{10}{9}$ for the noble metals, and (2) reduces to the simple form

$$B = 2\pi^3 / (\hbar v_F^2 k_F^3) . \quad (3)$$

Calculated values of B , based on the free-electron values of v_F and k_F , are given in Table I; we have also shown there the values calculated using the belly velocities from the de Haas-van Alphen effect.¹² In general, the agreement between the theoretical and experimental values is good, the latter being 3–4 times less than the former. This is quite reasonable, since Ziman indicates¹⁰ that the Born approximation overestimates the electron-electron scattering by a factor of about 5. The relative magnitudes of the observed values are also satisfactory: Certainly, Cu and Au are in the correct ratio. Ag is perhaps a bit low when the belly velocities are used; however, Ag has a very large ratio of belly-to-neck velocities, and this should lead to an enhancement of the scattering through a sort of two-band effect.¹³ Our experimental values have also the right order of magnitude when com-

pared to low-temperature effects usually associated with electron-electron scattering. One would expect the effects in the noble metals to be of the order of $(v_e/v_d)^2 \sim 10^2$ smaller than in transition metals¹⁴; the experimental results for the latter,¹⁵ where there are no special enhancement effects as occur in Ni or Pd, give a B of the order of $(8-10) \times 10^{-4}$ cm/W, which is in the right ratio to our results.

The explanation of the deviation in the high-temperature L_e of the noble metals in terms of electron-electron scattering is therefore very plausible: It gives the experimentally preferred temperature variation and the right magnitude whether compared to theory or previous low-temperature results.

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¹M. J. Laubitz, *Can. J. Phys.* **45**, 3677 (1967); **47**, 2633 (1969).

²J. M. Ziman, *Electrons and Phonons* (Oxford U. P., Oxford, England, 1960), p. 389.

³G. K. White, *Australian J. Phys.* **13**, 255 (1960).

⁴K. A. Gschneidner, *Solid State Phys.* **16**, 275 (1964).

⁵The maximum experimental error in L_e , obtained by adding the magnitudes of errors of all possible contributing sources, is about 0.8%; the probable error should not exceed 0.5%.

⁶J. P. Moore, D. L. McElroy, and R. S. Graves, *Can. J. Phys.* **45**, 3849 (1967); J. G. Cook and M. P. van der Meer, *ibid.*, **48**, 254 (1970); T. Matsumura and M. J. Laubitz, *ibid.*, **48**, 1499 (1970).

⁷Values of S were taken from N. Cusack and P. Kendall, *Proc. Phys. Soc. (London)* **72**, 898 (1958).

⁸Deviations in L_e quadratic in temperature can be related to second-order effects, expressible as derivatives of the "conductivity function" $\sigma(\epsilon)$ (Ref. 2, p. 385). Our experimental results, when interpreted in that way, give $(d^2 \ln \sigma / d\epsilon^2) \sim -0.4 \text{ eV}^{-2}$. This is about a factor of 2 larger than the first derivative of this function, related to the thermopower of the metal, and thus seems too large. Unfortunately, nothing further can be said on that matter, because all the difficulties connected with the explanation of the thermopower of the noble metals [see, for instance, J. M. Ziman, *Advan. Phys.* **10**,

1 (1961)] enter, to an even larger extent, into the second derivative of $\sigma(\epsilon)$.

⁹G. Baym and C. Ebener, *Phys. Rev.* **170**, 346 (1968).

¹⁰Reference 2, p. 170.

¹¹This formula differs from the one given in Ref. 2, p. 417, in its functional dependence on some of the parameters. Ziman's formula, which appears to be in error by a factor of 2, has been derived under the implicit assumption that $c \sim \pi b^3$ (in our notation). Although this approximation is not valid generally, it is suitable for the monovalent metals if, as we have done, one assumes that $q = 4\pi e^2 N(\epsilon_F)$.

¹²D. Shoenberg, *Phil. Trans. Roy. Soc. London* **A255**, 85 (1962).

¹³J. S. Dugdale and Z. S. Basinski, *Phys. Rev.* **157**, 552 (1967). Such an effect would also lead to contributions in $\rho \propto T^2$, but these would be difficult to distinguish from the electron-phonon T^2 terms in ρ . There would still be a depression of L_e , since for interband electron-electron scattering $L_{ee} \sim \frac{5}{12} L_0$ [M. J. Rice, *Phys. Letters* **26A**, 86 (1967); *Phys. Rev. Letters* **20**, 1439 (1968)].

¹⁴Reference 2, p. 416.

¹⁵C. K. White and S. B. Woods, *Phil. Trans. Roy. Soc. London* **A251**, 35 (1959); J. T. Schriempf, *J. Phys. Chem. Solids* **28**, 2581 (1967).