

ascribed its weak isotope dependence to the fact that it involved an acoustic mode in which the heavier fluorine ion has most of the displacement. Our spectral resolution was not high enough to reveal isotope shifts. For the 252.5-cm^{-1} band any shift must have been less than 1 cm^{-1} . In the future we plan to look for such shifts with higher resolution. In addition we are currently modifying the shell-model calculation for NaCl to bring it into better agreement with our experimental data. A similar calculation for LiF, including a detailed analysis of the behavior of the optical absorption in the neighborhood of critical points, is also in progress.

The authors would like to thank Professor R. O. Pohl for supplying the isotopically enriched samples of LiF used in this investigation. Thanks also go to Dr. G. Dolling for making available his results on LiF prior to publication.

†Work supported in part by the Advanced Research Projects Agency under Contract No. SD-131.

¹A. J. Sievers, Phys. Rev. Letters **13**, 310 (1964).

²A. J. Sievers and S. Takeno, Phys. Rev. **140**, A1030 (1965).

³R. Weber, Phys. Letters **12**, 311 (1964).

⁴R. Weber and P. Nette, Phys. Letters **20**, 493 (1966).

⁵H. F. Macdonald and M. V. Klein, in Proceedings of the International Conference on Localized Excitations in Solids, University of California, Irvine, California (to be published).

⁶R. F. Caldwell and M. V. Klein, Phys. Rev. **158**, 851 (1967).

⁷E. Burstein, in Proceeding of the International Conference on Lattice Dynamics, Copenhagen, Denmark, 1963, edited by R. F. Wallis (Pergamon Press, Oxford, England, 1965).

⁸B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949).

⁹A. A. Maradudin, Astrophysics and the Many Body Problem (W. A. Benjamin, Inc., New York, 1963).

¹⁰G. Benedek and G. F. Nardelli, Phys. Rev. **155**, 1004 (1967).

¹¹M. V. Klein, in Physics of Color Centers, edited by W. B. Fowler (Academic Press, Inc., New York, to be published).

¹²P. D. Thacher, Phys. Rev. **156**, 975 (1967).

¹³V. Nüsslein and U. Schröder, Phys. Status Solidi **21**, 309 (1967).

¹⁴R. Loudon, Proc. Phys. Soc. (London) **84**, 379 (1964).

¹⁵G. Dolling, H. G. Smith, R. M. Nicklow, P. R. Vijayaraghaven, and M. K. Wilkinson, Bull. Am. Phys. Soc. **12**, 557 (1967), and Phys. Rev. **168**, 970 (1968).

¹⁶C. B. Pierce, Phys. Rev. **135**, A83 (1964).

¹⁷A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

¹⁸A. E. Hughes, Proc. Phys. Soc. (London) **88**, 449 (1966).

THREE-TERM ANALYSIS OF THE IDEAL THERMAL AND ELECTRICAL RESISTIVITIES OF TRANSITION METALS

J. T. Schriempf

U. S. Naval Research Laboratory, Washington, D. C. 20390

(Received 4 March 1968)

Recently there has been considerable interest in the influence of electron-electron interactions on the low-temperature thermal and electrical resistivities of the transition metals. The theoretical treatments¹⁻³ have typically yielded the resistivities due only to electron-electron scattering; it has generally been assumed (sometimes tacitly) that the effects of other types of scattering can be included by simple addition of the resistivities due to each scattering mechanism. Thus, in analyzing experimental measurements, the following expressions are commonly employed for the low-temperature region:

$$\rho = \rho_0 + AT^2 + BT^5, \quad (1a)$$

$$wT = (wT)_0 + \alpha T^2 + \beta T^3. \quad (1b)$$

Here T is the absolute temperature, ρ the electrical and w the thermal resistivities, respec-

tively; and A , B , α , β , ρ_0 , and $(wT)_0$ are the constants. The latter two represent, of course, the behavior of the resistivities in the limit $T \rightarrow 0$, where only impurity scattering is effective. Equation (1b) assumes, as is usually the case, that heat transport via the lattice can be neglected. The terms in T^2 are the electron-electron effects, while BT^5 and βT^3 represent the influence of phonon scattering. In order to compare data with the electron-electron theories, the usual practice^{2,4,5} is to deduce A and α from the low-temperature slopes of the data on plots of ρ vs T^2 and wT vs T^2 . This method avoids the problem of precise determinations of ρ_0 and $(wT)_0$, which dominate ρ and wT at the lower temperatures; on the other hand, it assumes that the phonon terms are negligible.

In a recent Letter⁵ we analyzed our simultaneous measurements of the thermal and electri-

cal resistivities of palladium according to the conventional scheme just described, and deduced a value for the electron-electron scattering Lorenz number $L_e = A/\alpha$. Recent refinements in the calibration of our germanium-resistor temperature standard have been developed at the National Bureau of Standards, and these small changes have been incorporated in the data.⁶ As shall be shown below, the inclusion of the phonon terms in the analysis of the data has a pronounced effect on the value deduced for α , but only a small effect on the value obtained for A . Thus reliable values for L_e require a data analysis which includes phonon terms, at least in the thermal case, and hence the problem of a precise determination of $(wT)_0$ must be solved. It is the purpose of this Letter to show that our data has sufficient precision for such an analysis, and to present the resulting values of A , α , B , and β .

Equation (1) can be rewritten in the following way:

$$(\rho - \rho_0)/T^2 = A + BT^3, \quad (2a)$$

$$[wT - (wT)_0]/T^2 = \alpha + \beta T. \quad (2b)$$

In fitting our data to Eq. (2), it was found that a fairly precise value of ρ_0 could be chosen, for the BT^3 term falls quite rapidly with decreasing temperature. The value of $(wT)_0$ was then obtained from $(wT)_0 = \rho_0/L_S$, where $L_S = 2.443 \times 10^{-8} \text{ V}^2/\text{deg}^2$ is the Sommerfeld value of the Lorenz number which obtains for elastic scattering. The results are shown in Fig. 1 in plots of $(\rho - \rho_0)/T^2$ vs T^3 and $[wT - (wT)_0]/T^2$ vs T . The thermal data show excellent agreement with Eq. (2b); it is felt that this indicates the validity of this technique (at least for Pd), especially since the precise Sommerfeld value of the Lorenz number can be used to treat the impurity scattering term. The electrical data at the lower temperatures are well represented by Eq. (2a), although the behavior is apparently somewhat more complex at temperatures above, roughly, 9°K. The use of least-squares technique and Eq. (2) yields the following values, where Ω , cm, W, and °K units have been employed: $A = 3.1 \times 10^{-11}$, $B = 1.1 \times 10^{-14}$, $\alpha = 2.9 \times 10^{-3}$, $\beta = 2.6 \times 10^{-4}$, $L_e = 1.1 \times 10^{-8}$, and a Lorenz number for phonon scattering, $L_p = BT^2/\beta = 4.3 \times 10^{-11} T^2$. These values have been obtained by using the thermal data at all temperatures and the electrical data for T less than 9°K. The 0.5% uncertainty in wT and the 0.1% uncer-

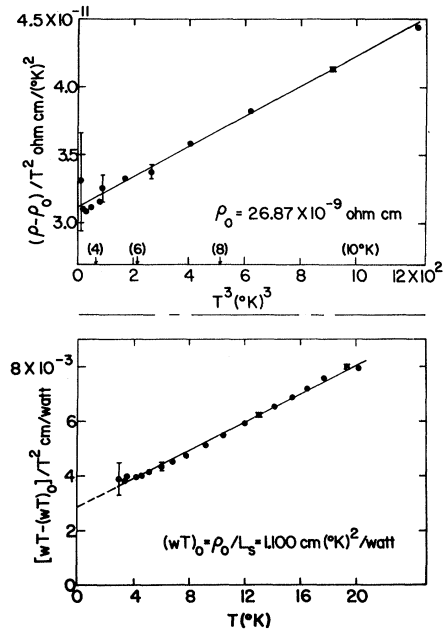


FIG. 1. Comparisons of the thermal and electrical resistivities of palladium with Eq. (2) of the text. In these plots the intercepts of the straight lines yield the coefficients in the electron scattering terms, while the slopes yield the coefficients in the phonon scattering terms. Error bars represent, respectively, $\pm 0.5\%$ and $\pm 0.1\%$ of the measured thermal and electrical resistivities. The straight lines were obtained by fitting the data to Eq. (2) with a conventional least-squares technique.

tainty in ρ yield an uncertainty in L_e of about 10%.

The value of L_e for Pd quoted above is somewhat larger than our previously reported value⁵ of 0.7×10^{-8} . It should be noted that the value of A obtained here is essentially the same as that deduced from the conventional analysis, whereas the new value of α is considerably smaller than the earlier value. This is consistent with the standard phonon scattering theory,⁷ which indicates that $B \sim \theta^{-4}$, whereas $\beta \sim \theta^{-2}$, where θ is essentially the Debye temperature. Thus the phonon term in the electrical resistivity (BT^3) decreases faster with decreasing temperature than does the phonon term in the thermal resistivity (βT^2).

The above analysis also works quite well for our rhenium data⁸ and yields a value of L_e of about $(0.9 \pm 0.3) \times 10^{-8}$. These new results, along with the White and Tainsh value of 1.0×10^{-8} in Ni,⁴ are in somewhat better agreement with Herring's prediction¹ of a single, universal value of L_e for all transition metals with complex Fermi surfaces. However, his numerical

estimate of 1.58×10^{-8} still appears to be somewhat high.

Very recently, Rice³ has calculated L_e as a function of the Stoner enhancement factor. His results predict an L_e which increases as enhancement decreases, and approaches a value of 1.02×10^{-8} in the limit where the enhancement factor reaches unity. In the light of this theory, our present results would seem to indicate that enhancement does not contribute to the L_e of pure palladium. For the present, however, this conclusion must be regarded as tentative, for current estimates of the enhancement factor of pure Pd range from 3 to 50.⁹

¹C. Herring, Phys. Rev. Letters 19, 167, 684(E) (1967).

²A. I. Schindler and M. J. Rice, Phys. Rev. 164, 759 (1967).

³M. J. Rice, Phys. Letters 26A, 86 (1967).

⁴G. K. White and R. J. Tainsh, Phys. Rev. Letters 19, 165 (1967).

⁵J. T. Schriempf, Phys. Rev. Letters 19, 1131 (1967).

⁶It is worth noting that very small discrepancies between the absolute temperature T and the laboratory temperature T_L can generate significant errors in the measurement of ΔT and, thus, in the thermal resistivity. For example, if the difference between T and T_L varies by, say, 5 mdeg over a 1-deg interval, the resulting error in ΔT is $\frac{1}{2}\%$. We have found that the small changes in our standards, of a few mdeg, caused changes in our measured values of ΔT of as large as 2%. At the lower temperatures these small changes play an important role, for the impurity terms are dominant and a high degree of precision is required to deduce the electron and phonon terms.

⁷P. G. Klemens, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1956), Vol. 14, p. 198.

⁸J. T. Schriempf, J. Phys. Chem. Solids 28, 2581 (1967).

⁹S. Foner and E. J. McNiff, Jr., Phys. Rev. Letters 19, 1438 (1967).

INTRA-ATOMIC COULOMB INTERACTIONS AND LOCAL EXCHANGE-ENHANCEMENT EFFECTS IN DILUTE TRANSITION-METAL ALLOYS

Pascal Lederer* and D. L. Mills†

Department of Physics, University of California, Irvine, California

(Received 7 December 1967)

A number of properties of pure transition metals may be interpreted by presuming the value of the intra-atomic Coulomb interaction U between two d electrons in the same unit cell varies from one metal to another in a systematic fashion. In this Letter, we shall discuss a number of striking properties of dilute alloys of $3d$ impurities in isoelectronic $4d$ or $5d$ hosts which can be interpreted by assuming the major effect of the impurity ion is to change the value of U locally.¹

The purpose of this Letter is to point out that very strong variations with concentration of the electronic specific heat of dilute alloys are predicted by the local exchange-enhancement model we have previously employed² to analyze susceptibility and electrical resistivity data on dilute alloys of Ni in Pd. Recent measurements of the specific heat of the Pd-Ni system³ show a striking, strong dependence of the electronic specific heat on Ni concentration. As Schindler and Mackliet³ have pointed out, an extension of the uniform-enhancement model⁴ to the disordered system obtained by introducing a concentration dependent, spatially averaged exchange-enhance-

ment factor deduced from susceptibility data fails to account for the magnitude and concentration dependence of the effect of alloying on the electronic specific heat of this system.

In this paper we present a discussion of the concentration dependence of the coefficient γ of the term linear in temperature in the specific heat for the case when the host exchange enhancement is unimportant. For this case, the structure of the theory is sufficiently clean that the essential physics is clearly exhibited, and the expression for $\gamma^{-1}d\gamma/dc$ is simple in structure. We apply our model to analyze recent NMR studies of Rh:Co alloys. This enables us to predict the value of $\gamma^{-1}d\gamma/dc$ near $c=0$. The extension of the theory to systems in which exchange enhancement is important in the host is discussed by Englesberg and co-workers.⁵

Consider first the Pd:Ni system. It is now well known that in pure Pd, the intra-atomic Coulomb interactions between the d electrons enhance the static magnetic susceptibility χ by roughly a factor of 10. This implies that in pure Pd, U is nearly large enough to produce a transition to the ferromagnetic state. Associated