Bloch-Boltzmann analysis of electrical transport in intermetallic compounds: ReO_3, $BaPbO_3$, $CoSi_2$, and Pd_2Si

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The shape and magnitude of the electrical resistivity $\rho(T)$ is analyzed for four intermetallic compounds, and electron-phonon coupling constants λ are extracted. ReO_3 is particularly interesting because a sharp departure from the Bloch-Grüneisen shape can be attributed to high-frequency optical vibrations. The λ values for the oxide metals seem too large to be consistent with the absence of superconductivity, but the results generally agree well with a conventional Fermi-liquid interpretation. The Hall coefficient R_H of ReO_3 is found to agree well with theory.

I. BASIS AND MOTIVATION

Because resistivities of complicated intermetallics (e.g., copper oxide superconductors) often appear peculiar,[1] it is useful to survey the literature to discover materials where a thorough analysis can be made, in order to provide benchmarks of either certifiably normal or certifiably peculiar behavior. For reasons to be explained below, a complete analysis requires input from band theory which is not generally available. Years ago certain $A15$-structure superconductors were shown[2] to be peculiar; non-Bloch-Boltzmann behavior in the form of resistivity "saturation" was connected to a phonon-limited electronic mean free path of ≈ 5 Å. Our recent analysis of NbO (Ref. 3) is perhaps the first complete certification of normal behavior for an intermetallic. Here we present four more cases where behavior is normal. Some of the basis and motivation of this work is summarized in the following eight observations.

(1) The Boltzmann equation is known theoretically[4] to provide a correct description of electrical transport provided propagating quasiparticles are well defined. Even strong electron-phonon interactions do not invalidate or alter the original Bloch version[5] of this equation as long as the mean free paths are long enough.

(2) Because of the variational nature of Boltzmann theory, an adequately accurate closed-form expression is available for $\rho(T)$ when phonons and impurities dominate the scattering,

$$\rho_{xx} = 4\pi/\Omega_{pxx}^2\tau_{xx}, \tag{1}$$

$$\Omega_{pxx}^2 = 4\pi e^2 \sum_k v_{kx}^2 \delta(\epsilon_k), \tag{2}$$

$$1/\tau_{xx} = 1/\tau_{xx}^{\rm imp} + 1/\tau_{xx}^{ep} + \cdots, \tag{3}$$

$$\hbar/\tau_{xx}^{ep} = 4\pi k_B T \int_0^{\omega_{\max}} \frac{d\Omega}{\Omega} \alpha_{xx}^2 F(\Omega) \left[\frac{\hbar\Omega/2k_BT}{\sinh(\hbar\Omega/2k_BT)}\right]^2, \tag{4}$$

$$\alpha_{xx}^2 F(\Omega) = N(0) \frac{\sum_{kk'} |M_{kk'}|^2 (v_{kx} - v_{k'x})^2 \delta(\epsilon_k)\delta(\epsilon_{k'})\delta(\Omega - \omega_{k-k'})}{\sum_{kk'} (v_{kx} - v_{k'x})^2 \delta(\epsilon_k)\delta(\epsilon_{k'})}. \tag{5}$$

Here $k = (\vec{k}n)$, $\hbar v_{kx} = \partial\epsilon/\partial k_x$ is the band velocity, Ω_p is the Drude plasma frequency, or, more exactly, $\Omega_{p\alpha\beta}^2/4\pi e^2$ is the $(n/m)_{\alpha\beta}$ tensor, and $M_{kk'}$ is an electron-phonon matrix element. This expression approximates the exact solution to typically better than 2% at $T \approx \Theta_D$; larger deviations (up to 100%) can be found by plotting ρ-ρ_0 on an expanded scale for $T < \Theta_D/5$.

(3) The shape of $\rho(T)$ is not especially sensitive to the details of the function $\alpha_{xx}^2 F(\Omega)$. The Debye approximation

$$\alpha_{xx}^2 F(\Omega) \to 2\lambda_{xx}(\Omega/\Omega_D)^4 \theta(\Omega_D - \Omega) \tag{6}$$

is usually sufficiently good on a coarse scale. When this is used in Eqs. (1)–(4), the result is the Bloch-Grüneisen theory.

(4) The coupling constants

$$\lambda_{xx} \equiv 2 \int_0^{\omega_{\max}} \frac{d\Omega}{\Omega} \alpha_{xx}^2 F(\Omega) \tag{7}$$

should be only weakly dependent on Cartesian direction x for noncubic metals, and should agree closely (typically $\approx 10\%$) with the superconducting λ.[6]

(5) Bloch-Grüneisen fits to $\rho_{xx}(T)$ determine three parameters $\rho_{xx}^{\rm imp}$, Θ_D, and $\lambda_{xx}/\Omega_{pxx}^2$. Although in principle the effective Debye temperature could vary with crystallographic orientation, in practice one expects this to be

a small effect. The anticipated weak dependence of λ_{xx} on the x direction means that most of the anisotropy of $\rho(T)$ should be explained by the anisotropy of Ω_p^2, i.e., by the anisotropy of the band velocity.

(6) Although Ω_{pxx}^2 is in principle contained in the optical constants

$$\epsilon_{xx}(\omega) = \epsilon_{xx,\mathrm{er}}(\omega) - \Omega_{pxx}^2/\omega(\omega + i/\tau), \tag{8}$$

in practice it is rare for the int*er*band term $\epsilon_{xx,\mathrm{er}}$ to be smooth enough to separate cleanly from the Drude part. Therefore band calculations of Ω_p using Eq. (2) are very useful.

(7) The correct evaluation of Eq. (2) requires a *quasiparticle* band theory, whereas essentially all calculations to date are based on density-functional theory in the local-density approximation (LDA). As a test of band theory, λ_{xx} can be approximated by λ if known from superconducting measurements. Resistivity then yields Ω_{pxx}, which can be compared with LDA theory. Surprisingly, there is no noticeable discrepancy between LDA and transport measurements for any metallic, nonmagnetic element.[7,8] However, the heavy-fermion compounds are cases where the comparison would surely fail. Experimental Drude plasma frequencies are expected to be smaller than LDA predictions in metals where correlation effects increase the band mass near the Fermi level. However, even in metals such as Pd the effect is apparently small. This test of LDA theory is one motivation for our work.

(8) An important consistency test is that the mean free path $\ell = \sqrt{\langle v_k^2 \rangle}\tau$ should be long enough that electrons can be assigned a propagation vector; that is, $k\ell \gg 1$ is required for the validity of the Boltzmann equation. Because $\Omega_{pxx}^2 = 4\pi e^2 N(0)\langle v_{kx}^2 \rangle$, band calculations of Ω_p contain the required Fermi-velocity information, and τ can be extracted from the resistivity. In the case of elements it has been observed[8] that as long as $\ell > 10$ Å, departures from Boltzmann behavior are too weak to see by eye in the data, whereas when $\ell < 10$ Å, characteristic "saturation" behavior occurs.

II. RESULTS

A. ReO_3

Transport measurements for ReO_3 were reported by King, Kirsch, and Geballe,[9] Tanaka *et al.*,[10] and Pearsall and Lee.[11] Data from Ref. 11 are shown in Fig. 1. As was noted by King, Kirsch, and Geballe, a single Bloch-Grüneisen curve does not fit the data. If a fit is made to the data for $T < 120$ K, then the data break sharply above the resulting Bloch-Grüneisen curve at T=150 K. However, as noted by King, Kirsch, and Geballe, a good fit can be achieved by using a mixed model for $\alpha_{xx}^2 F$ with both a Debye and an Einstein part,

$$\alpha_{xx}^2 F(\Omega) = 2\lambda_D(\Omega/\Omega_D)^4\theta(\Omega_D - \Omega) + \tfrac{1}{2}\omega_E\lambda_E\delta(\Omega - \omega_E). \tag{9}$$

The fitted curve and the separate Debye and Einstein parts are also shown in Fig. 1. The parameters of our

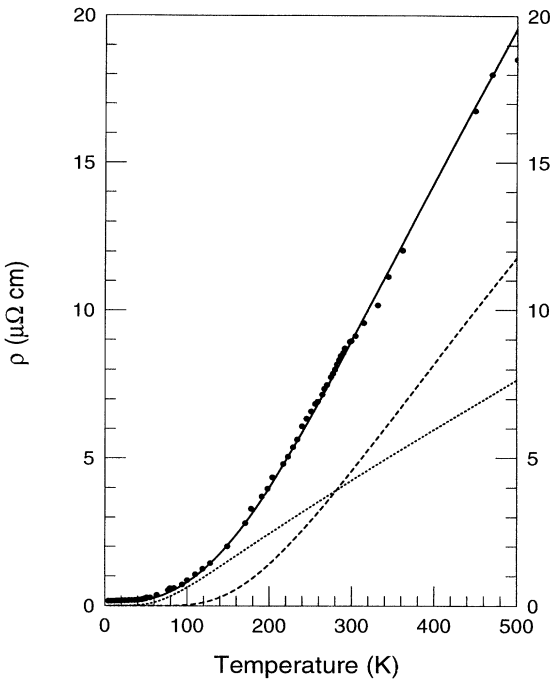

FIG. 1. Temperature dependence of the resistivity of ReO_3. The dashed line is the Einstein contribution, the dotted line the Bloch-Grüneisen part, and the solid curve is both electron-phonon parts, plus a constant residual resistivity. The solid circles are experimental data from Ref. 11.

fit to the data of Ref. 11 are Θ_D=450 K, Θ_E=900 K, λ_D=0.12, and λ_E=0.23. The Drude plasma frequency was taken to be Ω_p=5.47 eV. We obtained this value by integrating Eq. (2) numerically using the tight-binding parameters fitted by Mattheiss to his augmented plane-wave band calculation.[12] The value 5.47 eV coincides perfectly with the experimental number 5.5 eV found by Feinleib, Scouler, and Ferretti[13] by infrared measurement. The large frequency window before the onset of strong interband optical transitions permits a particularly accurate infrared measurement in this case. Using the same value of Ω_p, the analysis by Tanaka *et al.*[10] of their own data yields the parameters Θ_D=330 K, Θ_E=800 K, λ_D=0.09, and λ_E=0.30, which agree to 25% with our fit to the data of Pearsall and Lee.[11]

It is unusual in our experience for a conventional electron-phonon mechanism to deviate so strongly from the Bloch-Grüneisen formula. The reason is that the integral of Eq. (4) is not especially sensitive to details of the function $\alpha_{xx}^2 F(\Omega)$. For metallic elements such as Nb,[14] the strong deviations of $\alpha_{xx}^2 F$ from the Debye form cause only small changes in $\rho(T)$ which are not much bigger than other changes of $\rho(T)$ caused by effects such as anisotropy which enter as corrections to the lowest-order treatment. Since our treatment is phenomenological, it makes little sense to adjust $\alpha_{xx}^2 F$ to fit minor details. On the other hand, if most of the phonon coupling involves high-energy vibrations (as is apparently true in ReO_3) the deviations from Bloch-Grüneisen form can be strik-

TABLE I. Data fitted to measured resistivities (rows 3–5); band-theoretical input (rows 7–9); derived results (rows 10 and 11). The Fermi velocities in row 9 are total magnitudes for the cubic materials but components in the indicated directions for Pd_2Si. The mean free paths in row 11 are total magnitudes and include only the electron-phonon scattering.

	ReO_3	$BaPbO_3$	$CoSi_2$	Pd_2Si c axis	Pd_2Si a axis
Ref.	11	17	25	28	28
ρ_0 ($\mu\Omega$ cm)	0.15	85.0	2.5	0.10	0.10
Θ_D (K)	see text	450	430	200	168
λ/Ω_p^2 (eV^{-2})	0.0116	0.23	0.0114	0.01106	0.01799
Ref.	this paper	19	26	29,30	29,30
N(0) [(eV f.u.)$^{-1}$]	1.00	2.88	1.16	0.56	0.56
Ω_p (eV)	5.5	1.59	6.2	3.69	3.36
$\sqrt{\langle v_F^2 \rangle}$ (10^6 m/s)	0.77	0.16	0.7	0.36	0.33
λ	0.35	0.58	0.44	0.15	0.20
ℓ (300 K) (Å)	89	11	64	135	135

ing. ReO_3 presents an ideal opportunity for such effects because of the very large mass ratio of the Re atom to the O atom, and the large ratio of light to heavy atoms. Apparently the other compounds studied here have smaller coupling to high-energy phonons and a less noticeable departure from Bloch-Grüneisen form. The parameters of the fit are very natural ones, and the resulting λ=0.35 seems also reasonable, although it is a little large considering that superconductivity has not been found down to 0.020 K (K. Andres, cited in Ref. 9). Using the modified McMillan equation[15] with $\omega_{\log}$=650 K, λ=0.35, and μ^*=0.1, T_c=1.2 K is predicted. This prediction rests on the assumption $\lambda_{xx} \approx \lambda$, which is not guaranteed to be accurate. Another way to estimate λ is by the formula $1 + \lambda = N_\gamma(0)/N(0)$, the ratio of densities of states at the Fermi level found by specific heat and by band structure. We denote this value of λ as λ_γ. Using the specific-heat measurement of King, Kirsch, and Geballe and the band value which we calculated and show in Table I, we get $\lambda_\gamma = 0.2$. The expected error of 10% in $1 + \lambda_\gamma$ means that the two λ values are consistent. Predictions of low values of T_c are notoriously unreliable, but it seems worth speculating that ReO_3 may be superconducting at an experimentally achievable temperature. It must be mentioned that King, Kirsch, and Geballe[9] have also fitted the resistivity and extracted a value λ=0.24, which would predict T_c <1 mK. We are unable to reproduce this value, which we think must be in error. The resistivity data of King, Kirsch, and Geballe give a larger λ than the data of Pearsall and Lee[11] which we have used, and we suspect the latter data are more reliable.

We have also calculated the Hall coefficient of ReO_3 using the formula

$$R_H = -\frac{e^3\tau^2\rho^2}{6N\Omega}\sum_k \mathbf{v}_k^T\{\mathrm{tr}(M_k^{-1}) - M_k^{-1}\}\mathbf{v}_k\delta(\epsilon_k). \quad (10)$$

Here $\hbar^2(M^{-1})_{\alpha\beta}$ is the inverse mass tensor $\partial^2\epsilon_k/\partial k_\alpha \partial k_\beta$. The result -24.9×10^{-11} m^3/C agrees adequately well with experiment[11] as shown in Fig. 2. Only a weak temperature dependence was noticed experimentally. This is consistent with expectations from the shape of the Fermi surface, namely, of the three sheets, two are completely electronlike, and the third, which has both electronlike and holelike character, is dominated by electronlike regions. Thus a moderate scattering anisotropy can cause modest deviations between theory based on Eq. (10) and experiment, and also a modest temperature dependence, but could not cause any dramatic effects, such as are seen in NbO,[3] but not in ReO_3. The shape of the T dependence shown in Fig. 2 is reminiscent of the well-documented effect in Cu, which can be ascribed to the effect of inelasticity of electron-phonon scattering at low T,[16] rather than to anisotropy.

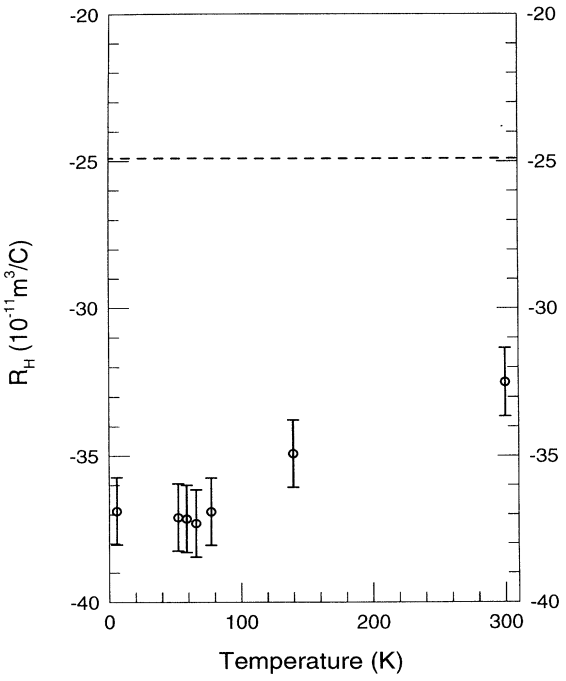

FIG. 2. Temperature dependence of the Hall coefficient of ReO_3. The open circles are experimental data from Ref. 11; the solid bars represent two standard deviations about the mean. The dashed line is the theoretical value according to Eq. (10).

B. $BaPbO_3$

This compound is an end member in the series $BaPb_{1-x}Bi_xO_3$ which includes superconducting metals with T_c up to 13 K and the very interesting insulator $BaBiO_3$. But $BaPbO_3$ itself is apparently a "vegetable" with a perovskite crystal structure weakly distorted,[17] but in a way apparently not closely related to the $BaBiO_3$ structure.[18] $BaPbO_3$ avoids being a semiconductor by overlap of the Pb(6s) band with the O(2p) bands. One electron and two hole bands intersect the Fermi level, a situation which permits complicated behavior of the Hall coefficient, which has not been calculated. Shannon and Bierstedt[17] report a temperature-independent value $R_H = -3.7 \times 10^{-8}$ m^3/C. Apparently the electronlike sheet, which has a larger velocity, dominates the Hall effect.

Mattheiss[19] has calculated the Drude plasma frequency in the cubic perovskite structure, obtaining Ω_p=1.59 eV, reasonably close to the value 1.07 eV found by infrared spectroscopy by Tajima *et al.*[20] The resistivity data[17] and a Bloch-Grüneisen fit are shown in Fig. 3. Fitted and derived parameters are given in Table I. The value λ=0.58 would predict T_c=7 K, contrary to the measured value $T_c < 0.02$ K.[21] A probable explanation for this discrepancy is that the resistivity is sensitive to sample quality. This effect has been seen dramatically in the superconducting bismuth-doped members of the family, where early resistivity measurements on polycrystalline samples (see, for example, Thanh, Koma, and Tanaka[22] gave results an order of magnitude larger than seen in subsequent measurements[23] on single crystals, which in turn are probably another order of magnitude larger than the true intrinsic resistivity. Even more interesting from a superconducting point of view are the potassium-doped materials $Ba_{1-x}K_xBiO_3$. Very recently high-quality thin-film samples have been grown. Data of Schweinfurth *et al.*[24] fit fairly well a Bloch-Grüneisen curve except at the lowest T where the data lie below the fitted curve. The measured resistivity of ≈ 500 $\mu\Omega$ cm is an order of magnitude smaller than previously reported in single crystals. The fitted value of λ/Ω_p^2 was 0.21, close to the present result of 0.23 for $BaPbO_3$. Perhaps the single-crystal samples have microscopic cracks which alter the effective sample size. The data of Ref. 17 might suffer from a similar problem, making the true value of λ small enough to agree with the absence of superconductivity.

C. $CoSi_2$

$CoSi_2$ is a cubic CaF_2-structure metal which is important because it can be grown epitaxially on Si. Resistivity of high-quality thin films (both single crystal and polycrystal) has been measured by Hensel *et al.*[25] The band structure has been calculated by Mattheiss and Hamann.[26] Figure 4 shows the resistivity of Ref. 25 and a Bloch-Grüneisen fit which agrees reasonably well with the data. Theoretical and experimental parameters are given in Table I. The resulting empirical value of λ_{tr} is 0.44, which agrees perfectly with the measured superconducting T_c=1.3 K (Ref. 27) using the McMillan equation and μ^*=0.13. The room-temperature mean free path is

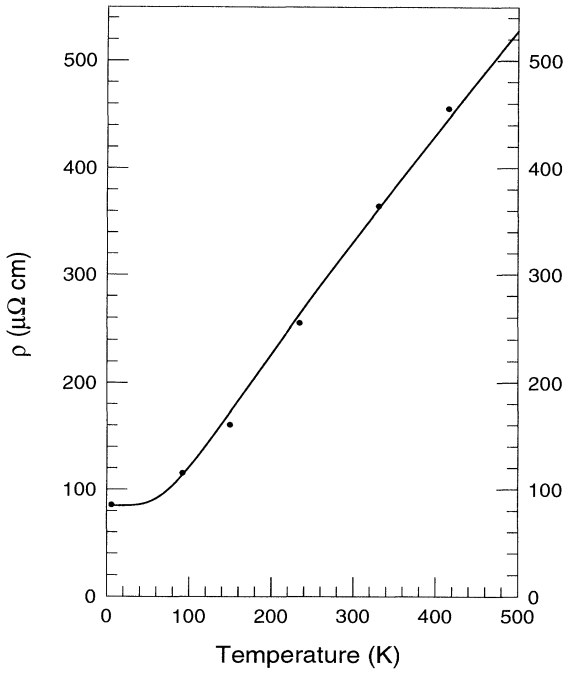

FIG. 3. Temperature dependence of the resistivity of $BaPbO_3$. The solid circles are experimental data from Ref. 17.

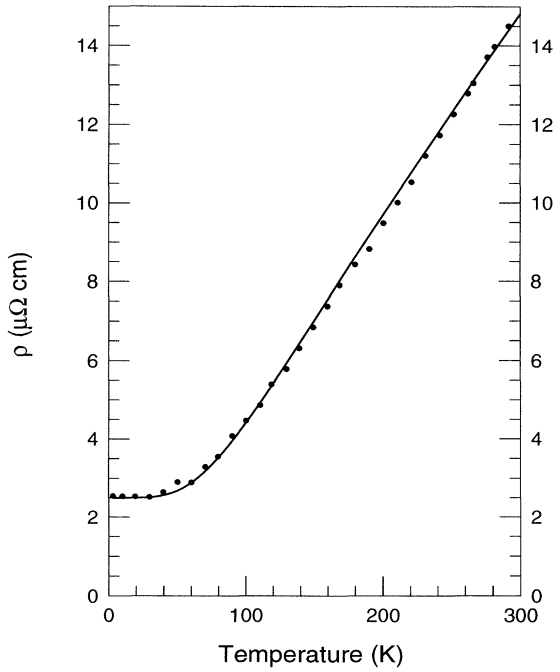

FIG. 4. Temperature dependence of the resistivity of $CoSi_2$. The solid circles are experimental data from Ref. 25.

64 Å, confirming that the Boltzmann approach is surely valid. This seems to be an absolutely conventional metal.

D. Pd_2Si

Pd_2Si is a hexagonal metal with a fairly low resistivity which has been studied because of its importance in silicon technology. Careful transport measurements both parallel and perpendicular to the c axis were reported by Marani *et al.*[28] Band calculations were made by Bisi, Jepsen, and Andersen,[29] and optical studies, both theoretical and experimental, were reported by Amiotti *et al.*[30]

Table I gives the Bloch-Grüneisen fitting parameters found by Marani *et al.* in both directions. Note that the Debye temperature was allowed to vary separately in the different directions, with the results disagreeing by almost 20%. Currents along the c axis relax more slowly and take less advantage of low-energy phonons than currents traveling in the ab plane. The ratio of resistivities $\rho_{ab}/\rho_c = 1.6$ at room temperature is only partly accounted for by the ratio of squared plasma frequencies, 1.21. The remaining anisotropy is assigned to anisotropy in the scattering rates, $\lambda_{xx}/\lambda_{zz} = 1.35$. The optical experiment of Amiotti *et al.* made a careful extraction of Drude parameters, giving $\Omega_{pzz} = 3.6$ eV, very close to theory, and $\Omega_{pxx} = 2.8$ eV, somewhat lower than theory. The squared ratio 1.65 agrees nicely with the resistivity ratio, as noted by Amiotti *et al.* However, it is our experience that LDA values are more reliable than experimental Drude plasma frequencies, and a glance at Figs. 3–5 of Ref. 30 shows why. The interband conductivity calculated theoretically is richly structured down to frequencies $\omega \approx 0.1$ eV. Experiment shows similar but very much milder structure, presumably because of lifetime broadening from various sources. By very careful comparison of theory and experiment and by working into the far infrared, it is perhaps possible to estimate Ω_p's, and probably this has been done as well as possible, but the sources of uncertainty are great. By contrast, LDA band theory gives an unambiguous number, although its meaning is clouded by the ambiguity of needing a quasiparticle property. But experience with both s- and d-band metals has shown the reliability of the LDA numbers so far, which justifies our preference for the theoretical values. At any rate, the differences are not especially large, and we can conclude that Pd_2Si has a very weak electron-phonon interaction, $\lambda \approx 0.18 \pm 0.03$, which suggests that superconductivity should not occur above 10^{-4} K, and would be very easily totally suppressed by residual magnetic impurities.

III. CONCLUSIONS

All four metals seem to behave normally, the only doubt being that the two oxides have large enough resistivities that one could expect them to be superconducting at temperature well above the temperatures at which superconductivity has been found absent. This result could be blamed on a systematic underestimate of the Drude plasma frequency by the LDA, but there is no other evidence favoring this, and it goes against the notion that correlations should diminish rather than enhance bandwidths near the Fermi energy. More likely possibilities include small errors remaining in the band calculations or, more likely, problems with the single-crystal samples of oxides, where cracks and grain boundaries can be chemically quite different from the bulk and act as good insulating barriers which cause inhomogeneous current distributions and distort the magnitudes of the measured resistivities.

In spite of this problem, it seems reasonable to assert that all four of these metals belong to the normal class of conventional band Fermi liquids, with electron-phonon interactions dominating the resistivity.

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