Electrical and Thermal Resistivities of the Nonmagnetic Transition Metals with a Two-Band Model*

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A two-band spherical model is used to represent the conduction electrons of the nonmagnetic transition metals with an incomplete d shell. It is shown by comparison with experimental results that phonon-induced interband s–d transitions are the major contributor to the electrical and thermal resistivities ρ and W at all but the lowest temperatures. Consequently, the momentum gap between the s and d bands is an important parameter of the theory and may be used to classify the behavior of ρ and W. At the lowest temperatures it is found that the experimental data for ρ of all the transition metals studied may be consistently interpreted if it is assumed that electron–electron scattering processes are important.

I. INTRODUCTION

THE nonmagnetic transition metals with incomplete d shells show a considerable variety in their low-temperature transport properties.[1] Since Mott's work[2] thirty years ago it has been realized that the existence of both a conduction band and an unfilled d band in these metals makes the electron scattering considerably more complex than for the monovalent metals.

In the ideal case (i.e., pure metals) there are two principal scattering mechanisms. First, conduction electrons are scattered by interaction with phonons. The phonons scatter electrons within each band and they also scatter electrons from one band to the other. The contribution to the resistivities from each process has it's own characteristic behavior. At low temperatures, for example, the intraband transitions contribute a term to the electrical resistivity $\propto T^5$ while interband transitions contribute a term $\propto T^3$. These s–d transitions are thought to give the main contributions to the electrical and thermal resistivities ρ and W at room temperatures.[3] At the lowest temperatures the contribution to ρ and W from phonon scattering of electrons will depend on the Fermi surface geometry. If the s and d surfaces do not intersect, then there will be a minimum wave vector for phonons which can induce s–d transitions, and below some characteristic temperature T_m, ρ and W will decay exponentially.

Second, the conduction electrons may be scattered by Coulomb interaction with one another. This mechanism gives rise to a significant resistivity only when s electrons are scattered by more "massive" d electrons; for it is only then that a momentum change in the current-carrying s electrons is effected. Baber[4] and, more recently, Appel[5] have calculated the contribution due to such a mechanism with the result that $\rho_{e-e} \propto T^2$. However, the only nonmagnetic transition metals for which ρ displays a T^2 dependence are W, Nb, Pd, and Pt, and it has not been clear that electron–electron scattering processes are important in the other transition metals.

The low-temperature behavior of the resistivities of the nonmagnetic transition metals is, then, determined by the sum of three characteristically different processes with their relative importance depending on the band structure of each metal. Since the band structure of these metals may differ greatly from one another it is not surprising that the behavior of ρ and W is so varied among them.

It seemed useful to attempt to separate the effects of the competing scattering mechanisms and to relate the differences in the transport properties of the transition metals to some parameter in a simplified model consisting of two spherical energy bands. This paper describes the results of such an attempt. The results of this investigation suffer the main limitation that umklapp processes have been neglected. Furthermore, our treatment is to be taken as phenomenological in that it is assumed that the Bloch–Grüneisen function appropriately describes the effects of intraband s–s transitions over the entire temperature range considered and that the Debye temperature is constant. While it is known that there are monovalent metals, e.g., rubidium, for which ρ deviates from the Bloch–Grüneisen function at low temperatures and that the effective Debye temperature is not strictly constant, we believe that the results of this investigation are at least qualitatively correct and indicate the relative importance of the three scattering processes mentioned.

In Secs. II and III of this paper, the data of White and Woods for ρ and W, respectively, are shown to be reasonably well fit by using a two-band model. The momentum gap between the Fermi surfaces of the s and d bands is used as a variable parameter. It is found that the temperature dependence of ρ and W obtained with this model displays the essential features of the experimental data if the momentum gap parameter is appropriately chosen and if it is assumed that electron–electron scattering processes are important in all of the transition metals at lowest temperatures.

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[3] A. H. Wilson, Proc. Roy. Soc. (London) **A167**, 580 (1938).
[4] W. G. Baber, Proc. Roy. Soc. (London) **A158**, 383 (1937).
[5] J. Appel, Phil. Mag. **8**, 1071 (1963).

II. THE ELECTRICAL RESISTIVITY

It is assumed that the conduction electrons of the transition metals may be represented by two spherical bands with effective masses m_s and m_d, that is

$$E(k,s)=\hbar^2k^2/2m_s$$
$$E(k,d)=A-(\hbar^2k^2/2m_d).$$

Electron–phonon scattering. Wilson calculated the electrical resistivity due to phonon scattering with such a model. In order to make the problem tractable he assumed that the phonons and the d electrons remain in thermal equilibrium. The resulting expression for the resistivity is given by

$$\rho_{\rm pho}(T)=\frac{2m_sP_{ss}3h^3}{16\pi(2m_s)^{\frac{1}{2}}e^2E_F}\left(\frac{T}{\theta_D}\right)^3 \times\left\{2^{-\frac{1}{2}}n^{-\frac{2}{3}}\left(\frac{T}{\theta_D}\right)^2J_5\left(\frac{\theta_D}{T}\right)+\frac{w_dm_dP_{sd}}{m_sP_{ss}} \times\left[J_3\left(\frac{\theta_D}{T}\right)-J_3\left(\frac{\theta_E}{T}\right)\right]\right\}.$$

Here n is the effective number of s electrons per atoms, w_d is the effective degeneracy number of the d band, P_{ss} and P_{sd} are the matrix elements for phonon induced s–s and s–d transition, respectively, E_F the Fermi energy, θ_D the Debye temperature, and $k\theta_E$ is the minimum energy of phonons that can induce s–d transitions. The functions $J_n(x)$ are the well-known transport integrals defined by

$$J_n(x)=\int_0^x\frac{z^ndz}{(e^z-1)(1-e^{-z})}.$$

In this investigation values for $J_3(x)$ and $J_5(x)$ were required over the range $0.05<x<1.0$ in small increments of x. Existing tables give only a few values in this region and it was necessary to construct a more complete table which we present as Table I. The first term in the above expression for $\rho_{\rm pho}(T)$ is the Bloch–Grüneisen function $\rho_{s-s}(T)$ which contains the effects of s–s transitions, while the remaining terms $\rho_{s-d}(T)$ are due to s–d transitions.

Near the Debye temperature, ρ_{s-s} and ρ_{s-d} are proportional to T. ρ_{s-d}, however, is larger than ρ_{s-s} by a factor $\gamma=w_dm_dP_{sd}/m_sP_{ss}$, which is of the order of 10.[6] This result has been given the physical interpretation that the d band acts as a trap with a high density of states into which s electrons are scattered and lost from the current. In any given low-temperature range, e.g., $0.05<T/\theta_D<0.1$; whether s–s or s–d processes are dominant depends critically on the parameter θ_E.

[6] An estimate of γ is obtained from electronic specific heat data if it is assumed that $P_{sd}=P_{ss}$.

TABLE I. Values of $J_n(x)$.

x	$J_3(x)$	$J_5(x)$
1.0	0.480	0.237
1.4	0.905	0.863
1.8	1.423	2.204
2.2	2.001	4.529
2.6	2.606	8.027
3.0	3.211	12.771
3.4	3.790	18.710
3.8	4.329	25.685
4.2	4.815	33.457
4.6	5.244	41.747
5.0	5.614	50.263
5.4	5.928	58.736
5.8	6.190	66.936
6.2	6.406	74.678
6.6	6.581	81.835
7.0	6.721	88.326
7.4	6.833	94.113
7.8	6.921	99.194
8.2	6.990	103.596
8.6	7.044	107.362
9.0	7.085	110.547
9.4	7.117	113.214
9.8	7.141	115.426
13.0	7.20−	123.14
20.0	7.21−	124.43

It is thus convenient to construct an analysis of $\rho_{\rm pho}(T)$ which separates the contributions from s–s and s–d scattering in some simple way and at the same time points up the effects of the momentum gap. This is achieved by projecting out the temperature dependence of $\rho_{s-s}(T)$ in a renormalization of $\rho_{\rm pho}(T)$ such that the contribution from intraband scattering is a constant. In this way we define

$$\tilde{\rho}_{\rm pho}(T)$$
$$=\rho_{\rm pho}(T)(m_sP_{ss}/w_dm_dP_{sd})/(T/\theta_D)^5J_5(\theta_D/T)$$
$$=\text{const.}\left[\frac{2^{-\frac{1}{2}}n^{-\frac{2}{3}}}{w_dm_dP_{sd}/m_sP_{ss}}+\frac{J_3(\theta_D/T)-J_3(\theta_E/T)}{(T/\theta_D)^2J_5(\theta_D/T)}\right] \quad (1)$$
$$=\text{const.}[\tilde{\rho}_{s-s}+\tilde{\rho}_{s-d}(T)].$$

As $\tilde{\rho}_{s-s}\approx\frac{1}{10}$ and $\tilde{\rho}_{s-d}(\theta_D)\approx 10$, $\tilde{\rho}_{\rm pho}(\theta_D)\approx\text{const.}\times\tilde{\rho}_{s-d}(\theta_D)$. The constant of proportionality is removed by writing

$$\frac{\tilde{\rho}_{\rm pho}(T)}{\tilde{\rho}_{\rm pho}(\theta_D)}=\frac{\tilde{\rho}_{s-s}}{\tilde{\rho}_{s-d}(\theta_D)}+\frac{\tilde{\rho}_{s-d}(T)}{\tilde{\rho}_{s-d}(\theta_D)}. \quad (2)$$

Electron–Electron scattering. The electron–electron scattering mechanism contributes a term to the resistivity ρ_{e-e} which is proportional to T^2. This term may then be a significant fraction of the total resistivity only at very low or very high temperatures. It is a good approximation to set

$$\rho_{\rm total}(\theta_D)=\rho_{s-d}(\theta_D).$$

In the renormalization scheme, the contribution of

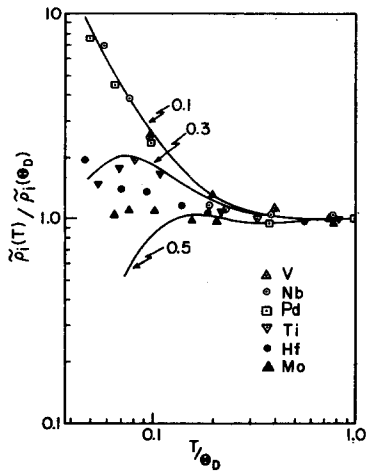

FIG. 1. White and Woods data for the ideal resistivity of metals with small and intermediate gap parameter plotted in renormalized form $\tilde{\rho}_i(T)=\rho(T)_{\rm exp}/(T/\theta_D)^5 J_5(\theta_D/T)$. The solid curves are the theoretical contributions to the renormalized resistivity from phonon-induced s–d transitions $[\tilde{\rho}_{s-d}(T)/\tilde{\rho}_{s-d}(\theta_D)]$ with the gap parameter θ_E/θ_D given to the right.

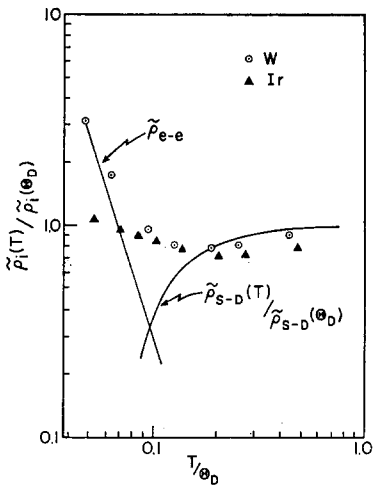

FIG. 2. Experimental data for the ideal resistivity of metals with large gap parameters plotted in renormalized form. The solid curves are the contributions from s–d transitions with $\theta_E/\theta_D=0.7$ and the contribution from electron–electron scattering.

ρ_{e-e} to $\rho_{\rm total}(T)$ is given by

$$\frac{\tilde{\rho}_{e-e}(T)}{\rho_{\rm total}(\theta_D)}=\frac{T^2\ \text{const.}}{(T/\theta_D)^5 J_5(\theta_D/T)\rho_{s-d}(\theta_D)}.$$

In the range $T/\theta_D<0.1$ this term is proportional to T^{-3}.

In principle, an estimate of the constant of proportionality could be obtained by fitting the experimental data. However, little is known about electron–electron scattering processes and such an estimate would serve little purpose. For example, no one has calculated the effects of electron–electron scattering when the initial states are $[s,d]$ or $[s,s']$ and the final state $[d',d'']$ These effects of these processes would be of the order m_d/m_s larger than the $[s,d]\rightarrow[s',d']$ processes computed by Baber.

Comparison with experimental results. The data of White and Woods for some of the nonmagnetic transition metals are plotted in Figs. 1 and 2 in the renormalized scheme. It is noted that as $\tilde{\rho}_{\rm exp}(T)/\tilde{\rho}_{\rm exp}(\theta_D)\gtrsim 1$ we may conclude from Eq. (2) that the effects of intraband scattering are negligible and the total resistivity is a sum of only ρ_{s-d} and ρ_{e-e}.

The data for V, Nb, and Pt are shown in Fig. 1 to be well fitted by $\tilde{\rho}_{s-d}(T)$ alone down to $T/\theta_D=0.05$ using $\theta_E/\theta_D=0.1$. Below this temperature the momentum gap becomes effective in inhibiting s–d transitions and ρ_{s-d} is proportional to $e^{-T_m/T}$. The fact that the temperature dependence of ρ_{s-d}, for $\theta_E/\theta_D=0.1$, is not significantly different from ρ_{e-e} to be sufficiently dominant below $T/\theta_D=0.05$ means that $\rho_{\rm total}\propto\rho_{e-e}$.

The data for Hf and Mo, on the other hand, display the characteristics of metals with slightly larger gap parameters, e.g., $\theta_E/\theta_D=0.4$, down to $T/\theta_D=0.1$. Below this temperature $\rho_{\rm exp}(T)$ deviates upwards from $\rho_{s-d}(T)$ as the electron–electron term becomes important.

The data for tungsten show, in Fig. 2, that near the Debye temperature $\tilde{\rho}_{\rm exp}(T)$ is monotonically decreasing as is characteristic of metals with $\theta_E/\theta_D\gtrsim 0.7$. For gap parameters this large, s–d transitions are significantly inhibited even near the Debye temperature. Consequently, at $T/\theta_D=0.05$, s–d effects are so depressed that electron–electron scattering effects are dominant and $\rho_{\rm total}\approx\rho_{e-e}$.

Similar estimates of the gap parameter θ_E/θ_D are made for the other metals and the results presented in Table II.

III. THE THERMAL RESISTIVITY

The thermal resistivity of the transition metals was computed for the two-band model described in Sec. II,

TABLE II. Estimates of the momentum gap parameter θ_E/θ_D[a] obtained from electrical and thermal resistance data.

Metal	Estimate obtained from ρ	Estimate obtained from W
Pd	S	S
Pt	S	S
Nb	S	S
Ta	S	S
Mo	I	I
Ti	I	I
Os	I	I
Ru	I	I
W	I	I
V	S	I
Hf	I	L
Zr	L	S
Ir	L	L
Rh	L	L

[a] θ_E/θ_D is taken as large (L), intermediate (I), and small (S) accordingly as $\theta_E/\theta_D>0.5$; <0.5, >0.3; <0.3.

using the variational principle of Kohler[7] and of Sondheimer.[8] The application of this method to solve the linearized Boltzmann equation involves a somewhat lengthy calculation. As the method is outlined by Wilson,[9] we merely quote the results:

$$W_{\rm pho}(T)=\frac{27m_sP_{ss}h^3T}{16\pi^5(2m_s)^{\frac{1}{2}}E_F^4}\left(\frac{T}{\theta_D}\right)^3\left(\frac{E_F}{kT}\right)^2 \times\left(J_5\left(\frac{\theta_D}{T}\right)+2^{-\frac{1}{2}}n^{-\frac{2}{3}}\left(\frac{T}{\theta_D}\right)^2 \times\left[\tfrac{2}{3}\pi^2J_5\left(\frac{\theta_D}{T}\right)-\tfrac{1}{3}J_7\left(\frac{\theta_D}{T}\right)\right]+\frac{w_dm_dP_{sd}}{m_sP_{ss}} \times\left\{\frac{2}{3}\left[J_5\left(\frac{\theta_D}{T}\right)-J_5\left(\frac{\theta_E}{T}\right)\right] +\frac{2\pi^2}{3}\left[J_3\left(\frac{\theta_D}{T}\right)-J_3\left(\frac{\theta_E}{T}\right)\right]\right\}\right).$$

The first three terms of this expression are the well-known results of the Bloch theory. The remaining terms are the contributions of interband scattering.

It is a good approximation to neglect the terms

$$2^{-\frac{1}{2}}n^{-\frac{2}{3}}(T/\theta_D)^2\left[\tfrac{2}{3}\pi^2J_5(\theta_D/T)-\tfrac{1}{3}J_7(\theta_D/T)\right]$$

with respect to the remaining terms in the expression for $W_{\rm pho}(T)$. In the low-temperature region these terms are depressed by a factor of $(T/\theta_D)^2$ and near the Debye temperature they are less than the terms due to s–d scattering by a factor of $w_dm_dP_{sd}/m_sP_{ss}$.

Near the Debye temperature $W_{\rm pho}(T)\propto(T/\theta_D)^2 \times J_3(\theta_D/T)$, which is in agreement with the empirical formula used by White and Wood to fit their data. This result may also be obtained by using Wilson's expression for $\rho_{s-d}(T)$ and invoking the Wiedemann–Franz law. At low temperatures the momentum gap becomes important in determining the temperature behavior of $W_{\rm pho}(T)$ and it is convenient to renormalize $W_{\rm pho}(T)$ by projecting out the temperature dependence of intraband effects. Thus we define

$$\tilde{W}_{\rm pho}(T)=\frac{W_{\rm pho}(T)(3m_sP_{ss}/2m_dw_dP_{sd})}{(T/\theta_D)^2J_5(\theta_D/T)} =\text{const.}\left[\frac{2^{-\frac{1}{2}}n^{-\frac{2}{3}}}{\frac{2}{3}(w_dm_dP_{sd}/m_sP_{ss})}+\frac{\pi^2[J_3(\theta_D/T)-J_3(\theta_E/T)]+[J_5(\theta_D/T)-J_5(\theta_E/T)]}{J_5(\theta_D/T)}\right] =\text{const.}\{\tilde{W}_{s-s}+\tilde{W}_{s-d}(T)\}.$$

As $\tilde{W}_{s-s}\approx\frac{1}{10}$ and $\tilde{W}_{s-d}(\theta_D)\approx20$ it is a good approximation to write $\tilde{W}_{\rm pho}(\theta_D)=\text{constant}\ \tilde{W}_{s-d}(\theta_D)$; hence, the constant of proportionality may be removed by writing

$$\frac{\tilde{W}_{\rm pho}(T)}{\tilde{W}_{\rm pho}(\theta_D)}=\frac{\tilde{W}_{s-s}}{\tilde{W}(\theta_D)}+\frac{\tilde{W}_{s-d}(T)}{\tilde{W}_{s-d}(\theta_D)}.$$

In Fig. 3, $\tilde{W}_{s-d}(T)/\tilde{W}_{s-d}(\theta_D)$ is displayed for various values of the parameter θ_E/θ_D. Electron–electron proc-

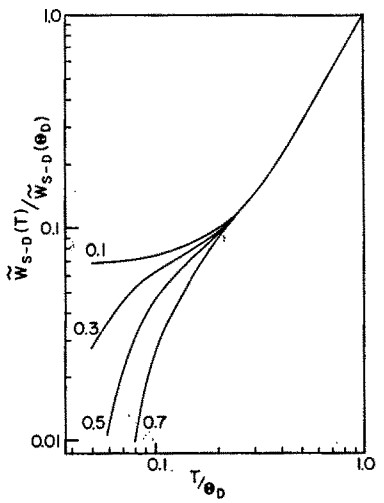

FIG. 3. Theoretical contribution of phonon-induced s–d transitions to the thermal resistivity, $W_{s-d}(T)$, plotted in renormalized form $W_{s-d}(T)=W_{s-d}(T)/(T/\theta_D)^2J_5(\theta_D/T)$ for various values of the parameter θ_E/θ_D.

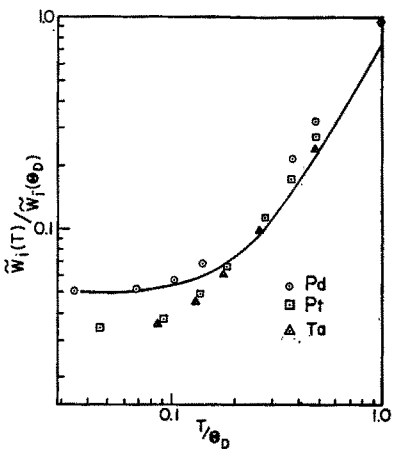

FIG. 4. Experimental data for the ideal thermal resistivity for metals with small gap parameter plotted in renormalized form along with the theoretical contribution due to s–d transitions using $\theta_E/\theta_D=0.1$.

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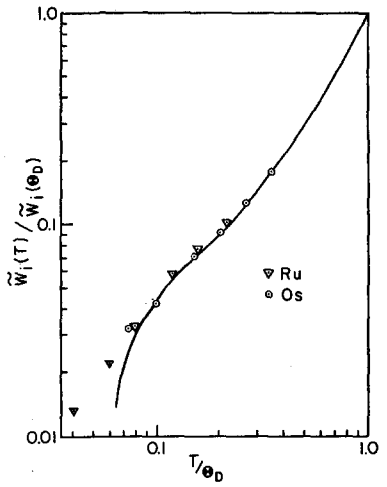

FIG. 5. Experimental data for the ideal thermal resistivity for metals with intermediate gap parameter plotted in renormalized form along with the theoretical contribution due to s–d transitions using $\theta_E/\theta_D=0.5$.

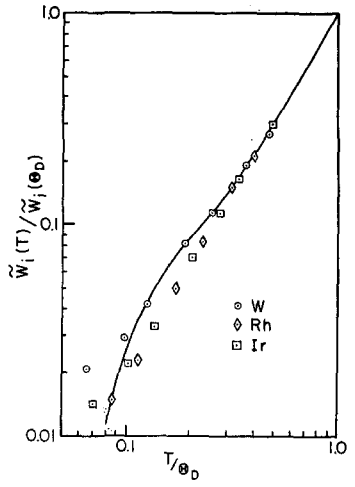

FIG. 6. Experimental data for the ideal thermal resistivity for metals with large gap parameters plotted in renormalized form along with the theoretical contribution due to s–d transitions using $\theta_E/\theta_D=0.7$.

esses contribute a term $W_{e-e} \propto T$. However there are sufficient differences in the behavior of $\tilde{W}_{\text{pho}}(T)$ above $T/\theta_D=0.1$, where electron–electron scattering processes are small, that we may obtain a classification of $\tilde{W}_{\text{exp}}(T)$ using the phonon part alone.

Comparison with experiment. In Figs. 4, 5, and 6 data for some of the transition metals are plotted in the renormalized scheme along with the theoretical curves of $W_{s-d}(T)$. The data are seen to be reasonably well fit above $T/\theta_D=0.1$ with $\tilde{W}_{s-d}(T)$ alone. Below this temperature the deviation of the data from $\tilde{W}_{s-d}(T)$ is assumed to be due to $\tilde{W}_{e-e}(T)$. In this way an estimate of the gap parameter θ_E/θ_D is obtained for each metal and the results are listed in Table II.

IV. DISCUSSION

The results of this investigation show that phonon-induced s–d transitions are the major contributor to the electrical resistivity at all but the lowest temperatures where electron–electron scattering is assumed to be important (phonon-induced intraband scattering being negligible at all temperatures). Consequently, the momentum gap between the s and d bands must be considered an important parameter of the theory.

The estimates of the gap parameter obtained from ρ and W independently for metals which are good conductors are consistent within the limits of our classification. Because of the crudeness of the spherical model and the neglect of umklapp processes this result is perhaps a bit surprising. Nevertheless, it seems to indicate that there is an effective gap expressed by the parameter θ_E which is characteristic of each metal. It is probable that the size of this parameter is a reflection of an average Fermi surface property and, in the case of simply connected Fermi surfaces, umklapp processes.

Finally, it should be mentioned that this analysis permits one to see some order in the experimental data that might have otherwise been obscured. For example, the fact that Nb, Pd, Pt, and W are the only metals for which ρ is proportional to T^2 at lowest temperatures may be attributed to the fact that these metals have very small or very large momentum gaps between their s and d bands. This allows ρ_{e-e} to either fit on smoothly to ρ_{e-d} or to dominate it completely. Although the other metals show no such low-temperature behavior, we believe that electron–electron processes are also operative in these materials. As a case in point, the data for Mo in our renormalized scheme show that $\tilde{\rho}_{\text{exp}}(T)/\tilde{\rho}_{\text{exp}}(\theta_D)$ is approximately constant or that $\rho_{\text{exp}}(T) \propto (T/\theta_D)^5 J_5(\theta_D/T)$, from $(T/\theta_D)=1$ to $(T/\theta_D)\approx 0.06$. Since this is the Bloch–Grüneisen function, one might be led to believe that intraband scattering is important throughout this range despite the fact that ρ_{exp} is an order of magnitude too large. Our analysis shows that, on the contrary, this result is fortuitous and is due to an interplay of the effects of interband and electron–electron scattering processes.

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