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Effect of Structure in the Electronic Density of States on the Temperature Dependence of the Electrical Resistivity*

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I discuss the effect of sharp structure in the electronic density of states on the temperature dependence of the interband–s-d–phonon-scattering resistivity. The *a priori* density of states of Pd is used to calculate the resistivity, which is found to be in excellent agreement with experimental high-temperature results.

The temperature dependence of the electrical resistivities of the pure transition metals[1] palladium and platinum, as well as the actinide metals[2] uranium, neptunium, and plutonium, exhibits high-temperature behavior that departs drastically from the classical linear T dependence. The low-temperature behavior has been found to obey a T^2 law that has led to descriptions in terms of spin fluctuations. Similarly many intermetallic compounds, especially those exhibiting finite superconducting transition temperatures,[3,4] exhibit high-temperature resistivities that tend to bend away from linear T behavior toward the temperature axis. These compounds are usually found to obey a T^3 law indicative of s-d phonon scattering at low temperature.

The present paper involves a generalization of the model[5,6] of interband s-d (or s-f) phonon scattering for cases in which there is sharp structure in the electronic density of states $N(\epsilon)$ in the vicinity of the Fermi level E_F. It is suggested that this interband–phonon-scattering mechanism is responsible for the high-temperature resistivity behavior. Because the model does not involve the exchange-enhanced spin susceptibility as does the spin-fluctuation model of the resistivity, simple model densities of states can be used to understand the temperature dependence of both the resistivity ρ and the spin susceptibility χ.

The density of states $N(\epsilon)$ of palladium is well known from relativistic augmented-plane-wave calculations,[7,8] and I will demonstrate the resistivity calculation using the *a priori* calculation of $N(\epsilon)$. The valence electrons in the transition metals are normally divided into two groups. The first forms an s band with a spherical Fermi surface; the second, a d band with a complex Fermi surface, but with a Fermi velocity much less than that in the s band. The lattice resistivity is then divided into three parts. The first, $\rho_{s\text{-}s}$, describes scattering of electrons within the s band; the second, $\rho_{s\text{-}d}$, is due to scattering of s electrons into the d band; and the third is due to d-d scattering. Since most of the current is carried by the s electrons, only the first two processes will contribute to the resistivity due to electron-phonon scattering. The contribution $\rho_{s\text{-}s}$ can be estimated from the resistivity of Ag, which is well behaved. We use an indirect model for the calculation of $\rho_{s\text{-}d}$. That is, we assume the momentum selection rule is always satisfied such that there are always phonons of sufficient size to cause interband scattering. This assumption will be invalid at very low temperatures where no phonons exist that can cause interband transitions. A Debye model for the phonon spectrum is then employed, and the resistivity is calculated following Ziman[6] except that the integral over $N(\epsilon)$ is treated generally; i.e., $N(\epsilon)$ is not assumed to be a slowly varying function of energy.

The resistivity due to phonon absorption is given by

$$\rho_{s\text{-}d}=\frac{\rho_0}{k_{\mathrm{B}}T}\int_0^{\Theta_{\mathrm{D}}}\frac{\omega^2\,d\omega}{\frac{1}{3}\Theta_{\mathrm{D}}^3}\,n(\omega)\int_0^{\infty}d\epsilon\,\frac{N_d(\epsilon+\omega)}{N(0)}\,f(\epsilon)[1-f(\epsilon+\omega)]\,, \tag{1}$$

where ρ_0 is a constant, k_{B} is Boltzmann's constant, T is the absolute temperature, Θ_{D} is the Debye temperature, $n(\omega)$ is the Bose function, $N_d(\epsilon)$ is the d (or f) fraction of the total density of states, and $f(\epsilon)$ is the Fermi function. Prange and Kadanoff[9] have demonstrated that the unrenormalized density of states enters the resistivity expression. To calculate the resistivity due to phonon emission, $n(\omega)$ is replaced by $n(\omega)+1$ and $\epsilon+\omega$ goes over to $\epsilon-\omega$ in the integral. The Fermi function depends on the value of the chemical potential μ, which is iteratively calculated at each temperature to hold the number of occupied states constant to within 5 parts in 10^7:

$$\int_0^{\infty}f(\epsilon,\mu,T)N(\epsilon)\,d\epsilon=\text{const.} \tag{2}$$

Equation (1) reduces to the functional form given by Wilson[5] either when $N_d(\epsilon)$ is a constant equal to $N_d(0)$, the density of d states at the Fermi level, or at sufficiently low temperatures, i.e., when $\rho_{s\text{-}d}$ is proportional to T^3 as $T\to 0$. For sufficiently high temperatures and a sufficiently narrow peak in $N_d(\epsilon)$, $\rho_{s\text{-}d}$ approaches a constant value.

In contrast to recent calculations[10] of the spin-fluctuation contribution to the resistivity, the only adjustable parameter in the present calculation is the coefficient ρ_0. Figure 1 illustrates the calculation of $\rho_{s\text{-}d}$ for palladium. $N_d(\epsilon)$ is taken as $N(\epsilon)$ of Mueller *et al.*,[7] $\Theta_{\mathrm{D}}=275°\mathrm{K}$,[11] and ρ_0 is set equal to 3.1 $\mu\Omega$ cm in order to fit the data[1] at 298°K. We assume the s density of states is a small free-electron-like contribution to $N(\epsilon)$. The contribution due to scattering within the s band, $\rho_{s\text{-}s}$, is estimated to be equal to the resistivity of Ag. Thus, comparison between theory and experiment is made between $\rho_{s\text{-}d}$ and $\rho_{\mathrm{Pd}}-\rho_{\mathrm{Ag}}$ in Fig. 1. The temperature dependence of $\rho_{s\text{-}d}$ is insensitive to the features of the phonon spectrum above about 100°K, i.e., once the resistivity is above the low-temperature T^3 regime. However, varying Θ_{D} does alter the magnitude of $\rho_{s\text{-}d}$ at high temperatures. The resolution, 1 mRy, in the palladium $N(\epsilon)$ calculation limits the accuracy of the calculated quantities below about 20°K. However, a remarkable fit to the resistivity data is obtained.

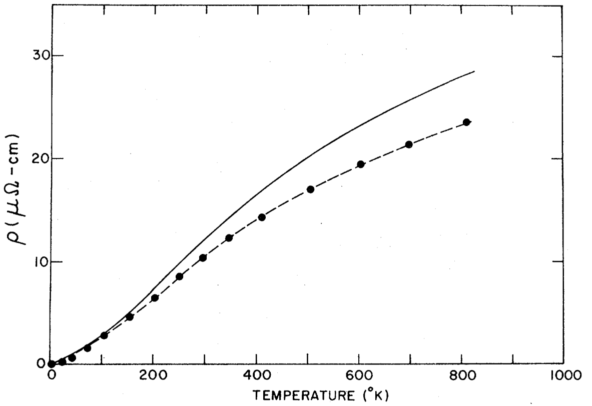

FIG. 1. Electrical resistivity of Pd. Solid line, experimental results (Ref. 1) for ρ_{Pd}; dashed line, $\rho_{\mathrm{Pd}}-\rho_{\mathrm{Ag}}$; circles, calculated values of $\rho_{s\text{-}d}$ normalized to $\rho_{\mathrm{Pd}}-\rho_{\mathrm{Ag}}$ at 298°K.

The coefficient ρ_0 due to normal processes can be estimated from[12]

$$\rho_{0\mathrm{N}}\approx 3m_s\lambda\omega_{\mathrm{D}}/e^2\pi^2k_{\mathrm{D}}^2(6\pi^2n_s)^{1/3}, \tag{3}$$

where m_s and n_s are the mass and number per unit volume of the current carriers, ω_{D} and k_{D} are the Debye frequency and wave vector, and λ is the mass enhancement. The contribution due to umklapp processes, $\rho_{0\mathrm{U}}$, is usually considered to be about a factor of 10 larger than $\rho_{0\mathrm{N}}$.[6] An order-of-magnitude estimate of $\rho_0=\rho_{0\mathrm{N}}+\rho_{0\mathrm{U}}$ based on a mass enhancement λ of 0.5 and 0.5 s electrons per palladium yields ρ_0 of order 1 $\mu\Omega$ cm. Thus, we find that the simple calculation of the resistivity due to s-d interband scattering gives a good accounting of the temperature dependence of the resistivity of Pd at high temperatures. The resistivity at very low temperatures, which follows a T^2 law,[1] is undoubtedly due to spin-fluctuation scattering. However, any treatment of the high-temperature resistivity must take full account of the effect of structure in $N(\epsilon)$ on the phonon-induced interband scattering.

Although $\rho_{s\text{-}d}$ is not sensitive to shifts in the Fermi level $E_{\mathrm{F}}\equiv\mu(T=0)$ of a few millirydbergs, the temperature dependence of the susceptibility is quite sensitive. The susceptibility is calculated from the indirect model ignoring matrix elements,

$$\chi_0(T)=(2\mu_{\mathrm{B}}^2/k_{\mathrm{B}}T)\int_0^{\infty}N(\epsilon)f(\epsilon)[1-f(\epsilon)]\,d\epsilon. \tag{4}$$

The value $\mu(T=0)=0.518$ Ry is used in both the $\rho_{s\text{-}d}$ and $\chi_0(T)$ calculations. Comparison is made

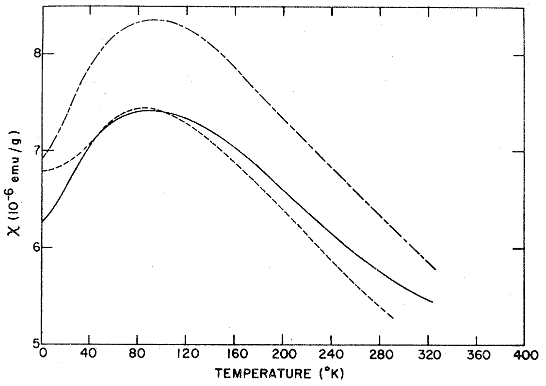

FIG. 2. Magnetic susceptibility of Pd. Dashed line, experimental results (Ref. 13); solid line, calculated values of χ with $S=7.6$; dot-dashed line, calculated values of χ with $S=8.4$.

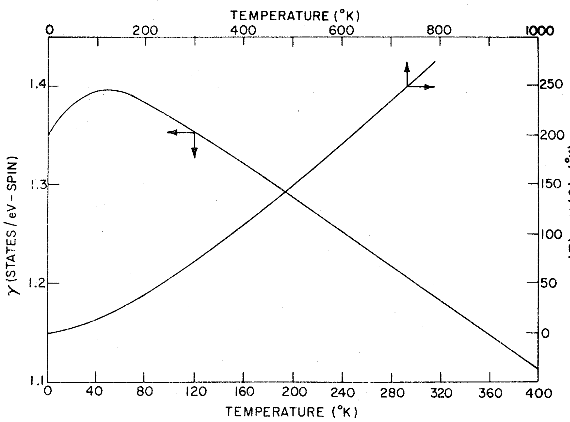

FIG. 3. Calculated temperature dependence of the electronic specific-heat coefficient γ and the shift in the chemical potential $\mu(T)-\mu(0)$ for Pd.

with the experimental[13] results in Fig. 2. The molecular-field approximation, which assumes a temperature-independent exchange interaction I, is used; i.e., $\chi(T)=\chi_0(T)/[1-I\chi_0(T)]$. Enhancement factors $S\equiv\chi(T=0)/\chi_0(T=0)$ of 7.6 and 8.4 are used in the calculated curves in Fig. 2. The departure of the experimental from the theoretical susceptibility below 40°K is due in part to the inaccuracies of the present calculation and to the assumptions made in subtracting the impurity contribution from the experimental data.[13]

The temperature dependence of the bare electronic specific-heat coefficient γ and the chemical potential are shown in Fig. 3. γ is calculated from

$$\gamma=(1/T)(\partial/\partial T)\int_0^\infty \epsilon N(\epsilon)f(\epsilon)\,d\epsilon. \qquad (5)$$

It is interesting to note that the electronic specific-heat coefficient γ changes by about 17% between 0 and 400°K. This is a considerably larger change than the unenhanced spin susceptibility χ_0 suffers. Also, the chemical potential increases by over 100°K for a temperature increase from 0 to 400°K. The breakdown of the lowest-order T^2 correction to γ and χ_0 is evident by 40°K.

The *a priori* band calculations for Pd have a number of inaccuracies of importance for the present calculation. Detailed comparisons between theoretical and experimental Fermi surfaces indicate that the relative position of the s and d bands is only known to within 1000°K.[8] However, near E_F nearly 90% of $N(\epsilon)$ is contributed by the purely d-like fifth band. The energies within this band are accurate to order 10°K. Thermal expansion[14] can give rise to a temperature-dependent $N(\epsilon)$ and possibly a temperature-dependent exchange interaction, which are not accounted for in the present calculation. Our calculated results use a Fermi level 2 mRy lower in energy than that of the *a priori* calculation of Mueller *et al.*[7] A similar calculation of $\chi_0(T)$ by van Dam and Anderson[15] based on the band structure calculation by Anderson[8] requires a shift of − 0.03 electrons or about 1 mRy to lower energy.

In conclusion, we find that interband s-d phonon scattering can explain the high-temperature electrical resistivity of Pd. This scattering mechanism is also capable of explaining the anomalous resistivity of other metals and intermetallic compounds that show curvature of the high-temperature resistivity toward the temperature axis, yet have weakly temperature-dependent susceptibilities with small enhancement factors. Examples are uranium, neptunium, and plutonium[2] and many intermetallic compounds.[4]

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Spectroscopically Observed Valence Mixing in SmS and Related Compounds*

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Photoemission spectra for semiconducting SmS and metallic $Sm_{0.5}Y_{0.5}S$ give evidence of strong configuration interaction of localized states near the Fermi level involved in semiconductor-to-metal phase transitions and in unusual trasport and magnetic properties. An analysis of the observed multiplet structure in photoemission spectra for semiconducting SmS shows a localized state of a mixed f^6+f^5d character.

Recently the samarium monochalcogenides have been widely studied because of their intriguing optical,[1-3] electrical,[4] and magnetic[5] properties. For example, SmS undergoes a pressure-induced semiconductor-to-metal phase transition at the remarkably low pressure of 6.5 kbar,[4] while certain mixed $Sm_{1-x}Gd_xS$ crystals undergo an explosive transition upon cooling at atmospheric pressure.[6] Also, certain $Sm_{1-x}Y_xS$ and $Sm_{1-x}La_xS$ crystals show an expansion upon cooling.[7] The unusual properties of these materials are associated with the presence of a highly correlated atomiclike six-electron configuration as the highest occupied electronic state.[1,4,5,8] The metal-to-semiconductor transition occurs when it becomes energetically favorable to delocalize one of these electrons[1,4,5] (i.e., the "valence" of the Sm ion changes).

We report photoemission energy-level measurements for semiconducting SmS and SmSe as well as for metallic $Sm_{0.5}Y_{0.5}S$ (actual composition $Sm_{0.54}Y_{0.46}S$). Both semiconducting SmS and SmSe show a valence-orbital binding-energy edge of ~0.3 eV below the Fermi energy E_F, while $Sm_{0.5}Y_{0.5}S$ is metallic. An analysis of the photoemission binding energies and spectral shapes of the emission from these localized states demonstrates that both semiconducting SmS and metallic $Sm_{0.5}Y_{0.5}S$ are in a "mixed-valence" state even at atmospheric pressure.

Photoemission energy distributions were taken with a previously described system[9] using synchrotron radiation from the 2.5-GeV storage ring at the Cambridge Electron Accelerator. Oriented (100) single-crystal specimens of 2 mm × 2 mm cross section were cleaved and measured *in situ* at about 2×10^{-10} Torr.

In a previous paper[8] we studied the valence electronic states of *s*, *p*, *d*, and *f* character as seen in photoelectron-energy-distribution curves. We identified the uppermost energy levels (for semiconducting SmS) at binding energies ~0.3 to 2.7 eV below E_F as being of primarily $4f$ character. These levels lie in the gap between the sulfur $3p$-derived valence bands (extending from ~3.4 to 7.5 eV below E_F) and the empty conduction bands.[8]

In this paper we concentrate upon the emission features associated with these localized states. The observed spectral shape of the emission from these localized electrons near E_F is complicated by the existence of final-state multiplet structures. As we shall describe, these structures can be used to identify the electronic configuration of the ground state. We need first to understand the expected spectral shape (i.e., final-state multiplet structure) for the limit of pure divalent Sm (six "*f*" electrons in the $^7F_0$ con-