VOLUME 48, NUMBER 1 PHYSICAL REVIEW LETTERS 4 JANUARY 1982

Mass and Lifetime Enhancement due to Disorder on $\mathrm{Ag}_c\mathrm{Pd}_{1-c}$ Alloys

G. M. Stocks and W. H. Butler
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 24 August 1981)

Residual resistivities of $\mathrm{Ag}_c\mathrm{Pd}_{1-c}$ alloys for $0.2 \leq c \leq 0.8$ were calculated from first principles using the Korringa-Kohn-Rostoker coherent-potential approximation and yielded quantitative agreement with experiment with no adjustable parameters. Some aspects of Mott's *sd* model are confirmed, but the *s* sheet velocities and lifetimes vary in a surprising manner with concentration because of the energy dependence of the disorder self-energy at the top of the *d*-band complex. These variations are analogous to electron-phonon mass and lifetime renormalization.

PACS numbers: 72.15.Qm, 72.10.Fk

The *sd* model of transport in transition metals and alloys was devised by Mott[1-5] in 1935. In this model, there are two types of valence electrons, nearly free *s* electrons and tightly bound *d* electrons. Electron transport is assumed to arise from the motion of the *s* electrons with the current being limited primarily by processes which scatter a mobile *s* electron into one of the more numerous but essentially immobile *d* states. The residual resistivity ρ_R of random alloys arises from the scattering of these *s* carriers by potential fluctuations. The *sd* model remains the basis for most discussions of transport in transition metals and transition-metal alloys.

In recent years, detailed band calculations have shown that the *sd* model is not so universally applicable as was once believed. The *s* and *d* bands hybridize so thoroughly that it is seldom possible to separate clearly the mobile carriers from the immobile traps. This separation can, however, be made in Pd and in its alloys with Ag. In this system the Fermi energy falls near the top of the *d*-band complex where all of the bands except one are very flat. The nonflat band of relatively high-velocity electrons is centered about the Γ point (the center of the Brillouin zone). As Ag is added this sheet expands and finally becomes the Fermi surface of pure Ag.

Recently, careful studies[6,7] of the electron-phonon interaction and the temperature-dependent phonon resistivity have confirmed the following aspects of the *sd* model for Pd: (1) Because of their high velocity, the electrons on the Γ-centered sheet carry most of the current (> 80%); (2) except at low T, where the electron-phonon interaction allows only small momentum transfer, the high-velocity electrons scatter primarily to the low-velocity sheets which hold the preponderance of the density of states; and (3) the momentum of an electron which scatters to one of the low-velocity sheets is no longer correlated with the momentum of the state from which it comes, i.e., the "scattering-in" term of the Boltzmann equation is negligible compared to the "scattering-out" term and the transport lifetime is equal to the quasiparticle lifetime. In our calculations of the residual resistivity, we assumed these three characteristics of electron-phonon scattering in Pd to apply to disorder scattering in Pd-rich $\mathrm{Ag}_c\mathrm{Pd}_{1-c}$ alloys. Characteristics (2) and (3) do not apply for Ag concentrations above 0.5 where the *d* band is filled; however, the difference between quasiparticle and transport lifetimes can be estimated.

The Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA)[8-10] method of calculating the electronic structure of substitutionally disordered alloys provides a basis for treating the electronic properties of these systems with roughly the same degree of rigor as band theory allows for ordered systems. The present KKR-CPA calculations use charge self-consistent potentials calculated by Stocks and Winter.[11] The only inputs to these calculations are the atomic number of the constituents and the experimentally determined crystal structure. Within the KKR-CPA the band-structure information is contained in the Bloch spectral density $A_B(\vec{k}, \epsilon)$.[9,12] In an ordered system $A_B(\vec{k}, \epsilon)$ consists of a set of delta functions at the band energies. As the system is disordered by the addition of substitutional impurities these delta-function peaks are broadened and shifted. If $A_B(\vec{k}, \epsilon)$ is plotted as a function of $\vec{k}$ at the Fermi energy ϵ_F, the locus of the peaks in $A_B(\vec{k}, \epsilon_F)$ define an alloy "Fermi surface." Such plots are shown in Figs. 21–26 of Pindor *et al.*[10] for some $\mathrm{Ag}_c\mathrm{Pd}_{1-c}$ alloys. These plots show a Γ-centered sheet consisting of relatively high-velocity electrons which retains its integrity throughout the concentration range and a complicated structure near the boundary of the Brillouin zone which arises from the multiply connected "jungle-gym" sheet of pure Pd. The "jungle gym" rapidly shrinks and becomes smeared out as Ag is added and vanishes for $c \simeq 0.5$. A plot of $A_B(\vec{k}, \epsilon)$ as a function of energy for a $\vec{k}$ which lies on the alloy Fermi surface shows a peak centered at ϵ_F. The width of this peak $\gamma_{\vec{k}}^{\epsilon}$ determines the k-dependent Fermi surface quasiparticle lifetime $\tau_{\vec{k}} = \hbar/2\gamma_{\vec{k}}^{\epsilon}$.

We calculated the residual resistivity ρ_R as a function of concentration using

$$\rho_R^{-1} = [2e^2\Omega/3(2\pi)^3] \int dS_k\, v_{\vec{k}} \tau_{\vec{k}},$$

where Ω is the volume per atom and $v_{\vec{k}}$ is the Fermi velocity obtained from the position of the peaks in $A_B(\vec{k}, \epsilon)$. The Fermi-surface integral was only evaluated for the Γ-centered sheet. The above formula for the resistivity can be derived trivially from the Boltzmann equation if the "scattering-in" term is neglected.

The results of our calculation (Fig. 1) are in very good agreement with experiment[13,14] considering the absence of adjustable parameters.[14] In silver-rich alloys, we overestimate the resistivity because the "scattering-in" term becomes important. We can estimate roughly the difference between transport and quasiparticle lifetimes using a formula appropriate to a low concentration of scatterers in a simple or noble metal,[15]

$$\tau^{qp}/\tau^{t} = [\textstyle\sum_l (l+1)\sin^2(\Delta\eta_{l+1} - \Delta\eta_l)]/[\textstyle\sum_l (2l+1)\sin^2\Delta\eta_l],$$

where $\Delta\eta_l = \eta_l^{\mathrm{Pd}} - \eta_l^{\mathrm{Ag}}$. For the phase shifts, η_l, appropriate to $\mathrm{Ag}_{0.8}\mathrm{Pd}_{0.2}$, we obtain $\tau^{qp}/\tau^{t} = 0.63$. When this correction factor is applied to the calculated resistivity values for this alloy, the result shown in Fig. 1 (bar) is obtained, in pleasing agreement with experiment.

Although our calculations of ρ_R agree with experiment, the calculated velocities and lifetimes differ significantly from Mott's *sd* model. His explanation for the asymmetry in ρ_R was based on the variation in the scattering rate or inverse lifetime which he assumed to have the form

$$(\gamma_{\mathrm{Mott}}^{\epsilon}) = c(1-c)n_s(\epsilon_F) + c(1-c)^2 n_d(\epsilon_F),$$

the first term coming from "*ss* scattering," the second from "*sd* scattering." n_s and n_d are the densities of states on the *s* and *d* sheets, respectively. This *Ansatz* for γ^{ϵ} is compared with our calculation in the top panel of Fig. 2. The second panel of Fig. 2 shows the variation of the Γ-sheet rms electron velocity, $\langle v^2\rangle^{1/2}$, as calculated here and in the rigid-band approximation.

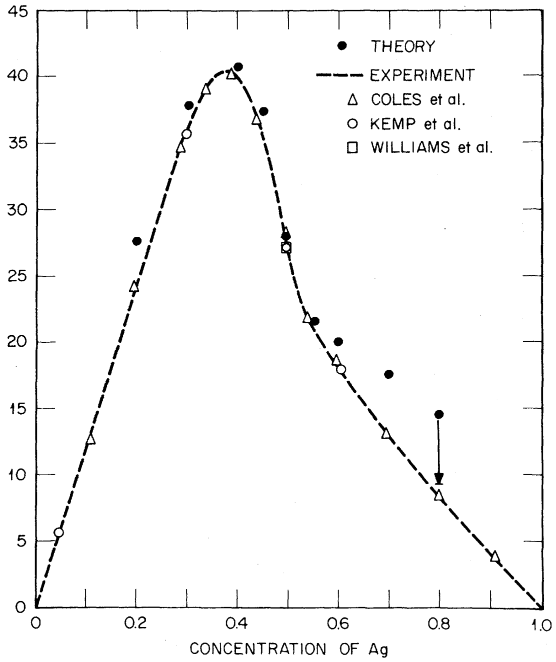

FIG. 1. Calculated and experimental residual resistivities in $\mathrm{Ag}_c\mathrm{Pd}_{1-c}$ alloys. The experimental results were taken from Refs. 4, 13, and 14.

Clearly, the concentration variation of the KKR-CPA γ^{ϵ} and $\langle v^2\rangle^{1/2}$ is different from that of the Mott model. Our calculations show that for low concentrations ($c \leqslant 0.2$ and $c \geqslant 0.8$) the effects on γ^{ϵ} of adding Pd impurities to Ag or Ag impurities to Pd are similar, i.e., $|(d\gamma^{\epsilon}/dc)_{c=0}| \simeq |(d\gamma^{\epsilon}/dc)_{c=1}|$. If it is to agree with experiment, the Mott model requires $|(d\gamma^{\epsilon}/dc)_{c=0}| \approx 2|(d\gamma^{\epsilon}/dc)_{c=1}|$ since $\langle v^2\rangle^{1/2}$ is assumed constant and $|(d\rho_R/dc)_{c=0}| \approx 2|(\rho_R/dc)_{c=1}|$. In our model, it is the fact that $(\langle v^2\rangle^{1/2})_{c=0} \approx 2(\langle v^2\rangle^{1/2})_{c=1}$ which accounts for the differences in ρ_R at the two ends of the concentration range. This in turn is related to the change in character, from *d* to *sp*, of the electrons on the Γ-centered sheet as Ag is added to Pd.

A further striking feature of our calculated γ^{ϵ} and $\langle v^2\rangle^{1/2}$ curves is the sharp dip near $c = 0.5$

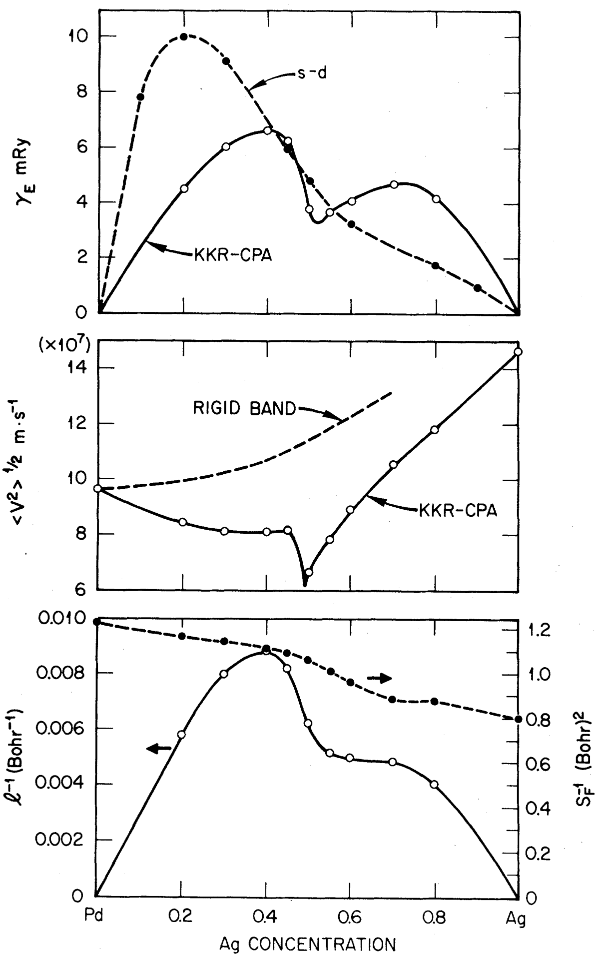

FIG. 2. Fermi-surface averages of various quantities involved in calculating the resistivity of $Ag_c Pd_{1-c}$ alloys. Upper frame: $\langle\gamma^\epsilon\rangle$ obtained in our KKR-CPA calculation; also shown is the form of γ^ϵ obtained for the Mott model. Middle frame: rms Fermi velocity obtained from our KKR-CPA calculation (solid line), and from the rigid-band model (dashed line). Lower frame: inverse of mean free path (solid line) and surface area of Γ-centered sheet (dashed line).

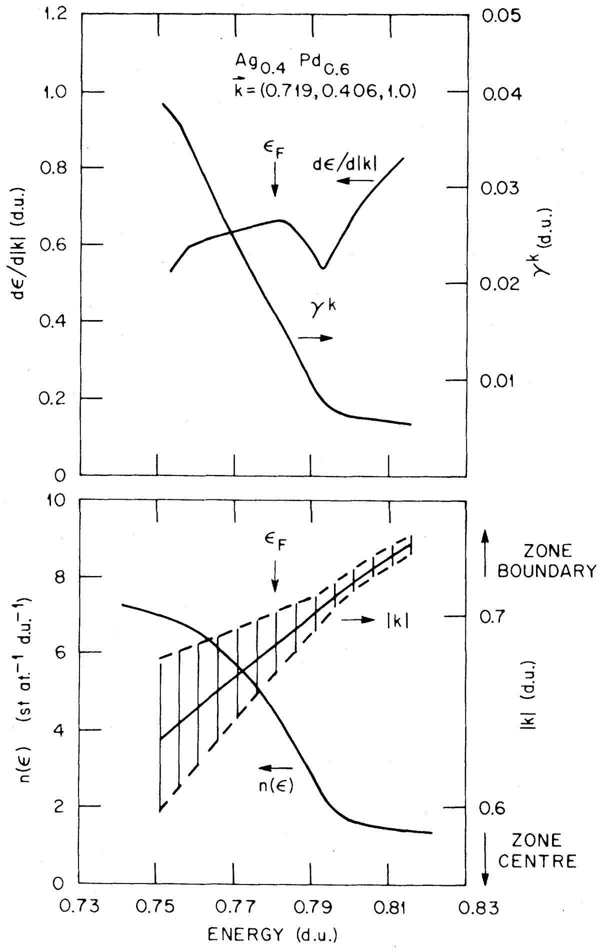

FIG. 3. Upper frame: width in $\vec{k}$, γ^k, and slope, $v_{\vec{k}} = |d\epsilon/dk|$, as a function of energy for the band which forms Γ-centered sheet of Fermi surface along the direction (0.719, 0.406, 1.0). Lower frame: ϵ vs $\vec{k}$ relation (solid line inside cross hatch) and width (cross hatch) of Γ-centered band for the above direction and total density of states (solid line) for the $Ag_{0.45}Pd_{0.55}$ alloy. The dimensionless units (d.u.) used in this figure may be converted to atomic units by multiplying by $(2\pi/a)^p$ where a is the lattice constant (7.494 a.u.) and $p = 1$ for k, γ^k, and $d\epsilon/dk$; $p = -2$ for $n(\epsilon)$.

(the density of states on the Γ-centered sheet has a corresponding hump). These features do not appear, however, in the ratio $\gamma_{\vec{k}}^{\epsilon}/v_{\vec{k}}^{k}$ which is physically the inverse of the mean free path shown in the lower frame of Fig. 2. Features similar to those in the concentration variation occur in the energy dependence of $\gamma_{\vec{k}}^{\epsilon}$ and $v_{\vec{k}}$ for a single alloy. An example is shown in Fig. 3 from which it is clear that the structure in $\gamma_{\vec{k}}^{\epsilon}$ and $v_{\vec{k}}$ is related to the fact that the band which forms the Γ-centered sheet is emerging from the high-density-of-states Pd d-band complex. In this same energy range $\gamma_{\vec{k}}^{k}$ decreases rapidly.

These rapid energy (or concentration) variations of $\gamma_{\vec{k}}^{\epsilon}$ and $v_{\vec{k}}$ can be viewed as velocity and lifetime renormalization effects analogous to those familiar from the theory of the electron-phonon interaction. If the disordered system Green's function is given by $G(\vec{k},\epsilon) = [\epsilon - \epsilon_{\vec{k}} - \Delta(\vec{k},\epsilon) + i\gamma(\vec{k},\epsilon)]^{-1}$ then the energy dependence of the real part of the self-energy $\Delta(\vec{k},\epsilon)$ must be included when calculating velocities and lifetimes. Thus, the renormalized velocities and lifetimes (generated automatically by the KKR-CPA) are related to the unrenormalized ones by $v_{\vec{k}} = v_{\vec{k}}^{\,0}/[1 - \partial\Delta(\vec{k},\epsilon)/\partial\epsilon]$ and $\tau_{\vec{k}} = \tau_{\vec{k}}^{\,0}[1 - \partial\Delta(\vec{k},\epsilon)/\partial\epsilon]$. The rapid variation in $\Delta(\vec{k},\epsilon)$ as a function of energy arises from the rapid falloff of the density of states at the top of the d-based complex. To a first approximation $\overline{\Delta}(\epsilon) = \sum_{\vec{k}}\delta(\epsilon - \epsilon_{\vec{k}})\Delta(\vec{k},\epsilon)/n(\epsilon)$ is given by the Hilbert transform of the density of states $n(\epsilon)$,[16] $\overline{\Delta}(\epsilon) = \int dz\, n(\epsilon)\,|V|^2/(\epsilon - z)$. We have evaluated $\overline{\Delta}(\epsilon)$ assuming that the matrix elements $|V|$ are independent of $\vec{k}$ and ϵ. We find that the rapid fall in $n(\epsilon)$ at the top of the d-band complex causes a peak in $\overline{\Delta}(\epsilon)$. The derivative of this peak $\partial\overline{\Delta}(\epsilon)/\partial\epsilon$ has structure of the proper magnitude and at the proper energy to explain the behavior of $v_{\vec{k}}$ and $\tau_{\vec{k}}$. Presumably, the KKR-CPA $\gamma_{\vec{k}}^{\,\epsilon}$ and $v_{\vec{k}}$ of Fig. 2 include these disorder renormalization effects at all concentrations, being smaller in Ag-rich alloys than in Pd-rich alloys, but it is only in the region of concentration where the Fermi energy is detaching from the Pd d-band complex where they introduce new structure. These renormalization effects cancel in the product $v_{\vec{k}}\tau_{\vec{k}}$ and, thus, do not affect the dc resistivity.

We acknowledge the help of Dr. F. J. Pinski and thank R. K. Williams and D. W. Yarbrough for their private communications. This research was sponsored by the Division of Materials Sciences, U. S. Department of Energy, under Contract No. W-7405-eng-26 with the Union Carbide Corporation.

---

[1] N. F. Mott, Proc. Phys. Soc. London 47, 571 (1935).

[2] N. F. Mott, Proc. Phys. Soc. London, Sect. A 153, 699 (1936).

[3] N. F. Mott, Proc. Phys. Soc. London, Sect. A 156, 368 (1936).

[4] B. R. Coles and J. C. Taylor, Proc. Roy. Soc. London, Ser. A 267, 139 (1962).

[5] J. S. Dugdale and A. M. Guenault, Philos. Mag. 13, 503 (1966).

[6] F. J. Pinski, P. B. Allen, and W. H. Butler, Phys. Rev. Lett. 41, 431 (1978).

[7] F. J. Pinski, P. B. Allen, and W. H. Butler, Phys. Rev. B 23, 5080 (1981).

[8] G. M. Stocks, W. M. Temmerman, and B. L. Gyorffy, Phys. Rev. Lett. 41, 339 (1978).

[9] B. L. Gyorffy and G. M. Stocks, in *Electrons in Disordered Metals and at Metallic Surface*, edited by P. Phariseau, B. L. Gyorffy, and L. Scheire (Plenum, New York, 1979), p. 89.

[10] A. J. Pindor, W. M. Temmerman, B. L. Gyorffy, and G. M. Stocks, J. Phys. F 10, 2617 (1980).

[11] G. M. Stocks and H. Winter, to be published.

[12] J. S. Faulkner and G. M. Stocks, Phys. Rev. B 21, 3222 (1980).

[13] W. R. G. Kemp, P. G. Klemens, A. K. Sreedhar, and G. K. White, Proc. Roy. Soc. London, Ser. A 233, 480 (1956).

[14] R. K. Williams and D. W. Yarbrough, unpublished.

[15] P. T. Coleridge, J. Phys. F 9, 473 (1979).

[16] S. Doniach and E. H. Sondheimer, in *Green's Functions for Solid State Physicists* (Benjamin, Reading, Mass., 1974), p. 107.