Possible coexistence of localized and itinerant states in connection with anomalies in the kinetic properties of high-resistivity alloys

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A polaron mechanism which leads to the existence of two groups of quasiautonomous electron states near the Fermi level in alloys with a special structural state (they contain disperse inclusions) is proposed. A qualitative explanation is offered for the unusual temperature dependence observed for the conductivity in titanium alloys, $V_{1-x}Al_x$, and other high-resistivity alloys. Anomalies in the concentration dependence of kinetic properties due to percolation in the system of disperse inclusions are discussed. © *1995 American Institute of Physics.*

An unusual temperature dependence of the static conductivity,

$$\sigma(T)=\sigma_0+\sigma_1\exp\left[-\left(\frac{T_0}{T}\right)^{\alpha}\right], \tag{1}$$

with $\alpha=1/4$ according to Ref. 1 and $\alpha=1/2$ according to Ref. 2, has been observed in numerous high-resistance metal alloys [$Ti_{1-x}Me_x$, where Me is a $3d$ metal,[1] and $V_{1-x}Al_x$ (Ref. 2); see Refs. 3 and 4 for some qualitatively similar curves for $W_{1-x}Re_x$ and $Cr_{1-x}Al_x$, respectively]. The temperature-dependent part of $\sigma(T)$ has been interpreted as a Mott conductivity with a variable hopping length, due to localized states which coexist with itinerant states at the Fermi level[5,6] (E_F). Expression (1) does indeed describe experimental data highly accurately over a fairly broad temperature range.[1,2] If we take this expression seriously, we are almost forced to assume a coexistence of localized and itinerant states. There is the difficulty that this expression does not conform to the general understanding of the electronic structure of disordered systems, since this expression would require a very strong suppression of hybridization between the two groups of states.[5] So far, no one has been able to propose a concrete physical mechanism which would lead to such a suppression. Empirical expression (1) thus remains puzzling. In the present letter we show that this expression can apparently be explained in a quite natural way in the picture of the structural and electronic states of high-resistance alloys which was drawn in Ref. 7. In the present letter we use this picture to discuss anomalies which have been observed in the concentration dependence of the magnetoresistance[6] and the thermal emf[2] of high-resistance alloys.

Experimental data on high-resistance alloys based on titanium[8] and on the alloys $Cr_{1-x}Al_x$ (Ref. 9), $V_{1-x}Al_x$ (Ref. 2), and $W_{1-x}Re_x$ (Ref. 3) point to a correlation between the unusual temperature dependence $\sigma(T)$ and the special structural state. For the titanium alloys and $Cr_{1-x}Al_x$, this state consists of a large number of small regions of "imperfect" ω phase.[7] In $W_{1-x}Re_x$ alloys, the corresponding role is played by regions of a χ phase, while in $V_{1-x}Al_x$ it is played by heterophase fluctuations with structures of the A15 and CsCl types. The possibility of a quantum size effect in these regions due to their small dimensions (20–60 Å in the case of the titanium alloys) and due to the presence of a deep pseudogap in the electronic structure of the ω phase near E_F was discussed in Ref. 7.

In this letter we show how this proposition, along with several natural assumptions, leads to an explanation of the behavior in (1) and thus makes it possible to take a fresh look at the problem of the "coexistence of localized and itinerant states in high-resistance alloys."

According to Ref. 7, as a zeroth approximation in a description of the electronic structure of titanium alloys near E_F we have two groups of electron states: localized (or "trapped") states in the small regions of ω inclusions, with a discrete energy spectrum (discrete because of the quantum size effect), and itinerant states of the matrix with a bcc structure (the β phase). The next step is to calculate the probability for transitions from certain states to others, i.e., the probability for a tunneling across the boundary of the ω regions. To do this we adopt a model with the Hamiltonian

$$\hat{H}=\varepsilon_0 a^+ a+\sum_i \lambda_i a^+ a(b_i^+ + b_i)+\sum_k \varepsilon_k c_k^+ c_k+\sum_k V_k(c_k^+ a+a^+ c_k)+H_{ph}. \qquad (2)$$

A similar model was used in Ref. 10 in connection with the mixed-valence problem, in which a coexistence of localized and itinerant states is again a key question.

Here the operators a^+, c_k^+, and b_i^+ create localized electrons, band electrons with a quasimomentum $\mathbf{k}$, and phonons (i is the index of the phonon mode), respectively; ε_0 and ε_k are the energies of the electrons, reckoned from E_F; λ_i and V_k are parameters of the electron–phonon interaction for the localized electrons and of the hybridization of localized and itinerant states; and H_{ph} is the phonon Hamiltonian (which was assumed in Ref. 10 to be harmonic). The seed width of the level ε_0 (in the case at hand, the penetrability of the barrier), $\Gamma_0=\pi\Sigma_k|V_k|^2\delta(\varepsilon_k)$, then undergoes a substantial renormalization according to Ref. 10 if Γ_0, $|\Delta|\leqslant\omega_{ph}$, where $\Delta=\varepsilon_0-E_p$, is the position of the localized level incorporating the polaron shift

$$E_p=\sum_i \lambda_i^2\int_0^\infty d\omega\,\frac{\rho_i(\omega)}{\omega}.$$

Here $\rho_i(\omega)$ is the spectral density of the ith phonon, and ω_{ph} is a characteristic frequency of the phonons. A formal renormalization-group analysis leads to the expression

$$\Gamma=\Gamma_0\exp(-\eta),\quad \eta=\sum_i \lambda_i^2\int_{|\Delta|}^\infty d\omega\,\frac{\rho_i(\omega)}{\omega^2}, \qquad (3)$$

which is valid under the condition $\Gamma \ll |\Delta|$. In the harmonic approximation we have $\rho_i(\omega) = \delta(\omega - \omega_i)$ and $\eta \sim E_p/\omega_{ph} \gg 1$. In our case, the electrons localized in the ω regions must interact fairly strongly with displacements of the $\beta \rightarrow \omega$ type, as can be seen from the fairly high sensitivity of the electron spectrum to such displacements.[7] This polaron mechanism for a narrowing of the quasilocal levels near E_F is probably responsible for the strong suppression of the effective hybridization which is necessary for the coexistence of localized and itinerant states.

The greatly anharmonic nature of the $\beta \rightarrow \omega$ oscillations is an important circumstance here. Because of it, much of the spectral density $\rho_i(\omega)$ is at frequencies $\omega \ll \omega_{ph}$. This assertion is a nontrivial consequence of the multiwell nature of the potential for $\beta \rightarrow \omega$ displacements.[11] Unfortunately, the detailed behavior of $\rho_i(\omega)$ in this situation is not known. For simplicity we use the approximation $\rho_i = \text{const}$ at $\omega < \omega_{ph}$, by analogy with the distribution of the energy of excitations in glasses associated with a two-well potential.[12] A simulation of strong anharmonic effects through simply a strong damping of phonons leads to the same result. Under the condition

$$\rho_i(\omega) = \frac{\gamma_i}{\pi} \frac{1}{(\omega - \omega_i)^2 + \gamma_i^2}$$

($\gamma_i \sim \omega_i$), we have $\rho_i \approx \text{const}$ at $\omega \ll \omega_i$. In this case the quantity $\lambda_i \sim (2M\omega_i)^{-1/2}$ (M is the mass of an ion) can also be replaced by a constant, since the "buildup" of spectral density at small values $\omega \ll \omega_{\max}$ is generally not due to a small value of the seed phonon frequency ω_i. By way of comparison we note that for acoustic phonons ($\omega_q \sim q$) we have $\lambda_q^2 \sim q^2/\omega_q \sim \omega_q$, and the quantity

$$\sum_q \lambda_q^2/\omega_q^2 \sim \int_0^{\omega_{\max}} d\omega \omega^{d-2}$$

converges at its lower limit ($d = 2,\ 3$ is the dimensionality of the space).

We then have $\eta = L/|\Delta|$, where $L = \Sigma_i \lambda_i^2 \rho_i$, and the probability for a phonon-induced transition from a level at a distance $|\Delta|$ from E_F at a temperature $T \ll |\Delta|$ is given by the following expression, which incorporates a polaron suppression of tunneling:

$$w(\Delta) \sim \exp\left[-\eta - \frac{|\Delta|}{T} \right] \equiv \exp\left[-\left(\frac{L}{|\Delta|} + \frac{|\Delta|}{T} \right) \right]. \tag{4}$$

Optimizing the argument of the exponential function with respect to $|\Delta|$, in the customary way in the theory of a Mott conductivity with a variable hopping length,[13] we find

$$w_{\text{opt}} \sim \exp[-2\sqrt{L/T}] \tag{5}$$

as the characteristic frequency of transitions between the electron subsystems. This result agrees with (1) in the case $\alpha = 1/2$ if we assume that the second term in (1) is due to transitions from localized states to collectivized states. Expression (5) is valid under the condition $\Delta_{\text{opt}} < \omega_{\max}$, from which we find $T < \omega_{\max}^2/L$. If we assume that $\rho_i(\omega)$ behaves in accordance with $\rho_i(\omega) \sim \omega^\beta$ ($0 < \beta < 1$), we find a dependence like (1) with $\alpha = (1-\beta)/(2-\beta)$ ($\alpha = 1/4$ for $\beta = 1/3$; $\alpha = 1/3$ for $\beta = 1/2$; etc.).

The most important circumstances in explaining (1) are thus the quantum size effect in the inclusions of the disperse phase, the fairly strong electron–phonon interaction in this phase ($E_p \gg \omega_{ph}$), and the highly anharmonic nature of the lattice dynamics. These considerations make it possible to understand the correlations between the unusual temperature dependence $\sigma(T)$ and the special structural state of high-resistance alloys, which has been mentioned on many occasions by experimentalists.[2–4,8,9]

We turn now to the anomalies in the concentration dependence of the kinetic properties of high-resistance alloys. The onset of a high-resistance state is accompanied by (in addition to an increase in the resistivity ρ) a sharp increase in the Hall coefficient[5] R_H and changes in the sign of the thermal emf α (Ref. 2) and the magnetoresistance $\Delta\rho(H)$ (Ref. 6). The concentration dependences $R_H(x)$ and $\alpha(x)$ seem to imply a change in conductivity type, from n-type to p-type, near the concentration x_c, at which $\rho(x)$ reaches a maximum. The most natural way to interpret this behavior is to take it as evidence of the onset of an additional conduction mechanism, e.g., a conduction resulting from the formation of a percolation cluster of ω-like regions which are in contact with each other. Such a cluster would form from spheres or ellipsoids with randomly distributed centers when the fraction of the volume which they occupy reaches a value on the order of $2.7/8 \approx 0.34$ (Ref. 13). This figure is extremely close to the fraction of the disperse ω phase which has been observed experimentally in the titanium-based high-resistance alloys.[7] At $x \approx x_c$, we would thus expect nonanalytic contributions to the energy dependence of the conductivity at the Fermi level, $\sigma(E_F) \sim |E - F_F|^s$, due to both a tendency toward an Anderson localization of matrix states, by virtue of resonant scattering by ω regions,[7] and a percolation through these regions. In the latter case we find $s \approx 1.6$–1.7 from the model of classical percolation.[13] In this case we find nonanalytic contributions to the thermal emf, $\alpha \sim \partial \ln \sigma(E_F)/\partial E_F$, and the conductivity becomes a function of the magnetic field due to a spin splitting:

$$\Delta\sigma(H) = \frac{1}{2}\left(\frac{\partial^2\sigma(E)}{\partial E^2}\right)_{E=E_F} (\mu_B H)^2 \sim -s(s-1)H^2(E-E_F)^{s-2}, \tag{6}$$

where μ_B is the Bohr magneton. As was shown in Ref. 6, the latter contribution provides a qualitative explanation for the anomaly in the magnetoresistance of the titanium-based high-resistance alloys.

Let us emphasize the two most important circumstances in the discussion above. First, there is the very fact that an electronic phase transition of a percolation type occurs at $x \approx x_c$. This transition seems natural on the basis of simple geometric considerations. Second, there is the question of the validity of the model of classical percolation and, in particular, the value of the critical exponent s. It is natural to assume that the percolation is classical if the temperatures are not too low (room temperature?), but in the limit $T \to 0$ we would definitely have to take quantum effects into account. Furthermore, according to the interpretation above, an "ω region" may be thought of as a gigantic atom, in which effects such as Hubbard repulsion could be important. A concrete description of the transition may thus prove to be very complex.

The coexistence of two electron subsystems and the fundamental importance of this coexistence for explaining features of the kinetic properties of titanium-based alloys were

stressed in Refs. 5 and 6. However, the picture of the nature of these subsystems which we have drawn in the present letter is quite different. The primary fundamental distinction between the new approach, proposed in Ref. 7 and pursued here, is the focus on the role played by the special structural state of high-resistance alloys.

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