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Localized Enhancement Effects in Pd-Ag Alloys

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Low-temperature electrical resistivities of Pd-Ag alloys show a positive T^2 temperature dependence in the concentration range above 60 at.% Ag. This behavior supplements the well-known resistivity minima observed in alloys with lower concentrations of Ag, and strongly favors the model of scattering from localized exchange-enhanced Pd d states, as against $s \rightarrow d$ scattering in the rigid-, or collective-, band description of the alloys.

Two conflicting models for the electronic structure of Pd-Ag alloys are currently being advanced as possible explanations of the electrical resistivity behavior of these alloys. The resistivity minima observed by Edwards, Chen, and Legvold[1] in Pd-Ag alloys in the concentration range between 25 and 55 at.% Ag have been explained by the authors in terms of scattering of conduction electrons from exchange-enhanced pockets of holes associated with statistical clusters of Pd atoms—a distinction being made between the localized density of d states and the itinerant d band, also associated with Pd atoms. However, Rowlands and Greig[2] who observed similar minima in the Pd-Rh system found the calculated value of the coefficient A of the T^2 term in the resistivity of an alloy containing 4% Rh (obtained by using the rigid-band model[3] approximation as applied to the Pd-Ag system by Coles and Taylor[4]) to be very close to the experimental value, and therefore they argued in favor of the rigid-, or collective-, band description of the alloys. This assertion is further supported, it is now claimed, by some recent resistivity measurements on the Pd-Ag system by Ahmad and Greig,[5] who have observed two resistance minima in a $\mathrm{Pd}_{0.60}\mathrm{Ag}_{0.40}$ alloy, as also found in the Cu-Ni system.[6] These authors have put forward a qualitatively plausible explanation of the anomaly as due to a combination of two terms in the resistivity—a term $\rho_0(1-AT^2)$ due to the reduction of $s \rightarrow d$ scattering cross section resulting from the broadening of the Fermi level within the d-band states,[4,7] and an ideal resistivity term $\rho_{\mathrm{ideal}} \sim BT^2 + CT^4$ at low temperatures which changes to a term linear in T at higher temperatures, giving rise to the maximum in the resistivity which follows the first minimum at lower temperatures. The second minimum results since the low-temperature $1-AT^2$ dependence is gradually modified and flattens off at high temperatures, as it must, leaving the linear term in the resistivity dominant. On the basis of this, the authors argue, the observed anomalies in the Pd-Ag and Cu-Ni systems may be regarded as caused by $s \rightarrow d$ scattering of conduction electrons into the d-band states.[4,7]

As suggested by Edwards, Chen, and Legvold,[1] of course, the $1-AT^2$ term in the resistivity discussed above could equally well be obtained from the process of scattering of conduction electrons from exchange-enhanced localized pockets of holes. Hence at first sight and on a qualitative basis it appears difficult to make a distinction between the two models. It is, however, useful to remember that direct evidence of a separate "band" associated with Pd in Ag-rich Ag-Pd alloys has been found in the optical absorption studies of the alloys by Myers, Wallden, and Karlsson.[8] Similar evidence is also seen in the photoemission experiments of Norris and Nilsson[9] and Norris and Myers.[10] The results have been explained by these authors in terms of a Friedel-Anderson virtual bound state[11] for Pd atoms in the Ag matrix, situated above the Ag d band and about 2 eV below the Fermi level. Formation of statistical near-neighbor clusters results in further broadening of the d states, but they remain localized on the Pd atoms, the authors suggest, until the concentration of Pd reaches 40 at.%. Also, Kjollerström[12] has shown that the dielectric-constant, the residual-resistivity, and the specific-heat data of dilute Ag-Pd alloys can be satisfactorily accounted for by the Anderson model using a half-width of 0.6 eV for the impurity state, which lies 2.2 eV below the Fermi level.

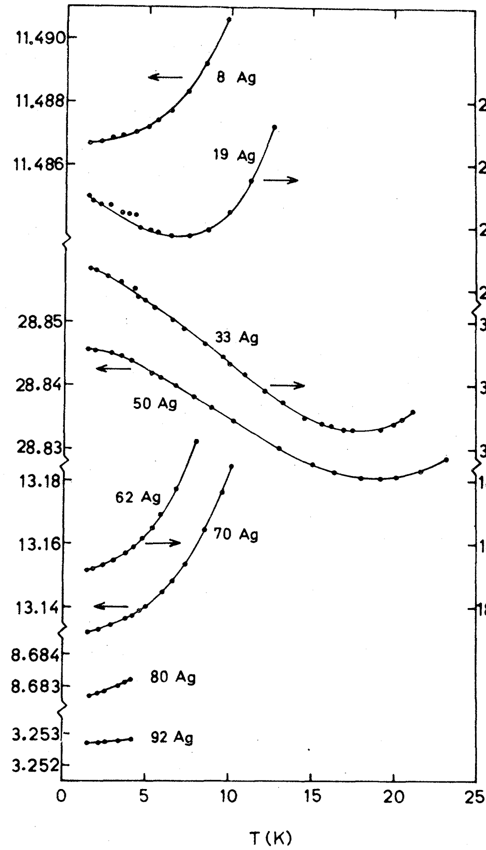

FIG. 1. Electrical resistivity of Pd-Ag alloys as a function of temperature. The concentration of Ag in the binary matrix is indicated on the respective curves. Note the changes of vertical scale, particularly between the alloys at the two ends and those in the middle of the series.

I wish to report here some preliminary measurements of the electrical resistivity of several Pd-Ag alloys which, I believe, lend strong support to the model of localized d-state formation in the alloy system. The low-temperature resistivity behavior in the concentration range above 60 at.% has, apparently, remained unmeasured so far despite an active interest in this alloy system for a long time.

The results are shown in Fig. 1 where the electrical resistivity is plotted as a function of temperature for a series of Pd-Ag alloys covering the whole concentration range. In the Pd-rich region with up to 50 at.% Ag, resistance minima are observed in good qualitative agreement with the results obtained by Edwards, Chen, and Legvold.[1] However, in the next concentration alloy with about 62% Ag the resistivity behavior changes dramatically and shows the positive T^2 temperature dependence (see Fig. 2). Further in-

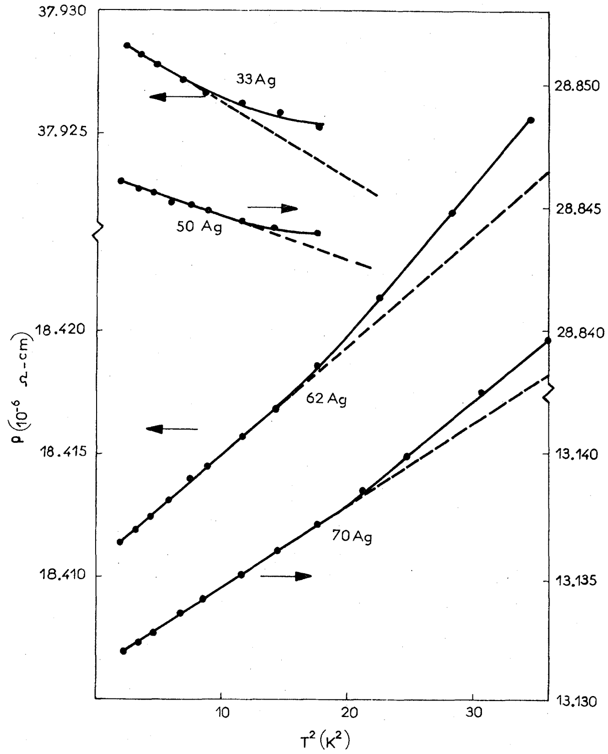

FIG. 2. Electrical resistivity plotted against T^2 for four Pd-Ag alloys containing Ag concentrations as indicated.

crease in the Ag concentration results in a decrease in the strength of the T^2 dependence, but it is possible that a maximum is reached at some concentration between 62 and 70 at.% Ag before this happens.

I argue that the localized–d-states model can account for the observed behavior in a quite natural way. As mentioned earlier, there is ample evidence that in Ag-rich alloys the localized states associated with statistical clusters of Pd atoms are situated below the Fermi level. Hence, at $T=0$ their contribution to the scattering of conduction electrons should be small. Any additional scattering from localized enhancement effects, or spin fluctuations, therefore gives an increasing contribution to the resistivity in a straightforward manner.[13,14] The appearance of holes in the d states when the concentration reaches above 40 at.% is accompanied by a change of slope in the residual resistivity versus concentration curve, which has been ascribed to the appearance of $s \rightarrow d$ scattering channel.[4] The situation is similar in some ways to that of *Pd*U where above a concentration of 8 at.% U, a large increase in the residual resistivity per atomic percent of U is observed as the "Fermi level becomes pinned to the U virtual f level."[15] If the $s \rightarrow d$ scattering in the present system gives rise to large phase shifts at $T=0$, then additional scattering due to spin fluctuations will result in a T^2-like decrease in the resistivity[14,16] as observed. In *Pd*U a change of sign of the T^2 dependence in the resistivity with concentration is also observed, but this is in opposite sense to the present one if the reduced diagram of the electronic specific-heat coefficient γ versus the electron/atom ratio is considered.[17] However, the mechanism for the anomaly is essentially the same for both systems. In *Pd*U the observed behavior is due to f levels in relatively dilute alloys, whereas in Pd-Ag alloys it is the localized d states on Pd atoms in alloys containing substantial Ag concentrations which are thought to give rise to the observed anomalies. I should mention, however, that the idea of localized pockets of holes existing in Pd-rich alloys is at variance with the claim by Norris and Myers[10] that Pd d states become itinerant above the concentration of 40 at.% Pd. It is nevertheless possible that d states on certain configurations of statistical clusters of Pd atoms remain localized (in some spatial sense) while others form "fully" itinerant band states.

The strong positive temperature dependence in the resistivity of Ag-rich alloys is more difficult to justify on band-model arguments than perhaps is the negative one (i.e., resistance minima). It should be noted, however, that the results of Edwards, Chen, and Legvold[1] indicate that the coefficient A of the T^2 term, which should roughly follow the depth of the minimum (even after due allowance for B), goes through a maximum value at around 40 at.% Ag in the binary matrix and becomes negligibly small in alloys with Pd concentrations above 80 at.%. This behavior would be impossible to obtain from the rigid-band formula of Coles and Taylor[4] taken together with the well-known specific-heat behavior of the Pd-Ag system.[18] (For instance, the value of A for the Pd–19-at.%-Ag alloy, Fig. 1, is an order of magnitude smaller than that expected from the formula of Coles and Taylor.) It also does not seem possible that an appropriately shaped d band or a two-band structure as considered by Dugdale and Guenault[19] for the Pd-Ag system and earlier by Coles[20] for the Cu-Ni system could simultaneously account for both the resistivity and the specific heat of the alloys. For the positive T^2 dependence the situation is even more clearcut, for band arguments require the Fermi level to be situated close to a minimum in the density of states.[7] It is difficult to imagine that any band model would indicate that it will remain fixed to a minimum over such a large concentration range of about 30–40 at.%.

I conclude by saying that the observed positive temperature dependence in the resistivity enables us, for the first time, to make an unambiguous choice of the model to describe the electronic structure of Pd-Ag alloys, regarding which considerable controversy exists in the literature. Although rigid-, or collective-, band arguments seem qualitatively appealing in the case of the negative temperature dependence, they fail completely when details such as the variation of the coefficient A of the T^2 term with concentration are considered. Even more important is the fact that the model is in direct conflict with the positive T^2 temperature dependence observed over a wide concentration range in silver-rich alloys. Scattering of conduction electrons from localized exchange-enhanced states associated with Pd atoms, on the other hand, can satisfactorily account for the T^2 resistivity behavior including the change in sign of the coefficient A. Hence this model seems to be the most appropriate description of this and similar alloy systems.

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Electronic Structure of the Tetracyanoquinodimethane (TCNQ) Molecule

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The electronic structure of an isolated TCNQ mulecule has been calculated by the self-consistent statistical-exchange multiple-scattering method. By using overlapping atomic spheres in place of nonoverlapping atomic spheres, a significant increase in physical realism has been achieved. The theoretical model provides a satisfactory account of the photoemission spectra of TCNQ vapor and solid TCNQ. The singlet-triplet splitting for the lowest optical transition is found to be 0.84 eV.

During the past few years, interest in the physics of organic solids has grown rapidly. Of particular interest are highly conducting charge-transfer salts[1-3] such as tetrathiofulvalinium-tetracyanoquinodimethanide (TTF-TCNQ).[4,5] Most current discussions of the physical properties of these organic solids are based on idealized one-dimensional models.[1-5] However, there are indications[6] that realistic three-dimensional models are required for a thorough understanding of these properties. Also, conclusive theoretical interpretations of the photoemission spectra of TCNQ vapor and solid TCNQ have not yet appeared.

In this paper we describe a simple theoretical model which can be used to generate realistic energy-level structures for large planar organic molecules such as TCNQ. Our calculations for the TCNQ molecule were carried out within the general framework of the self-consistent statistical-exchange ($X\alpha$) multiple-scattering method.[7,8] In an initial effort,[9] the calculations were carried out on the basis of the standard muffin-tin model[7,8] by which we mean nonoverlapping atomic spheres embedded in an intersphere region, all surrounded by a bounding outer sphere (cf. Fig. 1). This type of model had been used previously to study other large planar organic molecules.[10] It was clear from the preliminary study of the TCNQ molecule[9,11] that the standard muffin-tin model was not sufficiently accurate for our purposes, and that a significant improvement in physical realism was necessary if we hoped to deal successfully with the TCNQ molecule.

It is possible to improve upon the standard muffin-tin model by introducing nonspherical terms