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Electrical resistivity and antiferromagnetism of chromium-palladium alloys between 77 and 700 K

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Electrical resistivity ρ has been measured as a function of temperature for binary chromium alloys containing 0.99, 1.48, and 1.99 at.% palladium. The Néel temperature, determined from the $d\rho/dT$ method, oscillates with palladium concentration, first decreasing to a minimum at ~0.6 at.% palladium and then rising again to a peak at ~1.5 at.% palladium. Similar behavior is observed for the temperature coefficient of resistivity in the paramagnetic regime. We attribute the initial decrease in both cases to competition between Fermi-surface nesting and resonant scattering of band electrons from palladium impurities. The observed oscillations may result from a small moment on palladium impurities coupling to the spin-density wave of the host.

I. INTRODUCTION

It is well known that the itinerant electron antiferromagnetism in pure chromium can be strongly influenced by dissolved solutes. One experimental technique which is particularly useful for exploring the general features of the above antiferromagnetism is the electrical resistivity. For this reason, we have been investigating this property on all binary chromium alloys containing elements soluble (1 at.% or more) in chromium. In this paper we report such measurements on the chromium-palladium system. In general, very little has been done on these alloys. The only known previous study is by Noor and Booth[1] who investigated the electrical resistivity and magnetic susceptibility of dilute chromium-palladium alloys and found that the Néel temperature exhibits a minimum below 1 at.% palladium.

II. EXPERIMENTAL CONSIDERATIONS

The chromium-palladium alloys containing 0.99, 1.48, and 1.99 at.% palladium were prepared by an arc melting method using procedures described before.[2] Details on the purity of chromium used for making these alloys are also given in Ref. 2. Palladium of purity 99.99% was purchased from Engelhard Industries, Inc.

The experimental facilities for determining the electrical resistivity have been described elsewhere.[2,3]

III. RESULTS AND DISCUSSION

Figure 1 shows the measured electrical resistivity, $\rho_{\text{expt}}(T)$, uncorrected for thermal expansion, as a function of the absolute temperature T between 77 and 700 K. The insert in Fig. 1 presents the residual electrical resistivity ρ_0 determined at 4.2 K, as a function of palladium concentration. The straight line, whose slope is about 5.8 $\mu\Omega$cm/at.% palladium, confirms the good quality of the prepared alloys.

The $\rho_{\text{expt}}(T)$ curves in Fig. 1 are typical plots for itinerant electron antiferromagnets with incommensurate magnetic structure. The anomalies are caused by the antiferromagnetic paramagnetic transitions. The Néel temperatures can be conveniently determined from the $d\rho_{\text{expt}}(T)/dT$ curves as temperatures where

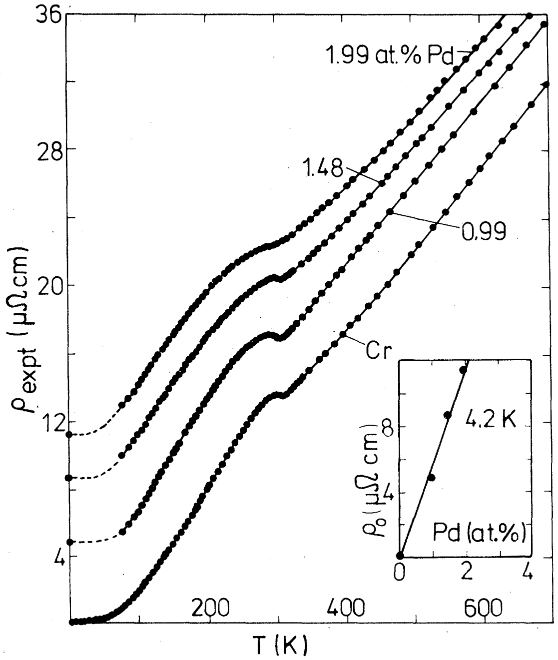

FIG. 1. Electrical resistivity of chromium-palladium alloys.

this derivative has its minimum value. The results are summarized in Table I and Fig. 2. Figure 2 also shows the values of T_N obtained by Noor and Booth.[1] Two observations can be made at once. First, the T_N determinations by the $d\rho_{\mathrm{expt}}(T)/dT$ method by us are in good agreement with the susceptibility values. Second, the T_N versus palladium content curve not only shows a minimum but exhibits an oscillatory behavior, i.e., the minimum is followed by a maximum at about 1.5 at.%. The only other binary chromium system which shows such characteristics are the chromium-cobalt alloys.[4]

According to Fedders and Martin,[5] the Néel temperature of dilute chromium rich alloys is given by

$$T_N = \Theta \exp(-1/\lambda) \ , \qquad (1)$$

where Θ and λ are parameters which depend upon the host band structure. The quantity λ for an itinerant two-band antiferromagnet is a function of several factors, but is most sensitive and proportional to the interaction area for the two nesting Fermi surfaces. Presumably palladium, which lies four places to the right of chromium in the Periodic Table, would act as a strong electron donor when substituted in the chromium matrix, thus improving the nesting of electron jack and hole octahedron and increasing T_N.

The chromium-palladium system is anomalous in that T_N initially decreases even though electrons are added. Two competing mechanisms are indicated here: in addition to the nesting effect there appears to be unusually strong impurity scattering which, by itself, is known to decrease T_N.[6] Similar anomalies observed in chromium alloys containing small amounts of iron, cobalt, and nickel have been attributed by some to resonant scattering of the band electrons by the dissolved solute.[7] We believe the same interpretation applies to our chromium-palladium alloys. In particular, a scattering resonance in the electronic spectrum of the alloy somewhat below the Fermi energy of pure chromium would capture (into virtual bound states) some of the host band electrons as well as any additional electrons donated by palladium impurities. The result would be a net reduction in the number of itinerant electrons, a smaller degree of nesting, and a lower Néel temperature. This process would continue only so long as the Fermi energy of the alloy E_F exceeds the resonance level E_r of the impurity scatterers; ultimately E_F becomes pinned somewhere near E_r and, in the absence of other mechanisms, T_N should level off. However, the increased Coulomb repulsion of the electrons "piled up" in virtual bound states at the impurity sites further serves to decrease T_N, even beyond the concentration needed for pinning the Fermi energy.

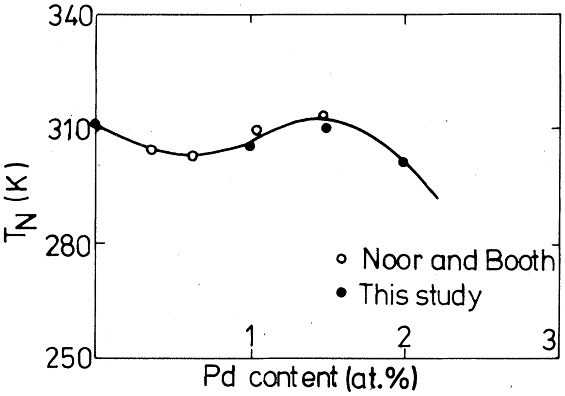

FIG. 2. The Néel temperature of chromium-palladium alloys.

TABLE I. The Neél temperature T_N and electrical resistivity coefficient A for dilute chromium-palladium alloys.

c (at.% Pd)	T_N(K)	A (10^{-6}/K^2)	R
0.00	312	−0.128	0.999 94
0.99	306	−0.237	0.999 87
1.48	310	−0.207	0.999 27
1.99	302	−0.296	0.999 75

This resonance model accounts qualitatively for all but the observed rise in T_N again at ~ 1.5 at.%. Such behavior is strikingly similar to that observed in chromium-cobalt alloys, and the same explanation should apply, i.e., we attribute this rise to impurity moments coupling to the host spin-density wave. These moments likely accompany the formation of virtual bound states. Based on his susceptibility investigations, Booth has dismissed the idea of local moments on palladium impurities in chromium. We note, however, that even a small moment could account for the slight rise of T_N from a minimum 306 K at ~ 1.0 at.% to a maximum 310 K at ~ 1.5 at.%—a swing of only 4 K. By comparison the T_N of chromium-cobalt alloys swings some 55 K from a minimum 270 K at ~ 1.5 at.% to a maximum 325 K at ~ 3.1 at.%. According to Shibatani[8] the impurity moment enhancement of T_N for itinerant antiferromagnets goes roughly as $(JS)^2$ where S is the impurity spin and J its coupling strength to the spin-density wave (SDW). From the known cobalt moment in chromium $\sim 2.8\mu_B$,[9] and assuming equal coupling strengths, we would predict a palladium moment $\sim 0.7\mu_B$ based on the swings in T_N. Our estimate is very crude; unequal coupling strengths could easily reduce this value by a factor of 2. Moreover, if, as we believe, the palladium moments result from the population of virtual bound states, T_N could be affected indirectly via exchange splitting of the resonant level. This would shift the Fermi energy of the alloy, with T_N changing accordingly. If anything, then, our analysis probably overestimates the moment size. Given the difficulty in analyzing the high-temperature susceptibility of chromium alloys, it does not seem impossible that impurity moments up to at least several tenths of a Bohr magneton might go unnoticed.

Further information concerning the electronic structure of our alloys can be had from the resistivity data in the paramagnetic regime above T_N. At elevated temperatures, i.e., for $T >> T_N$, it is reasonable to assume that $\rho(T) - \rho_0 = \rho_{e-p}$ results primarily from the $s-d$ type electron-phonon scattering, i.e.,

$$\rho_{e-p}/T = \text{const}(1+6\gamma\alpha T)(1-AT)^2 \ . \tag{2}$$

The quantity $\rho(T)$ is the total electrical resistivity corrected for thermal expansion, α the coefficient of linear thermal expansion, and γ the Grüneisen constant. Aside from thermal expansion effects, the departure of $\rho(T)$ from linearity at high temperatures is determined by A, a quantity whose value is fixed by the electronic band structure of the alloy, and which may be positive or negative. Jones[10] gives for A

$$A = \tfrac{1}{6}\pi^2 k_B^2 \left[3\left(\frac{1}{N_d}\frac{dN_d}{dE} \right)^2 - \frac{1}{N_d}\frac{d^2N_d}{dE^2} \right] \Bigg|_{E=E_F} \ , \tag{3}$$

where k_B is Boltzmann's constant, N_d the density of d-electron states, and E_F the Fermi energy. In our analysis we also have employed an alternate form for A:

$$A = \left[-\frac{eQ}{2T}\frac{1}{N}\frac{dN}{dE} + \frac{6}{\pi^2 k_B^2}\left(\frac{eQ}{2T} \right)^2 + \frac{e}{2T}\frac{dQ}{dE} \right] \Bigg|_{E=E_F} \ , \tag{4}$$

which follows from the well-known theoretical relation between conductivity σ and thermoelectric power Q:

$$Q = \frac{\pi^2 k_B^2 T}{3e}\frac{d}{dE}(\ln\sigma) \Bigg|_{E=E_F} \ . \tag{5}$$

Equation (4) is interesting in that it relates A to another measurable property Q, but its usefulness is limited since thermopower data on alloys are often unavailable.

In Ref. 2, we have shown that, using the first-order approximation for the thermal expansion effects, i.e.,

$$\rho(T) = \rho_{\text{expt}}(T)(1+\alpha T) \ , \tag{6}$$

the following equation is valid:

$$B/T^3 = \text{const}(1/T^2 - A) \ , \tag{7}$$

where

$$B = \frac{\rho_{\text{expt}}(T)(1+\alpha T) - \rho_0}{1+6\alpha\gamma T} \ . \tag{8}$$

This implies that plots of B/T^3 vs $1/T^2$ should be straight lines, from which one could determine the quantity A. In our previous work on the chromium-gold alloys, we found that the straight-line behavior was observed not only in these alloys but also in pure chromium for $T \gtrsim 450$ K. The chromium-palladium alloys behave in a similar fashion for $T \gtrsim 500$ K. Figure 3 shows this behavior for all our alloys. The quantities α and γ needed for the calculations of B were obtained from Refs. 11 and 12, respectively. At lower temperatures deviations from the straight line are observed (not shown in Fig. 3) which result from a precursor effect[13] associated with the onset of antiferromagnetism. A least-squares fit to the data of Fig. 3 gives the values for A listed in Table I. Also tabulated there are the linear correlation coefficients R, from which it is apparent that the data follow closely the straight-line behavior predicted by Eq. (7).

From Table I we see that values of A, as for the chromium-gold system, are negative. The quantity A as a function of palladium concentration is shown in Fig. 4. For the chromium-gold alloys, A decreases linearly with the gold content; in contrast, the plot of A versus palladium content is oscillatory, with A reaching a local maximum at ~ 1.5 at.%. The general behavior of A is consistent with that of T_N noted earlier, suggesting that both anomalies are due to the same underlying mechanism, viz., the formation of virtual bound states accompanied by local moments on the impurity atoms. To our knowledge, the effect on A of impurity moments has never been investigated; the solid line in Fig. 4 is the prediction of Eq. (3) when only resonance scattering is operative. Specifically, we used

$$N_d(E) = N_d^0(E) + \delta N(E) \ , \tag{9}$$

where N_d^0 is the host density of states and δN the change due to alloying. We approximated N_d^0 with

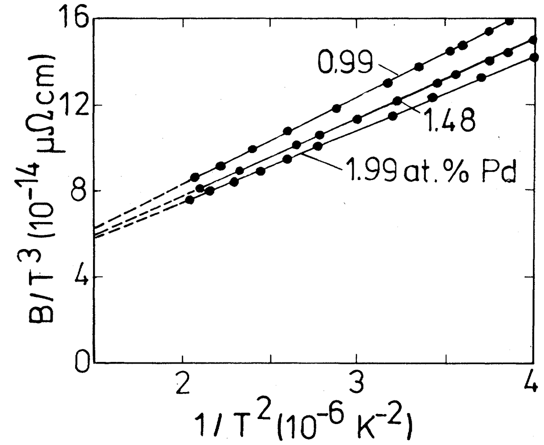

FIG. 3. The quantity B/T^3 as a function of $1/T^2$ of chromium-palladium alloys.

the first three terms in a Taylor expansion around E_F^0, the Fermi energy of unalloyed chromium; for δN we took the form expected near a scattering resonance[14]

$$\delta N(E)=\frac{\delta n_r c}{\pi}\frac{\Gamma/2}{(E-E_r)^2+(\Gamma/2)^2}\ . \qquad (10)$$

E_r and Γ are the position and width of the resonance, respectively, δn_r its degeneracy, and c the solute concentration. The Fermi energy in the alloy E_F was found from

$$N^0(E_F^0)(E_F-E_F^0)=\delta nc+\frac{\delta n_r c}{\pi}\arctan\left[\frac{\Gamma}{2(E_F-E_r)}\right]\ , \qquad (11)$$

which is consistent with the assumed form Eq. (9) for the alloy density of states. Here $\delta n\,(=4)$ is the number of electrons donated to the host per palladium atom. The solid curve of Fig. 4 was generated using the values $E_r-E_F^0=-0.21$ eV, $\Gamma=0.22$ eV, and $\delta n_r=6$ (as befits a d resonance split by the cubic crystalline field of the chromium lattice). The difference between this and the experimental points, then, is the contribution to A from the presumed palladium moments and, again, may reflect some exchange splitting of the resonant level.

The resonance parameters obtained from the data fit in Fig. 4 may not be reliable, since Eq. (3) assumes the energy dependence of $\sigma(E)$ enters solely through the state density N_d. This is not exact and probably exaggerates the variation of A, especially near resonance. In turn, the use of Eq. (3) leads to Γ values which may be too large. To remedy this would require an adequate theory for A in transition-metal alloys, but any such theory must overcome many difficulties, both conceptual and computational. The complexity of the problem is evident from our expression for A in terms of thermopower Q [Eq. (4)]. We need only remark that the thermoelectric power of transition metals and their alloys is, at best, only qualitatively understood at the present time. Nonetheless, Eq. (4) affords an alternative computational method for A if *thermopower data* for the chromium-palladium alloys were available. Alas, this, too, is not the case. However, such data have been reported for chromium and some chromium-ruthenium alloys, thus enabling us to calculate A from Eq. (4) at least for pure chromium.[15] We estimate from the data of Ref. 16, $Q/T\simeq 0.026\ \mu\mathrm{V/K}^2$ and $dQ/dc\simeq -0.877\ \mu\mathrm{V/K\,at.\%}$ at $T=727$ K. Assuming the addition of ruthenium donates two electrons per impurity atom to the Fermi sea, and taking for the chromium density of states $N^0(E_F^0)=1.28/\mathrm{eV}$ atom,[17] we find

$$\frac{1}{T}\frac{dQ}{dE_F}\bigg|_{E_F^0}\simeq -0.077$$

expressed in $\mu\mathrm{V/K}^2$. Even for pure chromium, the slope of the density of states at the Fermi level $dN/dE\big|_{E_F^0}$ is not known accurately. Substituting the above values and the measured value for A from Table I into Eq. (4) gives

$$\frac{1}{N}\frac{dN}{dE}\bigg|_{E_F^0}\sim 7.8$$

in eV^{-1}. This can be compared with rough estimates made from the band-structure calculations of Yasui *et al.*[18]:

$$\frac{1}{N}\frac{dN}{dE}\bigg|_{E_F^0}\sim 1.2$$

again in eV^{-1}. In view of the many approximations involved, the agreement should be considered encouraging.

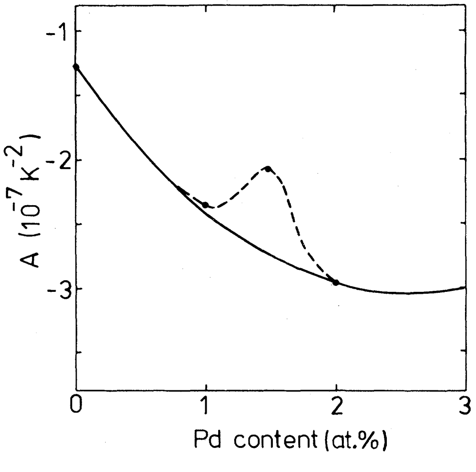

FIG. 4. The quantity A of chromium-palladium alloys. The solid curve is the theoretical prediction of Eq. (3) assuming resonance scattering; experimental values are denoted by ●.

IV. SUMMARY

In summary, we conclude that the high-temperature-resistivity data of our chromium-palladium alloys follow the form expected on the basis of the s-d scattering mechanism. Moreover, the initial-decrease with palladium content of the resistivity temperature coefficient A and the Néel temperature T_N is consistent with the existence of a scattering resonance in the electronic spectrum of these alloys somewhat below the Fermi energy of pure chromium. It is suggested further that the anomalous oscillations of A and T_N with palladium concentration are signatures of the existence of a small magnetic moment on the palladium impurities.

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[1] S. S. Abdul Noor and J. G. Booth, Phys. Lett. A 43, 381 (1973).

[2] A. Eroglu, S. Arajs, C. A. Moyer, and K. V. Rao, Phys. Status Solidi B 87, 287 (1978).

[3] S. Arajs, K. V. Rao, Y. D. Yao, and W. Teoh, Phys. Rev. B 15, 2429 (1977).

[4] S. Arajs, G. R. Dunmyre, and S. J. Dechter, Phys. Rev. 154, 448 (1967).

[5] P. A. Fedders and P. C. Martin, Phys. Rev. 143, 245 (1966).

[6] J. Zittartz, Phys. Rev. 164, 575 (1967).

[7] S. N. Behera and K. S. Viswanathan, Can. J. Phys. 47, 477 (1969).

[8] A. Shibatani, J. Phys. Soc. Jpn. 31, 1642 (1971).

[9] J. G. Booth, J. Phys. Chem. Solids 27, 1639 (1966).

[10] H. Jones, in *Encyclopedia of Physics,* edited by S. Fluge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 227.

[11] *American Institute of Physics Handbook,* 3rd ed. (McGraw-Hill, New York, 1972).

[12] K. A. Gschneidner, Jr., in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1965), Vol. 16, p. 412.

[13] C. H. Chin, M. H. Jericho, and R. H. March, Can. J. Phys. 49, 3010 (1971).

[14] J. Callaway, J. Math. Phys. 5, 783 (1964).

[15] We assume that the main alloy contribution to Q in dilute Cr-Ru alloys results from Fermi-level shifts.

[16] T. F. DeYoung, S. Arajs, and E. E. Anderson, J. Less-Common Met. 29, 93 (1972).

[17] F. Heiniger, E. Bucher, and J. Muller, Phys. Kondens. Mater. 5, 243 (1966).

[18] M. Yasui, E. Hayashi, and M. Shimizu, J. Phys. Soc. Jpn. 29, 1446 (1970).