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Spin-Fluctuation Effects in the Resistivity of Dilute *Pt*Fe Alloys*

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Measurements are presented of the electrical resistivity of a series of dilute *Pt*Fe alloys containing between 0.03- and 1.0-at.% Fe, over the temperature range 0.4 to 50 °K. The alloys containing less than 0.1-at.% Fe have a resistivity which increases approximately logarithmically with increasing temperature, and which scales linearly with concentration. Results are consistent with a spin-fluctuation model for the *Pt*Fe system with a characteristic spin-fluctuation temperature of (0.4 ± 0.2) °K, a value which is supported by recent Mössbauer-effect and thermoelectric-power measurements. The effect of interactions on the resistivities of the more concentrated alloys is discussed, and a simple phase-shift calculation is presented which relates the temperature dependence of the non-spin-flip scattering to the temperature dependence of the impurity magnetic moment, and which accounts qualitatively for the sign of the temperature coefficient in the resistivities of the *Pt*Fe and other Pt- and Pd-based alloys.

I. INTRODUCTION

Experimental investigations of alloys of second- or third-row transition-metal hosts containing low concentrations of first-row transition-metal impurities have revealed two more or less distinct types of behavior. In one category there are those systems which exhibit well-defined impurity moments, and which undergo magnetic ordering at low temperatures. These alloys, of which *Pd*Fe[1] and *Mo*Fe[2] are typical examples, exhibit a negative magnetoresistance[2,3] and magnetization curves which may be expressed (in the low-concentration limit) as a simple function of H/T[4] (where H is the applied magnetic field and T is the temperature). The second group, exemplified by the *Rh*Fe system, does not exhibit free-spin behavior in a magnetic field, and in fact has an effective moment per impurity which decreases at low temperatures.[5] The magnetoresistance is positive,[6] and low-temperature magnetic ordering does not occur. A distinctive feature of *Rh*Fe and related systems is an impurity resistivity which increases with increasing temperature.[6]

Previous investigations have shown that *Pt*Fe exhibits many of the characteristics of the first groups of systems, namely, a well-defined impurity moment of the order of $6\mu_B$,[1] ferromagnetic ordering at a relatively low Fe concentration,[1] and a negative contribution to the magnetoresistance which can be expressed as a simple function of H/T.[7] However, the resistivity of *Pt*Fe, which is the subject of the present investigation, is shown to have a temperature dependence which resembles that of *Rh*Fe, and the effect of interactions on the resistivities of more concentrated alloys is considerably more complicated than that observed in, for example, *Pd*Fe[8] and exhibits certain features which more closely resemble the effect of interactions in *Rh*Fe.[9] These results suggest that the distinction between the two categories may be less well defined than has been assumed hitherto. The resistivity and other properties of the *Pt*Fe system will be discussed in the light of recent theories.

II. EXPERIMENTAL DETAILS

The alloys were prepared by melting appropriate amounts of pure Pt and a Pt-5-at.% Fe master alloy in a copper-boat levitation furnace. The samples were inverted and remelted several times to ensure homogeneity. The metals used were 99.999% pure Pt, obtained from Metals Research Co., Cambridge, England, and 99.9% pure Fe, obtained from Johnson Matthey and Co. The alloys were etched and rolled into strips approximately 0.01 cm thick, 0.2 cm wide, and 8 cm long. The specimens were then given an homogenizing anneal at 1400 °K for 24 h, and rapidly quenched in water, to reduce the possibility of clustering. The geometrical factor (length/area) of the specimens was determined with an uncertainty of approximately ±0.3% using a technique described previously.[10] Resistivity measurements on a pure-Pt sample and on six *Pt*Fe alloys containing between 0.03- and 1-at.% Fe were made in the temperature range 0.4 to 300 °K, using a standard four-terminal potentiometric technique and a He_3 cryostat, details of which have been described elsewhere.[10] The Fe concentrations in each of the specimens, as determined by chemical analysis, are presented in Table I.

III. RESULTS

The pure-platinum sample used in the present investigations has an ice-point resistivity of 9.95 μΩ cm and a resistivity ratio of 780. At temperatures below 15 °K the resistivity is well described by the expression

$$\rho_{\mathrm{Pt}}(T)=A+BT^2+DT^5 ,$$

where $A=0.0128$ μΩ cm, $B=(1.6\pm0.2)\times10^{-5}$ μΩ cm $°K^{-2}$, and $D=(1.4\pm0.2)\times10^{-8}$ μΩ cm $°K^{-5}$. These values are in fair agreement with the values $B=1.4\times10^{-5}$ μΩ cm $°K^{-2}$ and $D=1.1\times10^{-8}$ μΩ cm $°K^{-5}$ found by White and Woods.[11]

In Fig. 1 the excess resistivity $\Delta\rho=\rho_{\mathrm{alloy}}(T)-\rho_{\mathrm{Pt}}(T)$ is plotted against temperature up to 50 °K, while in Figs. 2 and 3 the excess resistivity per atomic percent of Fe, $\Delta\rho/c$, is plotted against T up to 12 °K and against $\log_{10}T$ up to 20 °K. These figures reveal two distinct contributions to the temperature-dependent resistivity. Below 8 °K the temperature dependence is dominated by Fe-impurity scattering. The rapid increase in the excess resistivity at higher temperatures is almost certainly a deviation from Matthiessen's rule, $\Delta(T)$, of the kind frequently observed in dilute nonmagnetic alloys.[12] These two contributions may be fairly readily distinguished because of the very rapid dependence of $\Delta(T)$ compared with the relatively weak temperature dependence of the impurity scattering.

Below 8 °K, the impurity resistivity of the three most dilute alloys varies approximately logarithmically with temperature and scales linearly with concentration (Fig. 3), this latter result demonstrating conclusively that the temperature dependence is not a result of interactions between impurities but reflects a temperature-dependent scattering of the conduction electrons from isolated impurities.

The expression

$$\Delta\rho=E+F\ln(T^2+\theta^2)^{1/2}+\Delta(T) ,$$

with $\Delta(T)=GT^5$, provides a good description of the resistivities of all but the 1-at.% alloy, at temperatures below 15 °K. The full lines in Figs. 2 and 3 represent the function

$$\Delta\rho=E+F\ln(T^2+\theta^2)^{1/2} \tag{1}$$

and the dashed lines at temperatures above 8 °K represent the same function plus the extra term GT^5. Values of the coefficients E, F, θ, and G, together with the nominal and chemically analyzed Fe concentrations, are presented in Table I.

IV. DISCUSSION

A. Deviation from Matthiessen's Rule

We shall first discuss the initial temperature dependence of the term $\Delta(T)$, which we ascribe to a deviation from Matthiessen's rule. As indicated in Figs. 2 and 3, a term proportional to T^5 provides a good fit to the results up to about 13 °K in the most dilute alloys, and up to 20 °K in the 1-at.% alloy. Attempts to fit the results to a term proportional to T^3, as recently predicted by Campbell, Caplin, and Rizzuto,[13] and by Mills,[14] were not successful. The deviation was also not simply proportional to ρ_{Pt} (which contains a large T^2 term), and no evidence was found for a contribu-

TABLE I. Nominal and chemically analyzed Fe concentrations and values of the coefficients E/c, F/c, θ, and G/D deduced from the resistivities of the *Pt*Fe alloys (where $D=1.4\times10^{-8}$ μΩ cm/$°K^{-5}$ is the coefficient of the T^5 term in the pure-Pt resistivity and c is the analyzed Fe concentration).

Nominal Fe concentration (at.%)	Analyzed Fe concentration (at.%)	E/c (μΩ cm/at.%)	F/c (μΩ cm/at.%)	θ (°K)	G/D
0.03	0.031	3.06	0.020 ± 0.003	0.4 ± 0.2	0.31
0.05	0.051	3.14	0.021 ± 0.003	0.4 ± 0.2	0.45
0.10	0.12	3.18	0.018 ± 0.003	0.4 ± 0.2	0.57
0.3	0.30	3.12	0.018 ± 0.003	1.6 ± 0.3	0.56
0.6	0.59	3.24	0.021 ± 0.003	3.0 ± 0.3	0.54
1.0	1.02	...	...	...	0.41

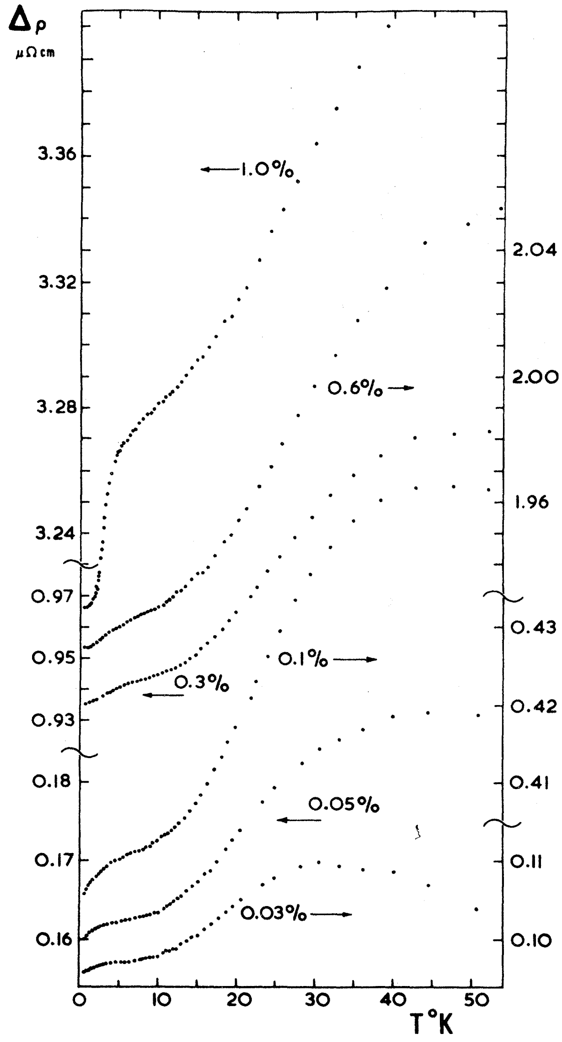

FIG. 1. Excess resistivity Δρ plotted against temperature T for the *Pt*Fe alloys. The nominal Fe concentrations are indicated in the figure in at.%.

tion proportional to T^2 which might have resulted from a modification of the paramagnon scattering of the host. The coefficient G of the T^5 term is approximately independent of the concentration (Table I) and is about half the magnitude of the T^5 term in the pure-Pt resistivity. The deviation can, therefore, be ascribed, possibly, to the differing anisotropies of the impurity and phonon scattering, as originally proposed by Kohler,[15] who predicts a deviation independent of concentration and proportional to the phonon resistivity at sufficiently low temperatures.

B. Impurity Resistivity of Alloys with Concentration ≤ 0.1-at.% Fe

At temperatures below 8 °K, $\Delta(T)$ is negligible, and the resistivity is determined simply by impurity scattering. As described above, the resistivities of the three most dilute alloys have an identical temperature dependence [identical values of θ and F/c in Eq. (1) within experimental error], and this implies a temperature-dependent scattering of conduction electrons from noninteracting Fe impurities. A positive temperature coefficient has been observed in the impurity resistivities of several alloys of first-row transition-metal elements dissolved in hosts taken from the second and third transition series, e.g., *Rh*Fe,[2,16,17] *Rh*Mn,[16] *Rh*Co,[16,18] *Pt*Co,[19] *Pd*Co,[20] *Ir*Fe,[21] *Pd*Ni,[22] and *Pt*Ni,[23] and it is tempting to assume that the origin of the temperature dependence is common to each of these systems. A comparison of some other properties of *Pt*Fe and these systems is therefore of interest. Magnetic-susceptibility measurements to very low temperatures on very dilute *Pt*Fe are not available, but Mössbauer-effect measurements down to 0.3 °K by Maley *et al.*[24] reveal significant deviations from free-spin behavior at temperatures below 1 °K. Above 1.5 °K free-spin behavior is observed (Mössbauer splitting[24] and NMR[25] are simple functions of H/T). While the low-temperature deviations could result from

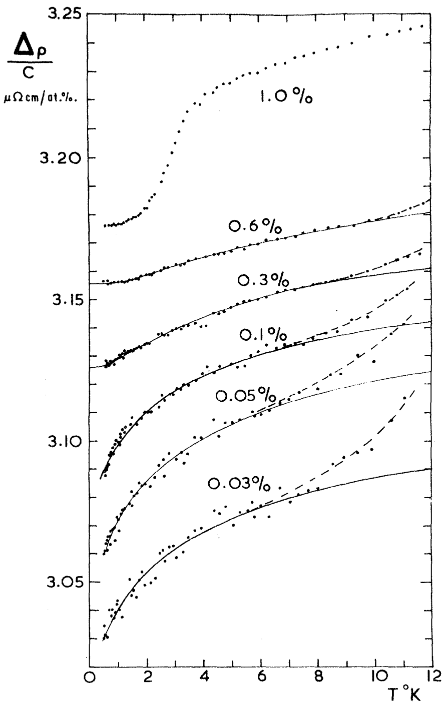

FIG. 2. Excess resistivity per atomic percent $\Delta\rho/c$ plotted against T. The ordinate scale refers to the 0.3-at.%-Fe alloy. Small vertical displacements have been applied to the other curves for clarity. The full lines represent Eq. (1) with values of E, F, and θ given in Table I. The broken lines include the additional term GT^5.

antiferromagnetic exchange interactions between Fe spins, the very low Fe concentration and the observation that the deviations are independent of concentration make this interpretation unlikely. Thus Mössbauer-effect measurements[24] are consistent with a gradual transition of the Fe atoms in Pt to a nonmagnetic state as the temperature falls below $\theta_{\rm MB} \sim 0.5\,^\circ$K, behavior which is similar to that observed in *Rh*Fe,[26] though in that system the characteristic temperature $\theta_{\rm MB} \sim 20\,^\circ$K.

Measurements by MacDonald[27] show that the thermoelectric power of a very dilute *Pt*Fe alloy exhibits a negative peak of approximately $-1\ \mu V/^\circ$K in the neighborhood of 1 °K. While this is an order of magnitude smaller than the "giant" thermopower observed in *Au*Fe alloys,[27] it is still very large compared with the thermopower of "normal" systems, and reflects an anomalously strong energy-dependent scattering of conduction electrons within an energy range of the order of 1 °K of the Fermi energy. The thermopower measurements can be represented approximately by the expression $S \sim -T/(T+\theta_s)$, where $\theta_s \sim 0.3\,^\circ$K is comparable with the value $\theta = 0.4\,^\circ$K obtained from the present resistivity measurements and the temperature $\theta_{\rm MB} \sim 0.5\,^\circ$K which characterizes the disappearance of a moment in Mössbauer measurements.

Measurements of the resistivity of a Pt-0.05-at.% Fe alloy[7] in an applied magnetic field and at temperatures above 1.5 °K reveal a large negative contribution to the magnetoresistance (after correction has been made for a positive Kohler[28] term) which is a simple function of H/T, and which is well described by the s-d model.[29] Thus it is consistent with the free-spin behavior observed in the Mössbauer splitting[24] and NMR[25] at a comparable temperature. Free-spin behavior of the magnetoresistance has also been observed in the *Pd*Co system,[3] which has a temperature-dependent resistivity[20] in zero applied field which is very similar to that of *Pt*Fe. *Rh*Fe[5] and *Pt*Co,[25] on the other hand, show a strongly reduced moment in the liquid-helium temperature range, and a *positive* magnetoresistance which cannot be expressed as a simple function of H/T.[30]

Several suggestions have been advanced to account for the positive logarithmic temperature dependence of the resistivity in *Rh*Fe and related systems, and we will consider these in relation to the *Pt*Fe system:

(a) Kondo[31] has shown that the spin resistivity in zero applied magnetic field, calculated to third order in the s-d exchange-coupling constant J, can be expressed as

$$\rho_{\rm spin} = AcJ^2 S(S+1)\,[1 - 4Jn(E_F)\ln(D/kT)]\ ,$$

where D is an energy of the order of the bandwidth and $n(E_F)$ is the density of conduction-electron states at the Fermi energy E_F. Using Yosida's result[29] that the decrease in resistance $\Delta\rho'$ in an applied magnetic field, for $g\mu_B H \gg kT$, is given to second order in J by $\Delta\rho' = AcJ^2(4S^2+S)$, we may deduce values of J and $n(E_F)$ using $S = 2.3$[7] and the values of $\Delta\rho'$ determined by magnetoresistance measurements on a Pt-0.05-at.% Fe alloy with $A = 9.23$ $\mu\Omega$ cm/at.% eV^2.[7] On these assumptions we find $J = +0.041$ eV, and $n(E_F) = 1.0$/eV atom. This value for $n(E_F)$ is four times larger than the density of states of the s band (assuming this to be parabolic with effective mass $m^*/m = 2.8$[32]) and is comparable with the value of 1.4/eV atom for the total density of states deduced from the electronic specific heat. The complexity of the band structure of Pt[32,33] does, however, throw some doubt on the

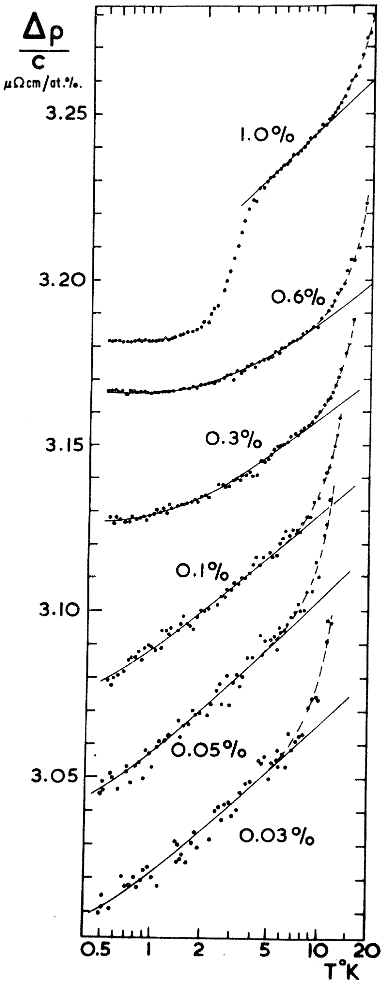

FIG. 3. Excess resistivity per atomic percent $\Delta\rho/c$ plotted against $\log_{10}T$. The ordinate scale refers to the 0.3-at.%-Fe alloy. Small vertical displacements have been applied to the other curves. The full lines represent Eq. (1) with values of E, F, and θ given in Table I. The broken lines include the additional term GT^5.

significance of these numerical estimates. It should also be pointed out that the decrease in moment observed in Mössbauer experiments and the large peak in the thermopower in the neighborhood of 1 °K would not be expected to result from a Kondo scattering with positive J.[34]

(b) Several authors[35] have demonstrated that the inclusion of a potential phase shift δ modifies the coefficient of the $\ln T$ term in the s-d expression for the resistivity by a factor $\cos 2\delta$. Thus, if $\delta > \frac{1}{4}\pi$, a positive logarithmic temperature dependence is predicted when J is negative. The decrease in moment at low temperatures in *Pt*Fe[24] and the peak in the thermopower[27] may then be associated with a spin compensation of the Fe spins by the conduction electrons with a Kondo temperature $T_K \sim 0.4$ °K. However, since the valence difference Z of solvent and solute in systems which exhibit a positive temperature coefficient never appears to exceed 2, we would expect the potential phase shift to be small in such systems. This is substantiated by their low residual resistivities which increase with increasing valence difference in Pd-, Pt-, and Rh-based alloys. We therefore reject this explanation.

(c) Knapp[36] has suggested a two-band model, in which s electrons are scattered from localized moments which are progressively compensated (as the temperature decreases) by electrons in the d band (which are assumed to make no contribution to the conductivity). This explanation can also be rejected as it would not yield a large anomaly in the thermoelectric power. The s-electron scattering, although strongly *temperature* dependent, would not be an assymetric function of *energy* in the vicinity of the Fermi surface, a condition which is a prerequisite for a large low-temperature thermopower.[37] It would also be difficult to explain the variation of residual resistivity with valence difference Z on this model as the excess charges are assumed to be screened by electrons which do not contribute to the conductivity.

(d) Following the success of Lederer and Mills's two-band model[38] of s-electron scattering from exchange-enhanced localized spin fluctuations on impurity sites in explaining the initial T^2 dependence of the resistivity of *Pd*Ni alloys, Kaiser and Doniach[39] have extended their theory to higher temperatures. They find that at low temperatures the resistivity varies as $(T/T_s)^2$, where T_s is a characteristic spin-fluctuation temperature given approximately by $kT_s \sim E_F/\alpha(T)$ and $\alpha(T)$ is the exchange-enhancement factor on the impurity sites. For $T \gg T_s$, the resistance varies as (T/T_s). Taking into account the temperature dependence of $\alpha(T)$, the universal curve predicted by Kaiser and Doniach closely resembles Eq. (1) over a wide range of temperatures, with θ replaced by T_s. With a suitable choice of T_s, excellent agreement with the observed resistivities of several systems has been obtained,[39] and the present results may be accounted for if we take $T_s = 0.4$ °K for the *Pt*Fe system.

The use of the random-phase approximation to calculate α leads to the prediction that $\alpha \to \infty$ (i.e., T_s and the spin-fluctuation rate tend to zero) at the Hartree-Foch magnetic instability.[39] The very large values of α required to yield the estimated values of T_s ($\alpha \sim 1000$ for $T_s \sim 1$ °K) imply that a surprisingly large number of magnetic impurities in Pt, Pd, and Rh are extremely close to this instability condition. This difficulty may perhaps be avoided if electron-hole correlations[40] and vertex renormalization[41] are taken into account. Schrieffer and Mattis[40] have, in fact, shown that the local enhancement factor can only become infinite if the Coulomb repulsion U between electrons of opposite spin on the impurity site tends to infinity. Hamann[42] has also shown on a rather different model that the spin-fluctuation temperature only tends to zero in the limit as $U \to \infty$. Thus the observed range of values for T_s may reflect a much wider range of parameters (U and local susceptibility) than is suggested by the Hartree-Foch theory.

The theory also suggests that the susceptibility is (exchange-enhanced) Pauli-like at all temperatures. Writing the susceptibility per impurity for $T > T_s$ as $\langle m^2 \rangle / 3kT$, where $\langle m^2 \rangle$ is the mean-square spin of the impurity, it is evident that $\langle m^2 \rangle \propto T$ if the susceptibility is temperature independent. While this behavior is observed at low temperatures,[5,43] $\langle m^2 \rangle^{1/2}$ cannot be expected to increase indefinitely with increasing temperature, but must tend to a constant value of the order of the moment expected if Hund's rule were obeyed. Thus at sufficiently high temperatures the susceptibility of a system of fluctuating moments must become increasingly Curie-like. This is reflected in the Kaiser and Doniach theory[39] by the decrease in $\alpha(T)$ at high temperatures. It may be conjectured that the s-d model for the resistivity will also be appropriate in this high-temperature region. Thus the observation of a large *negative* magnetoresistance in the systems *Pt*Fe[7] and *Pd*Co,[3] which can be expressed as a simple function of H/T for $T > 1.5$ °K, and which is well described by the s-d model, may simply reflect the fact that $\langle m^2 \rangle^{1/2}$ has reached an essentially temperature-independent plateau[24] (i.e., $T \gg T_s$). In *Rh*Fe[5] and *Pt*Co,[25] $\langle m^2 \rangle^{1/2}$ at 1.5 °K is substantially below the high-temperature plateau, and a positive magnetoresistance is observed.[6]

Spin fluctuations in magnetic impurities have been approached from somewhat different directions by several authors,[42,44-48] who have shown that the transition (as a function of U and T) from the nonmagnetic to the magnetic state is a gradual one, with a susceptibility that is constant for $T \ll T_s$[45,47] and Curie-like for $T \gg T_s$.[45,47,48] Where the resistivity has been calculated,[44-47] this is generally found to increase towards the unitarity limit with decreasing temperature, which is not in agreement with the present results.

We may correlate, in a simple phenomenological manner, the temperature dependences of the resistivity and of the effective moment on the impurity by a phase-shift calculation, if we assume that the conductivity and the charge screening take place within a common band, and if we also assume that the number of electrons of up and down spin on the impurity are related to the electron phase shifts by the Friedel sum rule.[49] For simplicity, we will assume a free-electron model, in which the excess charge Z is screened entirely by $l=2$ partial waves, i.e., phase shifts $\delta_l = 0$ unless $l=2$. If $\delta_\uparrow$ and $\delta_\downarrow$ are the $l=2$ phase shifts for the electrons at the Fermi surface of spin parallel and antiparallel to an impurity of excess charge Z and spin m, then the Friedel sum rule[49] yields for the excess number of up-spin electrons on the impurity site $\frac{1}{2}Z + m = (5/\pi)\delta_\uparrow$ and for the excess number of down spins yields $\frac{1}{2}Z - m = (5/\pi)\delta_\downarrow$. The cross section for non-spin-flip scattering of up-spin electrons is thus

$$\sigma_\uparrow = \frac{20\pi}{k_F^2}\sin^2\delta_\uparrow = \frac{20\pi}{k_F^2}\sin^2 \tfrac{1}{5}\pi\left(\tfrac{1}{2}Z + m\right). \qquad (2)$$

If we average this cross section over all possible magnitudes of the spin m, we have

$$\begin{aligned}\sigma_\uparrow &= \frac{20\pi}{k_F^2}\sum_m P(m)\sin^2\tfrac{1}{5}\pi\left(\tfrac{1}{2}Z+m\right)\\ &= \frac{20\pi}{k_F^2}\Big[\sin^2\tfrac{1}{10}\pi Z + \cos\tfrac{1}{5}\pi Z\sum_m P(m)\sin^2\tfrac{1}{5}\pi m\\ &\qquad + \tfrac{1}{2}\sin\tfrac{1}{5}\pi Z\sum_m P(m)\sin\tfrac{2}{5}\pi m\Big]\,, \qquad (3)\end{aligned}$$

where $P(m)$ represents the probability that the impurity has a spin m during the very short time ($\sim 10^{-15}$ sec) that the scattering takes place. For a system of fluctuating moments, $P(m)$ will be a continuous function of m and may be temperature dependent. $P(m)$ will also be symmetric about $m=0$ in the absence of an applied magnetic field H and, therefore, in this case the last term in Eq. (3) will be zero. An identical expression is then obtained for $\sigma_\downarrow$.

Equation (2) shows that the scattering cross section contains a term proportional to $\langle m^2\rangle$, provided $\langle m^2\rangle^{1/2} \ll \frac{5}{2}$, where $\langle m^2\rangle = \sum_m P(m)\,m^2$ is the mean-square spin on the impurity site. This result is in agreement with a many-body calculation of the scattering cross section integrated over all frequencies of the fluctuations of the system.[50] At temperatures high compared with the characteristic energy of these fluctuations (i.e., $T \gg T_{\mathrm{SF}}$) the mean-square spin is related to the impurity susceptibility $\Delta\chi(T)$ by $\langle m^2\rangle \sim 3k_B T\Delta\chi(T)$. Fluctuations of the spin system persist at $T=0$, and a simple application of the fluctuation-dissipation theorem[50] and assuming the spectral density function derived by Kaiser and Doniach,[39] show that $\langle m^2\rangle \sim 3k_B T_{\mathrm{SF}} \times \Delta\chi(0)$ in this limit. However, in a scattering process, only fluctuations of energy less than of the order of kT may be absorbed from the impurity, and for the case of an electron at the Fermi surface, the Pauli exclusion principle prevents the emission of fluctuations of energy greater than kT (due to absence of available final states for the electron[39]). Thus only thermally excited fluctuations contribute to the scattering of an electron, and as these tend to zero at very low temperatures, the impurity scatters as if it were nonmagnetic, i.e., $\delta_\uparrow$ and $\delta_\downarrow$ are equal, in the limit $T \to 0$. The situation is entirely analogous to the scattering of electrons by thermally excited phonons—the density fluctuations in the crystal which persist at $T=0$ making no contribution to the resistivity. The scattering of a beam of neutrons, on the other hand, in which the Pauli exclusion principle plays no role, is affected by the entire spectrum of fluctuations at $T=0$ in both the phonon and impurity problems.

In order to calculate the resistivity, we may take account of the effects of the exclusion principle described above, if we replace $P(m)$ by $P(m)_{\mathrm{th}}$, a probability density of thermally excited fluctuations. The resistivity may then be written

$$\Delta\rho(T) = 5c\rho'\left[\sin^2\tfrac{1}{10}\pi Z + \cos\tfrac{1}{5}\pi Z\textstyle\sum_m P(m)_{\mathrm{th}}\sin^2\tfrac{1}{5}\pi m\right], \qquad (4)$$

where ρ' is the unitarity limit for s-wave scattering.

At $T=0$, $P(m)_{\mathrm{th}} = 0$ unless $m=0$, and we have

$$\Delta\rho(0) = 5c\rho'\sin^2\tfrac{1}{10}\pi Z\,. \qquad (5)$$

In the low-temperature region $T \ll T_{\mathrm{SF}}$ we find

$$\Delta\rho(T) = \Delta\rho(0) + \frac{\pi^2}{5}c\rho'\cos\tfrac{1}{5}\pi Z\,\langle m^2\rangle_{\mathrm{th}}\,,$$

where $\langle m^2\rangle_{\mathrm{th}}$ is the mean-square thermally excited spin per impurity. Assuming that the spectral density function is linear in frequency at low frequency,[39] $\langle m^2\rangle_{\mathrm{th}}$ is of the order of $\langle m^2\rangle\,(T/T_{\mathrm{SF}})^2 \sim \Delta\chi(T)\,T^2/T_{\mathrm{SF}}$. Since the susceptibility tends to a constant as $T \to 0$, the resistivity is proportional to T^2 for $T \ll T_{\mathrm{SF}}$ as found by Lederer and Mills.[38] Finally, at high temperatures $T \gg T_{\mathrm{SF}}$, when all the fluctuations may be considered to be thermally excited, $\langle m^2\rangle_{\mathrm{th}} \to \langle m^2\rangle \sim kT\Delta\chi(T)$, and thus in this region a resistivity proportional to $T\Delta\chi$ is predicted, in agreement with the conclusion of Kaiser and Doniach,[39] provided $\langle m^2\rangle^{1/2} \ll \frac{5}{2}$. If this latter condition is not satisfied, the more general expression Eq. (4) is required. For the purposes of comparison with experiment, we will assume that at sufficiently high temperatures $T \gg T_{\text{SF}}$, Eq. (4) may be written

$$\Delta\rho(T \gg T_s) = \Delta\rho(0) + 5c\rho' \cos(\tfrac{1}{5}\pi Z)\sin^2(\tfrac{1}{5}\pi S) , \qquad (6)$$

where S is of the order of the impurity spin deduced from high-temperature susceptibility measurements. As the temperature increases from $T=0$, the resistivity should vary monotonically between $\Delta\rho(0)$ at $T=0$ and $\Delta\rho(T \gg T_s)$ at high temperatures. The sign of the temperature coefficient is determined by the sign of the term $\cos(\frac{1}{5}\pi Z)$ and is positive for $Z < \frac{5}{2}$ or $> \frac{15}{2}$ and is negative within the range $\frac{5}{2} < Z < \frac{15}{2}$.

Equations (5) and (6) may easily be modified to include phase shifts other than δ_2. Using the free-electron expression for the resistivity[51]

$$\Delta\rho = c\rho' \textstyle\sum_l (l+1)\sin^2(\delta_{l+1} - \delta_l)$$

and assuming $\delta_l = 0$ for $l > 2$, we have

$$\Delta\rho(0) = c\rho'[\sin^2 \tfrac{1}{2}\pi(\tfrac{1}{3}Z_1 - Z_0) + 2\sin^2 \tfrac{1}{2}\pi(\tfrac{1}{5}Z_2 - \tfrac{1}{3}Z_1) + 3\sin^2(\tfrac{1}{10}\pi Z_2)] \qquad (7)$$

and

$$\Delta\rho(T) \gg T_s) = \Delta\rho(0) + c\rho' \sin^2(\tfrac{1}{5}\pi S)[2\cos\pi(\tfrac{1}{5}Z_2 - \tfrac{1}{3}Z_1) + 3\cos(\tfrac{1}{5}\pi Z_2)] , \qquad (8)$$

where

$$Z_0 = \frac{2}{\pi}\delta_0 , \quad Z_1 = \frac{6}{\pi}\delta_1 , \quad \text{and} \quad Z_2 = \frac{5}{\pi}(\delta_{,} + \delta)$$

are the number of excess charges screened by s, p, and d partial waves, respectively, and $Z = Z_0 + Z_1 + Z_2$.

In Fig. 4 the impurity resistivities at fixed temperatures for impurities in Pt and Pd are plotted against Z. These values serve to indicate the magnitudes of the resistivities and their temperature coefficients, but only in some cases do they approximate to the resistivities in the limits $T \ll T_s$ or $T \gg T_s$. The continuous curves represent Eqs. (5) and (6) with $\rho' = 1$ $\mu\Omega$ cm/at.% and $S = \frac{1}{2} + \frac{1}{2}|Z|$. This corresponds to spin values of $\frac{1}{2}$, 1, $\frac{3}{2}$, 2, and $\frac{5}{2}$ for Ni, Co, Fe, Mn, and Cr impurities, respectively, in approximate agreement with high-temperature spin values deduced from neutron-scattering measurements in *Pd*Co[52] and *Pd*Fe[53] and susceptibility measurements in *Pd*Mn.[54] (We assume that similar values for S obtain for Pt-based alloys.) On this simple model, a positive temperature coefficient is predicted for $|Z| < \frac{5}{2}$ in agreement with that observed in Pd and Pt containing Ni and Co, and in the present *Pt*Fe system. A negative temperature coefficient is predicted, and observed, in Pd and Pt containing Cr.[55] No temperature dependence in the paramagnetic region has been reported in *Pd*Fe [8] or *Pd*Mn,[54] but this may reflect the fact that the characteristic temperature T_s for a transition from the nonmagnetic to magnetic state is extremely low in these systems. Since well-defined moments are observed in each case, the resistivities should correspond to the "high-temperature" curve $\Delta\rho(T \gg T_s)$. The model also predicts that the step height $\Delta\rho(T \gg T_s) - \Delta\rho(0)$ has a maximum positive value for Co impurities, and a maximum negative value for Cr impurities. The step height is expected to be rather small in alloys containing Ni, Fe, or Mn. These conclusions are in general agreement with available experimental evidence.

It is commonly assumed that a two-band model is appropriate to Pd and Pt alloys, in which the current is carried by the s electrons and the charge screening is confined to the d band. It is, therefore, necessary to justify the present assumption that conduction and screening take place, at least to some extent, within a common band. The large s-electron effective mass and low Fermi velocity deduced from band-structure calculations of Pt[32,33]

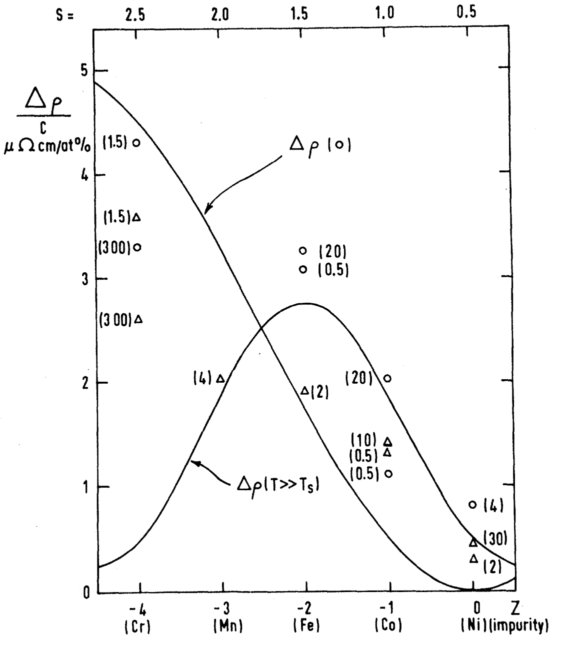

FIG. 4. Values of the excess resistivities per at.% ($\Delta\rho/c$ $\mu\Omega$ cm/at.%) of first-row transition-metal impurities in Pd(Δ) and Pt (○) at fixed temperatures (shown in brackets in °K for each system). The curves $\Delta\rho(0)$ and $\Delta\rho(T \gg T_s)$ [given by Eqs. (5) and (6)] represent an approximate estimate of the resistivities on a simple phase-shift model at $T=0$ and at very high temperatures, respectively. We have taken $\rho' = 1$ $\mu\Omega$ cm/at.% and the values of S for each alloy are given in the figure.

(which results from strong s-d hybridization) and the anomalously low Hall coefficient in Pt[56] suggest that, in this metal at least, a substantial fraction of the current is carried by d-band holes. This is also probably true, though to a lesser extent, in Pd alloys.[32,33,57] Furthermore, the observed variation of residual resistivity with Z provides strong evidence that charge screening and conductivity are provided (at least partially) by a common band, since if the two-band model were strictly valid, the residual resistivity would be approximately independent of Z. It seems likely that the true situation lies somewhere between the two extremes of a single-band and two-band model, and the rather low value of ρ' required to simulate the experimental results suggests that the s electrons do, to some extent, "short out" the resistivity of the d band. An improved fit to the results shown in Fig. 4 can be obtained using Eqs. (7) and (8), with plausible values of Z_0 and Z_1, and in particular, the inclusion of phase shifts other than δ_2 can readily account for the finite resistivity at $T = 0$ of the isoelectronic systems *Pt*Ni and *Pd*Ni. However, uncertainties resulting from the two-band character of the Pd and Pt hosts render such a refinement inappropriate. Examination of Eq. (8) shows that the value of Z at which the temperature coefficient changes from positive to negative is not substantially affected by the inclusion of these other phase shifts, and this almost certainly lies in the range $2 < | Z | < 3$.

Although they did not include potential scattering in their theory, Kaiser and Doniach emphasize[39] that the negative temperature coefficient of the impurity resistivity in systems such as *Al*Mn could be accounted for by their theory if resonant potential scattering were included. Coles *et al.*[16] have also suggested that resonant potential scattering could explain the small negative temperature coefficient which they observe in the *Rh*Cr system, in contrast to the positive temperature coefficient observed in Rh containing Co, Fe, and Mn, in which the potential phase shift is smaller. Examination of Fig. 5, in which Coles's Rh-based data[16] are compared with Eqs. (7) and (8), shows that their suggestion is substantiated by the present model. The curves $\Delta\rho(0)$ and $\Delta\rho(T \gg T_s)$ have been calculated assuming $\rho' = 1.4$ $\mu\Omega$ cm/at.% and $Z_0 + Z_1 = -0.3$. We have also assumed $\delta_0 = 2\delta_1$, following Blatts's calculation for normal-metal alloys.[58] The variation with Z of the resistivity of $T = 0$ and the signs and magnitudes of the temperature coefficients are in rather good agreement with the predictions of the model.

C. Impurity Resistivity of Alloys with Concentration between 0.1- and 1-at.% Fe

We will now discuss the resistivities of the more concentrated *Pt*Fe alloys. The resistivities of the 0.3 and 0.6 at.% alloys may be described by Eq. (1) (see Figs. 2 and 3) with values of F/c which are comparable with those of the more dilute alloys, and values of θ which increase approximately linearly with concentration (Table I). The behavior of the 1-at.% alloy is strikingly different from that of the other alloys, exhibiting a pronounced change of slope at 4 °K and a substantial reduction of the resistance at lower temperatures. This behavior is strongly suggestive of magnetic ordering of the kind observed in *Pd*Fe[8] alloys, though the transition temperature (4 °K) is an order of magnitude lower than that observed in *Pd*Fe alloys of a comparable concentration.[8] The nature of the ordered state (ferromagnetic or antiferromagnetic) may be inferred rather directly from a comparison of the decrease in resistance on ordering in internal magnetic fields and the decrease on ordering in a large applied magnetic field. If the ordered state is ferromagnetic, the change in resistance should be the same,[29] but if the ordering is antiferromagnetic, the change in resistance is reduced, according to the s-d model, by a factor of $4S + 1$.[29] Magnetoresistance measurements on a Pt-0.05-at.% Fe alloy[7] show that the resistance decreases with complete spin alignment by 0.36 $\mu\Omega$ cm/at.%, and a comparable decrease (per at.%) would be expected to result for complete ferromagnetic alignment in the 1-at.% alloy. In fact a decrease of only 0.045 $\mu\Omega$ cm/at.% between T_c (4 °K) and $T = 0$ is observed in this

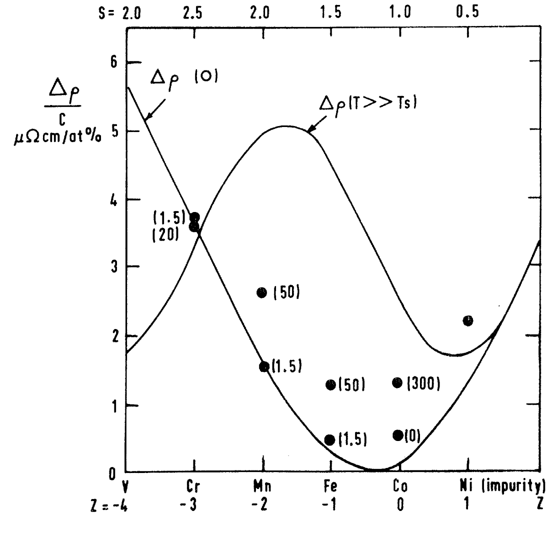

FIG. 5. Values of the excess resistivities per at.% ($\Delta\rho/c$ $\mu\Omega$ cm/at.%) of first-row transition-metal impurities in Rh as determined by Coles *et al.* (Ref. 16) taken at fixed temperatures (shown in brackets in °K for each system). The curves $\Delta\rho(0)$ and $\Delta\rho(T \gg T_s)$ represent Eqs. (7) and (8), respectively, with $\rho' = 1.4$ $\mu\Omega$ cm/at.% and $Z_0 + Z_1 = -0.3$. The values of S appropriate to the curve $\Delta\rho(T \gg T_s)$ are shown at the top of the figure.

alloy (Figs. 1–3). Using the spin value $S = 2.3$ deduced from magnetoresistance measurements[7] we would expect on the basis of the *s-d* model a decrease in resistance of 0.036 $\mu\Omega$ cm/at.% if the ordering were entirely antiferromagnetic. A simple analysis shows that the measured step heights are consistent with approximately 65% of the Fe spins parallel and 35% antiparallel in the ordered state. A similar effect has been observed in Pd–0.1-at.% Fe and Pd–0.1-at.% Co alloys,[3] in which a significant number of the spins are aligned antiferromagnetically in the ordered state. Pd containing 1 at.% of Fe or Co has, however, been found by this technique to be completely ferromagnetically ordered.

These conclusions may be readily understood if we consider the nature of the spin polarization surrounding an impurity in an exchange-enhanced host. The range of the polarization parallel to the impurity is extended by exchange enhancement,[59] leading to "giant" impurity moments and long-range ferromagnetic ordering at rather low concentrations. At large distances from the impurity the polarization is oscillatory[59] leading to antiferromagnetic ordering at sufficiently low concentrations. The critical concentration is expected to be lower in Pd-based alloys, in which the enhancement factor is of the order of 7,[60] than in Pt-based alloys in which the enhancement factor is of the order of 1.8.[61] Indeed, a spin polarization parallel to the impurity is not expected to extend much beyond the nearest-neighbor distance in Pt alloys.[59] These conclusions are supported by the dramatic increase in slope of the Curie temperature against concentration curve deduced from magnetic[1] and Mössbauer-effect[62] measurements, which occurs at about 0.2 at.% in *Pd*Fe and 2 at.% in *Pt*Fe.

It is of interest to consider whether the temperature dependence of the 0.3- and 0.6-at.% alloys can be attributed to magnetic ordering. Although the existence of a decrease in spin scattering due to ordering in these alloys cannot be ruled out, the decrease in resistance of the 0.6-at.% alloy between 10 °K (which should be well above T_c for this alloy) and $T = 0.5$ °K (where the resistance is essentially temperature independent) is only 0.02 $\mu\Omega$ cm/at.% (Fig. 2), which is considerably smaller than the decrease expected for antiferromagnetic ordering on the *s-d* model (0.036 $\mu\Omega$ cm/at.%). This, coupled with the fact that the temperature dependence of the resistivity of the 0.3- and 0.6-at.% alloys is well described by Eq. (1) with the same values of F/c as for the more dilute alloys, but with increased values of θ, suggests that the spin scattering is actually being *increased* by interactions between Fe atoms. This effect, which has been observed in *Rh*Fe[10] and *Pt*Co[63] alloys, may possibly be explained qualitatively if the spin on the Fe atoms is increased by interactions between impurities. Equation (6) then predicts an increase in spin scattering due to this cause, provided $|Z| < \frac{5}{2}$, as is the case for *Pt*Fe, *Rh*Fe, and *Pt*Co. The decrease in resistivity resulting from the freezing out of spin-flip scattering and from the interference of non-spin-flip and potential scattering, which is predicted on the basis of the *s-d* model,[29] should also be present. The sign of the magnetoresistance and the sign of the resistivity change per at.% resulting from magnetic ordering will, in general, be positive or negative depending on the relative magnitudes of these two effects, i.e., an increase due to a field-dependent increase in spin and a decrease due to a modification of the up- and down-impurity-spin populations resulting from an applied magnetic field or interactions between impurities. The negative contribution should dominate at temperatures $T \gg T_s$ (and $H \gg T_s$), when the mean-square moment has reached its maximum value (and is thus almost field independent). The dominance of a negative term in the 1-at.% alloy may thus result from the fact that $T_c \gg T_s$ (and hence $H_{\text{internal}} \gg T_s$) in this alloy. For $T \ll T_s$, when the spin is well below its maximum high-temperature value, and is thus strongly field dependent, a positive magnetoresistance (for $|Z| < \frac{5}{2}$) may be expected. As mentioned above, a positive term was, in fact, observed in the magnetoresistance of the Pt–0.05-at.% Fe alloy, and this was attributed[7] entirely to a Kohler[28] contribution. The possibility that this resulted, at least in part, from a field-dependent increase in spin, cannot be discounted.

V. SUMMARY

It has been shown that the impurity resistivity of *Pt*Fe alloys contains a positive logarithmic temperature dependence, similar to that observed in *Rh*Fe,[6] which can be fitted over the temperature range 0.5 to 8 °K, to Eq. (1), with a value of $\theta = (0.4 \pm 0.2)$ °K for alloys containing $c \leq 0.1$ at.% Fe. This behavior, and also perhaps the low-temperature Mössbauer effect[24] and thermopower[27] data is consistent with a spin-fluctuation model for the *Pt*Fe system, with a spin-fluctuation temperature $T_s \sim (0.4 \pm 0.2)$ °K. It must be emphasized that the limiting low temperature T^2 dependence of Eq. (1) has not been observed in these more dilute alloys, the temperature dependence being approximately linear at the lowest temperatures reached in the present investigation. The function was chosen since it has been used successfully to describe the resistivities of a variety of other systems,[64] and because it approximates to the universal curve predicted by Kaiser and Doniach.[39] An expression of this form has also been predicted on the Kondo theory when interactions between impurities and impurity-spin-lattice-relaxation processes are included.[64]

A simple model has been described which relates the non-spin-flip part of the resistivity to the experimentally determined temperature dependence of the mean-square spin of the impurity, on the assumption that the number of electrons of up and down spin on the impurity site are related to the phase shifts by the Friedel sum rule. It is shown that the positive temperature coefficient of the resistivity of *Pt*Fe follows directly from this assumption, and satisfactory agreement with the sign of the temperature coefficient in a variety of Pd-, Pt-, and Rh-based alloys is also obtained.

In many respects—the decrease in moment at low temperatures,[24] the large thermopower,[27] the large negative contribution to the magnetoresistance,[7] and Curie susceptibility at high temperatures[24,25]—the *Pt*Fe system resembles systems such as *Au*Fe, which have previously been interpreted in terms of the Kondo effect. Indeed, the characteristic temperature ($\theta \sim 0.4\,^{\circ}\mathrm{K}$) of *Pt*Fe is comparable to the estimated Kondo temperature of *Au*Fe[10] ($T_K \sim 0.2\,^{\circ}\mathrm{K}$). The systems differ only in the sign of the temperature coefficient of the resistance. It is evident from the foregoing discussion that this difference need not represent a fundamental difference in scattering mechanism. Equation (8) does, in fact, predict a negative temperature coefficient for the resistivity of *Au*Fe, and there seems little reason to postulate different mechanisms to explain the behavior of "Kondo" systems such as *Au*Fe and "spin-fluctuation" systems such as *Rh*Fe and *Pt*Fe. Finally, we have suggested that the low-temperature increase in spin resistivity per impurity for $c = 0.3$ at.% Fe and 0.6 at.% Fe and the decrease for $c = 1$ at.% Fe may result from a competition between two factors—a positive term due to an increase in impurity spin (resulting from interactions) and a negative term resulting from a modification of impurity spin-up and spin-down populations, the latter term dominating in the most concentrated alloy for which the Curie temperature $T_c \gg T_{\mathrm{SF}}$.

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Insulator-Metal Transition and Long-Range Magnetic Order in EuO[†]

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Several aspects of the insulator-metal transition below the magnetic-ordering temperature in EuO have been examined. The conductivity above 50 K is shown to be thermally activated, with an activation energy which depends linearly on the long-range magnetic order. Below 50 K the conductivity is metallic. This insulator-metal transition is observed only in samples which are slightly oxygen deficient, presumably in the form of vacancies. The magnitude of the exchange interaction between the conduction electron and localized spins is shown to be about 0.1 eV.

INTRODUCTION

The conductivity of EuO may increase by many orders of magnitude as the temperature is decreased below the ferromagnetic-ordering temperature ($T_c = 69.3$ K). This behavior has been reported by Oliver, Kafalas, Dimmock, and Reed[1-3] and by Petrich, von Molnar, and Penney.[4] We have grown additional crystals and extended our measurements to cover a wider range of conductivities, both with and without an applied magnetic field. Typical data are shown in Fig. 1. It is evident that the insulator-metal transition below T_c is related to the onset of magnetic order. It is our purpose to explore the nature of this relationship. Furthermore, we shall discuss the preparation and stoichiometry of EuO and show that the crystals which exhibit the insulator-metal transition are oxygen deficient, probably in the form of oxygen vacancies.

The conductivity σ shown in Fig. 1 may be divided into four regions. Between room temperature and 125 K, $\log\sigma$, if plotted against $1/T$, shows thermally activated conduction with a 0.285-eV activation energy. Between 125 and 70 K the conductivity was masked by leakage currents. Below T_c, there is a 13-order-of-magnitude increase in σ which we may well call an insulator-metal transition. Below 50 K, conduction is essentially metallic.

Hall-effect measurements have been made at 5 K and near room temperature, but could not be made in the 50–70 K region due to the very large magnetoconductance. The results for three samples (89B, 89A, and 73) showing the insulator-metal transition are summarized in Table I. The expression $\sigma(T)$