LONG-RANGE ANTIFERROMAGNETIC SPIN CORRELATIONS IN SCANDIUM METAL*†

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Alloys of Sc with magnetic impurities show strong anomalies in the concentration dependence of the impurity interaction temperature. This is interpreted with exchange enhancement of the susceptibility of metallic Sc near a finite wave vector.

Correlations of the conduction-electron spins in a metal may be measurably reflected in the interactions between magnetic impurities embedded in it. The field dependence of the magnetization of very dilute alloys of Sc:Gd indicates long-range impurity interactions, in contrast to the abnormally short range suggested by the low Néel temperature in alloys of Sc with intermediate Gd concentrations.[1,2] A simple molecular-field model makes both results consistent. The model assumes an indirect impurity interaction through the d electrons of the Sc matrix, and a mutual correlation of the d spins over many lattice sites through an antiferromagnetic interaction. Similar d-spin correlations are well known in Pd metal, where they arise, however, from a ferromagnetic interaction.

The magnetization of carefully prepared dilute alloys of Sc:Gd was measured at 0.38°K in fields up to 11 kG. The magnetization of the scandium base material, measured at the same temperature before alloying, was subtracted.[3] Figure 1 shows the magnetization per Gd ion as a function of H/T for three alloys and for noninteracting Gd^{3+} ions. The theoretical saturation of free Gd^{3+} is 99.5% at the experimental limit $(H/T)_{max}$ = 30 kG/°K. Clearly only the 76-ppm alloy saturates. The average saturation moment of five alloys, prepared independently for the 100-ppm range, is $(9.3 \pm 0.3)\mu_B$. The enhancement by more than 30% over the free Gd^{3+} value ($7\mu_B$) is consistent with the somewhat smaller modification of the effective moment on Gd found by Nigh et al.[1] at higher concentration. Gd in Sc shows the largest modification of a rare-earth moment observed in any metal so far, indicating an unusual magnetic polarizability of the Sc matrix, which is larger than that of Pd. (The saturation moment of Gd in Pd is $5.7\mu_B$,[4] a 20% decrease from the free-ion value.)

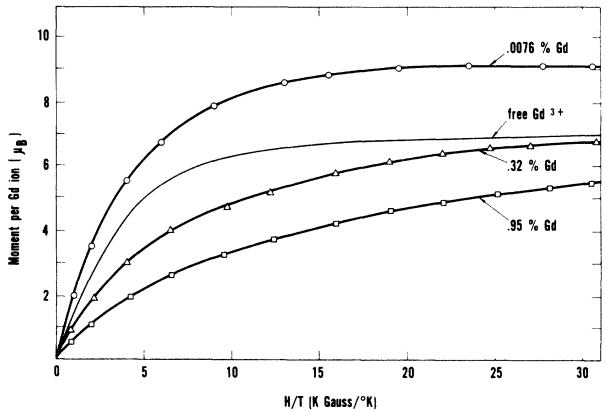

FIG. 1. Saturating magnetization curves of dilute Sc:Gd alloys. The saturation moment per Gd ion is 30% enhanced with respect to free Gd^{3+}. The failure of the 0.32% and 0.95% alloys to saturate indicates strong interactions between the impurities.

In the 0.32% and 0.95% samples, the magnetization is well below that of the most dilute alloy. For an estimate of the strength of the interaction which prevents saturation, we write

$$M(T,H,c) = M_{sat} B_J[H/\{T-\theta(c)\}], \quad (1)$$

where c is the Gd concentration, $B_J(H/T)$ is the magnetization curve for the Gd impurity with its polarization cloud at infinite dilution, and $\theta(c)$ is the interaction temperature. Alloys in the 100-ppm range show no concentration dependence of the normalized magnetization within experimental error. Thus the curve of the 76-ppm alloy may be taken as a direct measurement of $B_J(H/T)$. The other two curves in Fig. 1 coincide with this isolated impurity magnetization if one chooses $\theta = -1.1 \pm 0.1$°K for the 0.32% alloy, i.e., $\theta/c = -3.4$°K/%, and $\theta = -2.0 \pm 0.5$°K for the 0.95% alloy, i.e., $\theta/c = -2.1$°K/%. This interaction is larger in magnitude than in Pd:Gd where Crangle[4] found a long-range interaction between Gd impurities with $\theta/c = +2$°K/% in the 1-2% range. For comparison, $\theta/c = 0.6$°K/% in La:Gd[5] at high dilution.

The long range of the interaction at low concentration is in apparent contradiction to the short range which one might deduce from the abnormally low interaction temperatures found in alloys of intermediate concentration (Fig. 2). The Curie-Weiss temperatures of ScGd alloys measured by Nigh et al.[1] extrapolate to zero at

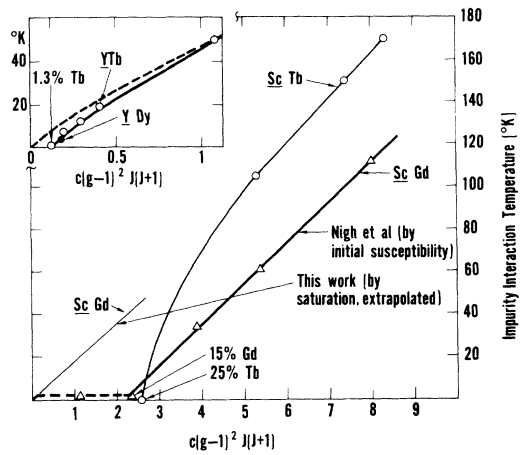

FIG. 2. Anomalies of the concentration dependence of the interaction temperatures of alloys of Sc and Y with magnetic rare earths. The data are taken from the following references: Y:Tb and Y:Dy, Ref. 5; Sc:Gd, Ref. 1; Sc:Tb, Ref. 2.

15% Gd, and the Néel temperatures of Sc:Tb alloys obtained by neutron diffraction by Child and Koehler[2] are less than 1.3°K below 25% Tb. Both concentrations correspond to about the same value of $\gamma = (g-1)^2 J(J+1)c \equiv \alpha c = 2.5$ (α is the de Gennes factor). Alloys of Y with Tb and Dy exhibit a similar but much weaker anomaly,[5] with the characteristic concentration at $\gamma = 0.13$ (Fig. 2). Since the anomalies scale with the de Gennes factor, they seem to reflect some property of Sc and Y rather than the impurity.

In Table I the values of θ/c are given as function of concentration between 0.3 and 65% Gd in the Sc:Gd system. A simplified calculation, based on the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction,[6] predicts θ/c to be independent of concentration for dilute alloys, in rough agreement with the experimental results in La:Gd,[7] Y:Gd,[8] Lu:Gd,[9] $(La_{1-x}Gd_x)_3In$,[10] $(La_{1-x}Gd_x)Sn_3$,[11] and Cu:Mn.[12] The table exhibits clearly the deviations of the Sc:Gd system from this behavior by the minimum of θ/c near $c = 15\%$ and by the high value of θ/c at the lowest concentration.

We propose a molecular-field model which is consistent with both anomalies and is based on three properties of the d electrons in Sc which can be derived from the temperature dependence of the susceptibility of the pure metal.

(1) The susceptibility shows Curie-Weiss behavior with $\mu_{eff} = 1.67\mu_B$ per d electron.[13] Since the effective moment of a completely delocalized electron is $1.73\mu_B$ and of a fully local d^1 electron $1.55\mu_B$, we conclude that the orbital moment on the d electron in Sc metal is not completely quenched.

Table I. Concentration dependence of the interaction energy per impurity ion.

c (at.%)	θ/c (°K/at.%)
65.7	2.59
50	2.18
35	2.06
25	1.60
15	1.07
7.4	<0.268
1.85	1.35
0.95	2.1
0.32	3.4

(2) The d-electron gas in Sc is highly polarizable. This can be inferred from the low value ($T_i \sim 100$°K[3]) of the point of inflection of the curve of susceptibility versus temperature for Sc (between the parabolic temperature dependence of the degenerate electron gas and the high-temperature Curie-Weiss behavior). This temperature T_i is a realistic measure for the energy required to locally flip a spin in the interacting electron gas by external forces (for instance by exchange or spin-orbit scattering on an impurity). It is expected to be a few electron volts (the Fermi energy) for a delocalized s-electron gas and is reduced in Sc for the d electrons by two orders of magnitude because of strong localization (narrowness of the d band), exchange enhancement,[14] and possibly many-body effects. Since T_i is smaller in Sc (~100°K) than in Pd (~400°K), we are not surprised to find a larger modification of the moment of Gd in Sc and also a longer range of the Gd-Gd interaction at low concentration.

(3) Neighboring d shells interact antiferromagnetically in Sc. The Curie-Weiss temperature is about −850°K.[3,13]

Our molecular-field model for the rare-earth impurity interaction in Sc and Y assumes that the d spins couple ferromagnetically to the impurity spin inside the impurity cell; this explains the increase of the impurity moment. Furthermore, we assume that the Fourier transform of the resulting polarization outside the impurity cell is strongly peaked at a wave-vector $\vec{\kappa}$ whose magnitude is of the order of $\frac{1}{2}$ the reciprocal lattice period and depends on the orientation of $\vec{\kappa}$ in the hexagonal Sc lattice. This peak is presumably due to the antiferromagnetic interactions between

neighboring d shells, which enhance the susceptibility in reciprocal space, $\chi(q)$, at the finite $q = \kappa$ (rather than near $q = 0$, as in Pd[15,16]). The peak in $\chi(q)$ is analogous to that of Cr above the Néel temperature (see, for instance, Arrott[17]).

The width Δq of the peak determines the range R of the polarization cloud about an impurity in real space by $R \approx (\Delta q)^{-1}$. It will be shown presently that the ratio of range to period, R/κ^{-1}, of the polarization outside of the impurity cell in Sc is significantly larger than for a polarization derived from the common RKKY interaction which neglects the interaction between the conduction electrons and gives $R/\kappa^{-1} \approx 1$.

The effective Hamiltonian for the ith ion interacting with the polarization clouds of the ions of its environment is

$$\mathcal{H}_i = -\vec{S}_i \cdot \sum_j F(\vec{r}_{ij}) \vec{S}_j \equiv g\mu_B \vec{S}_i \cdot \vec{H}_i, \tag{2}$$

where $\vec{H}_i$ is the molecular field, $\vec{S}_i, \vec{S}_j$ the spins of the ions, and $F(\vec{r}_{ij})$ reflects the oscillatory polarization outside of the jth impurity cell and the coupling strength between impurity and conduction electron spin. The sum is over the range. Because of the random spatial distribution of the ions, there will be a large variety of environments within the range and a distribution of $\mathcal{H}_i$ about a mean $\mathcal{H}_{av}$ with a mean-square deviation $\Delta\mathcal{H}$. In zero applied field the thermal average $\langle S_{jz} \rangle$ is zero for all j far above a certain temperature but finite far below. This temperature is defined by $\mathcal{H}_{av}$ or by $\Delta\mathcal{H}$, whichever is the larger:

$$k\theta \equiv |\mathcal{H}_{av}| \text{ or } \Delta\mathcal{H}. \tag{3}$$

If range and oscillation period of $F(\vec{r}_{ij})$ are not very different ($R/\kappa^{-1} \approx 1$), as in the RKKY interaction or in the long-range ferromagnetically enhanced interaction in Pd and Pt,[15,16] the principal contributions of $F(\vec{r}_{ij})$ to $\mathcal{H}_i$ are all of the same sign. This leads to the prediction of constant θ/c.[7] If, however, $R/\kappa^{-1} \gg 1$, $\mathcal{H}_{av}$ and thus $k\theta$ will be reduced with respect to the case of nonoscillatory interaction of equal range and magnitude because of a partial cancellation of the contributions of the $F(\vec{r}_{ij})$ to $\mathcal{H}_i$. At constant concentration this cancellation will be the stronger, the larger R/κ^{-1}. At sufficiently low concentration the distribution of $\mathcal{H}_i$ becomes symmetric about $\mathcal{H}_i = 0$, in which case $\Delta\mathcal{H}$, the width of the distribution, will determine the interaction temperature. We suggest that the cancellation becomes noticeable in Sc and Y at elevated concentrations and is responsible for the minimum of θ/c in ScGd near 15% Gd concentration. (This minimum is even more striking in ScTb, where $\theta/c < 0.05$ °K/% near 25% Tb.) We suspect that the distribution of $\mathcal{H}_i$ is symmetric about zero in Sc below $\gamma = 2.5$ and in Y below $\gamma = 0.13$. This is consistent with the deviation of the paramagnetic Curie temperature from the Néel temperature (as derived from the susceptibility maximum) in YTb alloys.[6]

Since the minimum of θ/c occurs at much higher concentrations in Sc ($\gamma = 2.5$) than in Y ($\gamma = 0.13$) and since we do not expect the oscillation period to be very different in these materials because of their similarity in band structure,[18] we conclude that antiferromagnetic spin correlations exist in both Y and Sc but are of significantly longer range in Sc.

It is possible to estimate the range of the interaction in Sc from the behavior of θ/c in Table I. The reduction of θ due to cancellation of the contributions of the $F(\vec{r}_{ij})$ depends on the number of jth ions within range. It is obvious that if the average impurity distance increases and approaches the range, the cancellation mechanism loses efficiency because the number of contributing ions will become of order unity. Then the interaction temperature will again reflect the actual magnitude of the two-ion interaction energy, i.e., the ratio θ/c will increase and become constant when the average impurity distance is larger than the range. Since θ_c/c is still increasing between the Sc:0.95% Gd and Sc:0.32% Gd samples, we estimate that the range of the antiferromagnetic spin correlation is more than seven lattice sites in Sc.

The existence of a long-range polarization in Sc and Y gives further support to the idea that with respect to their electronic properties these metals belong to a special class together with Pt and Pd. The first such indication came when it was recognized that with a reasonable extrapolation of the effective electron-phonon interaction parameter from other transition metals the simple BCS theory predicts superconductivity in Sc, Y, and Lu as well as in Pd and Pt.[19] The absence of superconductivity in Sc, Y, and Lu may be due to paramagnons which accompany the incipient antiferromagnetism of these metals.

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MAGNETIC ORDERING IN PALLADIUM-IRON ALLOYS

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We have studied the temperature dependence of the electrical resistivity of palladium-iron alloys in the composition range 0.5-12 at.% Fe with particular emphasis on the neighborhood of the magnetic-ordering temperature. Values of the critical temperature T_C determined from the temperature of the maximum of $d\rho/dT$ fall consistently below those obtained from saturation-magnetization measurements. The dependence of T_C on Fe concentration is discussed and correlated with other properties of this system.

The ferromagnetic-ordering temperature in palladium-iron alloys has been studied by a variety of methods including saturation magnetization,[1,2] Mössbauer effect,[2,3] heat capacity,[4] and electrical resistivity,[5,6] but there are significant discrepancies between the ordering temperatures deduced from the different measurements. We report here a systematic study of the electrical resistivity in a series of Pd:Fe alloys ranging in composition from 0.5 to 12 at.% Fe with particular emphasis on the temperature dependence in the neighborhood of the magnetic-ordering temperature where pronounced anomalies in the temperature dependence of the electrical resistivity are observed. As the criterion for determining the ordering temperature (T_C) we take the temperature at which there is a maximum in the temperature derivative of the resistivity, $d\rho/dT$. The recent measurements of Craig et al.[7] on ferromagnetic nickel have demonstrated the relevance of such a criterion, but we might also mention that this choice gives values for T_C which are consistent with values obtained from the most reliable analysis of the data obtained by other methods.

The measurements were made using the standard four-point probe technique on samples which were usually about 3×10^{-3} cm thick, 2 mm wide, and about 2 cm long prepared from homogenized ingots. Data for all the samples were obtained between 4.2 and 300°K. For each sample $d\rho/dT$ was obtained from the $\rho(T)$ data by point-by-point differentiation using a computer. The temperature dependence of ρ and $d\rho/dT$ in the neighborhood of the ordering temperature for a sample of