Magnetic properties of gadolinium-rich alloys

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The change in the saturated magnetic moment and the depression of T_c caused by different nonmagnetic solutes in Gd suggest that the basic Ruderman-Kittel-Kasuya-Yosida theory for the $4f$—conduction-electron interaction is not directly applicable to alloys. The saturated moment, a local property, is found to vary linearly with the c/a ratio. Remarkably, no correlation with c/a is found for T_C, a global property; rather, T_C is found to vary nearly linearly with the residual resistivity. It is shown that the T_C dependence can be understood by taking into account the decreased $4f$-$4f$ coupling caused by the finite mean free path of the conduction electrons in the alloys.

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The kaleidoscopic magnetic structures and properties displayed by rare-earth alloys are of increasing interest for utilization in applied devices and for studying basic magnetic interactions. As functions of concentration and temperature, these alloys exhibit multicritical points and may serve as good candidates for studying critical phenomena and spin-glass behavior.[1-3] The fundamental mechanism governing the magnetic properties of these alloys is the $4f$—conduction-electron interaction, which seems well understood for the pure rare-earth metals [Ruderman-Kittel-Kasuya-Yosida (RKKY) theory]. Indeed, with insight from RKKY theory progress has been made recently using molecular-field theory to describe the observed phase transformations.[2] We present new experimental evidence indicating the straightforward application of RKKY theory to the alloy systems is in need of modification. In particular, the finite mean free path of the conduction electrons is important in determining the $4f$-$4f$ coupling and should be taken into account.[4]

According to RKKY theory, the saturated magnetic moment at low temperatures in excess of the seven Bohr magnetons from each Gd $4f$ shell is proportional to the strength of the $4f$—conduction-electron interaction (given by j_{d-f}, the exchange integral) and the density of states at the Fermi level $N(E_F)$.[5] The measured excess magnetic moment μ per Gd atom, as reported by White *et al.*,[6] is shown in Fig. 1 as a function of c/a and volume for seven different alloys systems with concentrations of nonmagnetic solutes up to 30 at.%. (The concentrations were low enough to keep the ordered state ferromagnetic.) It is clear that the excess moment increases linearly with decreasing c/a and that there is no obvious correlation with volume. This result indicates that the product $j_{d-f}N(E_F) \sim \mu$ is sensitive to the c/a ratio and, using RKKY theory for the ordering temperature

$$3kT_C = S(S+1)j_{d-f}^2 N(E_F) \quad , \tag{1}$$

where S is the spin of local moment, one would predict that the Curie temperature of these alloys should also vary systematically with c/a. Measurements of the depression of the Curie temperature ΔT_C vs c/a for the 10% alloys yielded the shotgun diagram of Fig. 2(a). Similar plots of ΔT_C versus a-axis parameter, c-axis parameter, and atomic volume were equally discouraging. Fortuitously, the electrical resistivity of two of the alloys had been measured several years ago,[7] and the high residual resistivity and large ΔT_C for Gd-Mg alloys suggested a relationship. Figure 2(b) shows our new finding that there is a striking correlation between the residual resistivity and the depression of T_C. Explanations for these results are given in the discussion later.

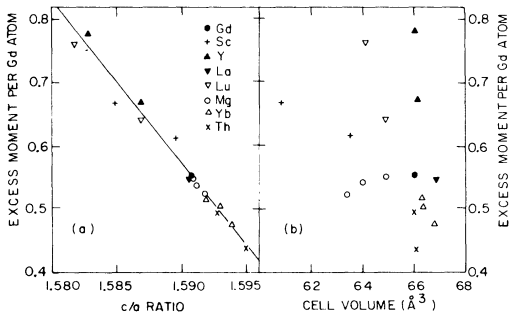

FIG 1. (a) Excess magnetic moment per Gd atom in units of μ_B vs the unit-cell axes ratio c/a for Gd (polycrystal mother) and the Gd alloys. The symbols indicate the solute atom (from Ref. 6). (b) Excess magnetic moment per Gd atom in units of μ_B vs the unit-cell volume for Gd (polycrystal mother) and the Gd alloys. The symbols indicate the solute atom (from Ref. 6).

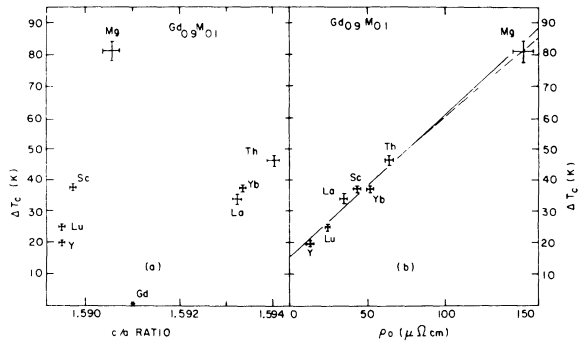

FIG. 2. (a) Depression of the Curie temperature ΔT_C of Gd alloys vs the hexagonal-lattice c/a ratio. The metal solute concentration is 0.1 for all samples as indicated by $M_{0.1}$. (b) Depression of the Curie temperature ΔT_C of Gd alloys vs the residual resistivity. The equation for the straight line shown is $\Delta T_C = 15 + 0.46\rho_0$ in K, the dashed curve is from the theory described in the text.

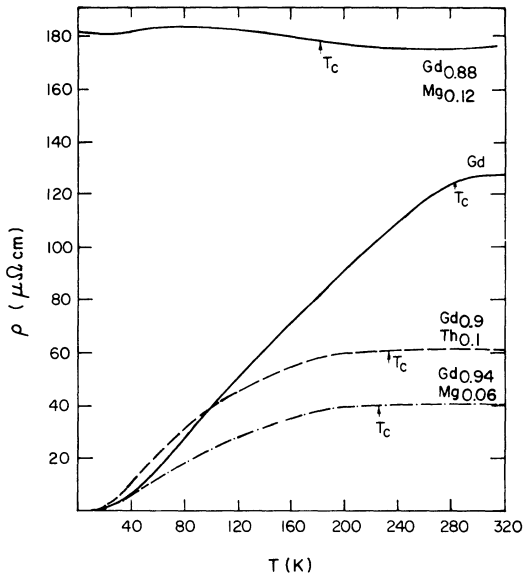

FIG. 3. Electrical resistivity vs T for several representative samples. Shown are the raw data for $Gd_{0.88}Mg_{0.12}$ from Ref. 7 and $\rho(T) - \rho(4.2)$ for the other samples. The polycrystalline data shown for Gd and for $Gd_{0.9}Th_{0.1}$ were calculated from data of Refs. 9 and 7 using $\rho_{poly} = \frac{1}{3}\rho_c + \frac{2}{3}\rho_a$.

The alloys of Gd with Sc, Y, La, Lu, and Th were arc melted over a water-cooled copper hearth in a helium atmosphere. Several inversions of the button were made to ensure homogeneity. The alloys were heat treated at 1100 °C for 2 h in a vacuum of 2×10^{-7} Torr to eliminate any dendritic segregation. The Gd-Yb and Gd-Mg alloys were prepared in sealed Ta crucibles inductively heated to 1350 °C. The crucibles were inverted and reheated several times to obtain proper mixing of the constituents. The Yb alloys were heated to 950 °C and then quenched while the Mg alloys were heated to 700 °C for 10 days and quenched so as to preserve the solid solutions. Metallographic and x-ray examinations established that the alloys had the hcp Gd structure. The starting metals were of high purity prepared in our laboratory by methods described previously.[8] The saturation moments and Curie temperatures of the alloys were measured in a vibrating sample magnetometer. In the course of the work, it was found that an extrapolation to the T axis of the $M^{3/2}$-vs-T plot for constant 200-Oe applied field gave the same T_C for pure Gd as did the Arrott plot (M^2 vs H/M for different T). Therefore, the simplified extrapolation procedure was adopted for determining the Curie temperatures of the alloys.

In Table I, we give a partial listing of samples studied, their ordering temperatures and the electrical resistivities at 4.2, 77, and 297 K. To complete the picture we have relied on more complete resistivity data taken earlier by Mellon and Legvold[7] and Nigh *et al.*[9] In Fig. 3 we display their data as adapted for

TABLE I. Partial listing of sample data.

Solute (at.%)	T_C (K)	ρ(297 K) ($\mu\Omega$ cm)	ρ(77 K) ($\mu\Omega$ cm)	ρ(4.2 K) ($\mu\Omega$ cm)	ρ(247 K) $-\rho$(4.2 K) ($\mu\Omega$ cm)	ρ(77 K) $-\rho$(4.2 K) ($\mu\Omega$ cm)
Sc 5	274	121	46	22	99	24
Sc 10	255	130	69	44	86	25
La 5	275	107	44	17	90	27
La 10	257	106	57	33	73	24
Lu 15	253	133	62	37	96	25
Y 15	259	135	47	21	114	26
Yb 10	256	147	85	52	95	33
Th 10	246	124	93	64	60	29
Mg 10	214	153	155	152	1	3

our purposes. The data for polycrystalline samples were calculated from the published single-crystal data using $\rho_{\text{poly}} = \frac{1}{3}\rho_c + \frac{2}{3}\rho_a$ for Gd (Ref. 9) and for $Gd_{0.9}Th_{0.1}$ (Ref. 7). The upper curve of Fig. 3 shows that the raw resistivity data for $Gd_{0.88}Mg_{0.12}$ is nearly temperature independent. The other curves show $\rho(T) - \rho(4.2\text{ K})$ versus temperature. The data for samples described in Table I would fall in the range between the curves for pure Gd and for $Gd_{0.9}Th_{0.1}$.

It has been known for some time that the ordering temperature of the pure rare-earth metals decreases with pressure[10] and from uniaxial stress measurements on Gd the decrease in T_C can be directly related to the increased stress along the c axis.[11] Thus in the pure metals, T_C *decreases with decreasing c/a* as stress or pressure is applied. From the relativistic augmented-plane-wave (RAPW) calculations of Fleming and Liu, who calculated the band structures corresponding to the normal lattice spacing and the spacing at 20-kbar pressure, the decreased T_C can be understood as a decrease in $N(E_F)$ [see Eq. (1)] resulting from the increased d-band width (with smaller volume).[12] Unfortunately, the saturated magnetic moment of Gd has not been measured under the application of uniaxial stress, however, the *increasing* excess moment with *decreasing c/a* shown in Fig. 1 is just the opposite correlation one might expect from the T_C results of the pure metals. To understand this c/a sensitivity better we have performed non-self-consistent band calculations on paramagnetic Gd for the normal volume but with a 5% decrease in c/a, and for the normal c/a with a 5% smaller volume. The results show a strong dependence of the bands crossing E_F on c/a, but only an overall increase in d-band width and corresponding decrease in $N(E_F)$ as the volume is decreased. The smaller c/a calculation showed that the band near E_F with predominantly d character was lowered with respect to a band with more s-p admixture, thus allowing for a stronger $4f$ conduction-electron coupling and the possibility of an increased moment.[13] These calculations were for the paramagnetic state of the pure metal, and we cannot, therefore, make quantitative statements about the density of states for the ferromagnetic state of the alloys. However, the calculations do indicate that the surprising c/a sensitivity of the observed magnetic properties are probably related to the band structure.

The excess moment is a local effect in the sense that it is a measure of the short-range interaction of a conduction electron with a local $4f$ moment on one site. The Curie temperature, on the other hand, is a measure of the conduction electron's ability to couple $4f$ spins on different sites. In these alloys the ordering is ferromagnetic (ordering wave vector $\vec{Q}=0$) so that the most important process is an electron "scattering" from one $4f$ moment (with $\vec{k}$ to $\vec{k}'=\vec{k}$) and interacting with another $4f$ moment. Since the residual resistivity ρ_0 measures the effectiveness of impurities to scatter electrons out of the forward direction ($\vec{k}=\vec{k}'$) it is not surprising to find a correlation between ΔT_C and ρ_0 as in Fig. 2(b). The straight line shown is simply a linear fit to the data and has the form $\Delta T_C = (a + b\rho_0)x$, where x is the concentration of solue, a and b are constants, and ρ_0 is the residual resistivity. Thus, ax is the ΔT_C axis intercept and gives the ideal dilution effect which would come from a nonmagnetic nonscattering impurity in the lattice (i.e., a compatible impurity which ideally would allow the conduction electrons to maintain an infinite mean free path at $T=0$).

The significance of resistivity for the RKKY theory was suggested by the work of de Gennes,[14] but it has not received much attention in recent years. de Gennes was especially concerned with the spin-disorder resistivity for the pure metals and its role in lowering T_C. However, the essential results of his investigation which has been confirmed experimentally by studies of dilute Mn in Cu alloys,[15] is that the strength of the conduction-electron polarization surrounding a local-moment site is damped by a factor $e^{-R/\lambda}$, where R is the distance from the site and λ is the conduction electron mean free path. This damping factor has also been obtained for the case of alloys.[4] The damping factor can be incorporated with RKKY theory to yield the theoretical dependence of T_C on ρ_0 as shown by the dashed curve in Fig. 2(b). One begins by considering the Fourier transform of the exchange interaction

$$J(\vec{q}) = \sum_j{}' J(\vec{R}_{ij})\, e^{i\vec{q}\cdot(\vec{R}_i - \vec{R}_j)} , \tag{2}$$

where $J(\vec{R}_{ij})$ is the exchange coupling (due to conduction electrons) between local moments located on sites $\vec{R}_i$ and $\vec{R}_j$. $J(\vec{q})$ is directly related to the magnon spectrum and values of $J(R)$ for the pure metals are available from fits to the magnon dispersion curves as measured by neutron diffraction.[16] For ferromagnetic ordering mean-field theory gives a relationship between $J(q=0)$ and the paramagnetic Curie temperature

$$kT_C = \tfrac{2}{3}S(S+1)J(0) . \tag{3}$$

For the alloys we now insert the exponential damping factor $\exp(-|\vec{R}_i - \vec{R}_j|/\lambda)$ into Eq. (2) and use Eq. (3) to predict T_C. In practice, what we have done is to use Lindgård's $J(R)$'s (uniformally scaled to account for the dilution effect which would lower the exchange coupling even if the mean free path remained infinite) and then used the measured ΔT_C for Mg to fix the constant of proportionality between ρ_0 and $1/\lambda$. The resulting dashed curve in Fig. 2(b) is thus a one-parameter fit to the data, the parameter yielding a value of $\sim$16 Å for the mean free path in the 10% Mg

alloy, which seems very reasonable. The agreement is good. Thus the near linear dependence of ΔT_C on ρ_0 can be understood from a fairly simple physical picture. We should also remark that neutron-diffraction measurements of the magnon-dispersion curves for alloy systems with short mean free paths should show a damping out of the higher Fourier components of Eq. (2). This already seems to be happening in the case of Gd, where structure in the dispersion curves is diminished with increasing temperature (smaller mean free path).[17]

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