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Magnetic ordering in terbium alloys

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The magnetic-ordering temperatures of alloys of Tb with the nonmagnetic diluents Sc, Y, La, Lu, Yb, Mg, and Th were investigated. The initial ordering temperature for transition into the helical structure is discussed in terms of the magnitude of the indirect-exchange-interaction strength. The second ordering temperature for transition into the ferromagnetic state was also determined. In the La, Yb, and Th alloys the helical structure is suppressed with increasing concentration of nonmagnetic diluents and the ferromagnetic transition is then associated with the initial ordered state. For the Sc, Y, Lu, and Mg alloys it is the ferromagnetic state which is suppressed relative to the helical state. The ordering temperatures drop particularly rapidly for the Mg alloys with the disappearance of the ferromagnetic transition occurring at only 7 at.%.

I. INTRODUCTION

The complex magnetic structures of rare-earth metals are generally understood in terms of a periodic exchange field which is strongly influenced by the conduction-electron Fermi surface.[1] For rare-earth alloys the picture is presently unfolding and Lindgård[2,3] has provided some theoretical guidance.

One of the simplest magnetic-rare-earth alloy systems consists of a magnetic element alloyed with a nonmagnetic element. It therefore might be expected that these systems should be most easily understood theoretically. The work reported here covers alloys of the magnetic element Tb with a number of nonmagnetic metal solutes. Among the latter Sc, Y, La, and Lu can be alloyed with Tb over the entire concentration range to form solid solutions (expect for La which induces the Sm crystal structure in Tb at about 15 at.% La). Of the other metals we were only able to find three which produce solid-solution alloys over a reasonable concentration range. These are Mg, Th, and Yb (Yb is also a rare earth but since it is in the nonmagnetic divalent state it will not form a wide range of solid solutions). Therefore, in this study we deal with alloys of Tb with Sc, Y, La, Mg, Yb, and Th.

II. EXPERIMENT

The alloys were produced by the melting together of carefully weighed quantities of high-purity metals which were produced at the Ames Laboratory. The alloys of Tb with Sc, Y, La, Lu, and Th were produced by arc melting the constituents over a water-cooled hearth. The Yb and Mg alloys were produced by melting the constituents inside of sealed, inert gas-filled tantalum crucibles in a vacuum induction-heated furnace. The freshly melted alloys were then annealed for three days in the tantalum crucibles followed by a cold water quench to retain single-phase alloys. Samples were cut from the resulting ingots with a jewelers saw and were electropolished prior to the experiments. In all cases the experiments were performed on polycrystalline samples.

The magnetic-ordering temperatures of the alloys were determined with a vibrating sample magnetometer. A calibrated copper-Constantan thermocouple provided the temperature measurements. In each case the magnetization of the sample was measured at a fixed field (typically 30 Oe) as a function of temperature. At these low fields the antiferromagnetic transition, Néel temperature T_N, is seen as a sharp cusp in the susceptibility. The ferromagnetic transition temperature T_C is seen as a sharp increase in the susceptibility followed by a flat plateau extending to low temperatures.

The resistivity of each alloy sample was also investigated to search for any correlation between magnetic ordering and the electrical resistivity. The electrical resistivities of $1 \times 1 \times 20\text{-mm}^3$ samples, cut from the sample ingots, were determined using the standard four-probe dc technique.

The method used in this study for determining the ordering temperatures of the alloys is illustrated in Fig. 1 which shows the data for pure Tb. In this case we see a sharp cusp in the susceptibility at 229.7 K which we identify as T_N. In all of the alloys, where T_N is observed, the cusp is less than 1 K wide so that the T_N values are accurate to about 0.5 K. The Curie temperature T_C is identified as the sharp increase in susceptibility that occurs at about 221 K. In this case we identify T_C to be the temperature corresponding to the maximum slope in the susceptibility which is

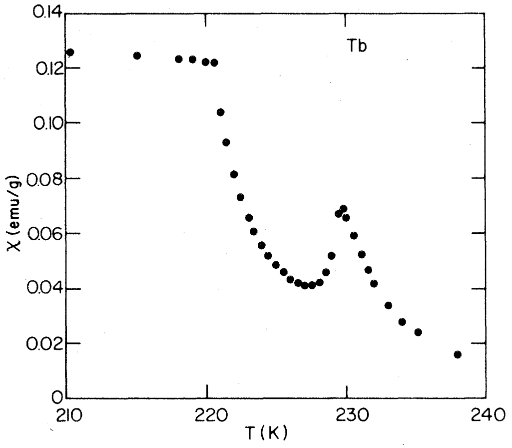

FIG. 1. Magnetic susceptibility of pure terbium as a function of temperature.

$T_C = 220.9$ K. Even though the temperature at the maximum slope is well defined, the ferromagnetic critical region is several degrees wide so that the critical T_C values are accurate to about 2 K.

In Fig. 2 we show the ordering temperatures for alloys of Tb with Sc, Y and Lu for diluent concentrations of up to 20 at. %. The Sc-alloy data of this work are shown along with similar data of Child *et al.*[4] There are minor variations in alloy composition. Considering the great sensitivity of the ordering temperatures to the Sc content the agreement between the data of this work and the previous values is satisfactory. In addition, the work of Child *et al.*[4] used neutron diffraction studies to find the ordering temperatures while this work used magnetic susceptibility. It is possible that some systematic differences between the two techniques could also affect the ordering temperatures. Figure 2 also shows data for Y alloys from this work along with data from Child *et al.*[5] and data for Lu alloys also with data from Child *et al.*[5] In the latter two cases the agreement between the present data and that from the previous work is quite good.

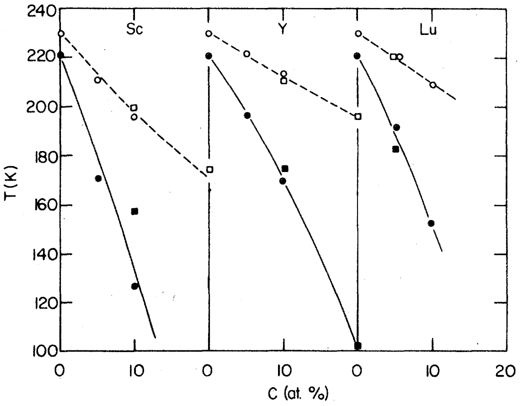

FIG. 2. Magnetic-ordering temperatures of terbium with scandium, yttrium, and lutetium. The open symbols are Néel temperatures and the filled symbols are Curie temperatures. The squares for the Tb-Sc alloys are from Ref. 4. The squares for the Tb-Y and Tb-Lu alloys are from Ref. 5.

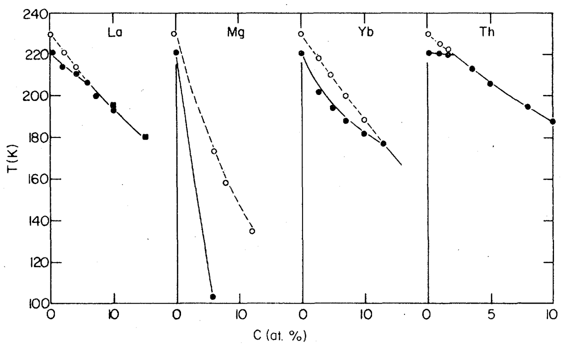

FIG. 3. Magnetic-ordering temperatures of terbium with lanthanum, magnesium, ytterbium, and thorium. The open symbols are Néel temperatures and the filled symbols are Curie temperatures. The squares for the Tb-La alloys are from Ref. 6.

Figure 3 shows data for alloys of Tb with Mg, Yb, Th, and La. In this figure there are two data points for the La alloys which are from Koehler[6] which agree very well with data from this work. The main feature of the La-alloy results is the tendency of La to favor ferromagnetism in Tb by suppressing the helical structure at about 5 at. % La. In the Th alloys the helical structure is also suppressed by about 2 at. % Th. Similarly the Yb alloys show this suppression of the helical structure at about 11 at. % Yb. It is of interest to note that the three alloy systems just mentioned all have similar ordering temperatures for a given alloy concentration. Finally, the Mg data show stabilization of the helical structure with complete elimination of ferromagnetism at less than 10 at. % Mg. In addition, the initial ordering temperatures of the Mg alloys are very low with respect to the other alloys with similar concentrations.

In Table I we present all of the ordering temperatures which were obtained for the alloys of this study along with the alloy composition, the Néel temperature T_N, the Curie temperature T_C, the residual resistivity and, for most of the samples, the lattice constants.

III. DISCUSSION

There are two aspects of the data which require analysis: the first is the initial (highest) ordering temperature and the second is the regime of the helical magnetic structure.

In his theoretical[3] work Lindgård used mean-field theory to obtain the following expression of the ini-

TABLE I. Alloy composition in atomic percent, Néel temperature, Curie temperature, residual resistivity for each alloy, and some of the alloy lattice constants.

Alloy	T_N (K)	T_C (K)	R_0 ($\mu\Omega$cm)	Lattice constants c (Å)	 a (Å)	 c/a
Pure Tb	229.7	221	3.1	5.6966	3.6055	1.579
5-at.% Sc	221	170	25			
10-at.% Sc	196	126	43	5.6493	3.5777	1.579
5-at.% Y	222	197	9			
10-at.% Y	215	170	14	5.7001	3.6098	1.579[a]
5-at.% Lu	220	192	13			
10-at.% Lu	209	153	25	5.6773	3.5963	1.579
2-at.% La	221	214	14			
4-at.% La	214	211	24			
6-at.% La	···	207	32			
8-at.% La	···	200	39	5.7320	3.6210	1.583
10-at.% La	···	193	46	5.7397	3.6246	1.583
6-at.% Mg	173	100	133	5.6701	3.5814	1.583
8-at.% Mg	158	69	160			
12-at.% Mg	135	···	182	5.6480	3.5613	1.586
2.5-at.% Yb	218	202	13			
4.5-at.% Yb	210	194				
7-at.% Yb	200	188	35	5.7172	3.6162	1.581
10-at.% Yb	188	182	49	5.733	3.623	1.582[b]
13-at.% Yb	···	177		5.7493	3.6319	1.583
1-at.% Th	225	220	19	5.7012	3.6061	1.581
1.6-at.% Th	222	220				
3.5-at.% Th	···	213	34	5.7048	3.6060	1.583
5-at.% Th	···	206	53			
8-at.% Th	···	195	68	5.7180	3.6061	1.585
10-at.% Th	···	188	75	5.724	3.599	1.591[b]

[a] Calculated from pure Y and pure Tb parameters.

[b] Interpolated from parameter data at other concentrations.

tial ordering temperature for alloys of rare-earth metals with nonmagnetic diluents:

$$3k_B(T_i-A_R)=(1-c)J_R(J_R+1)(g_R-1)^2 j_R^2 \times [c\bar{\chi}_M(Q)+(1-c)\bar{\chi}_R(Q)]. \qquad (1)$$

In this equation the subscript R refers to the rare-earth metal with concentration $1-c$ and M stands for the nonmagnetic metal. The j_R is the average exchange coupling between the localized $4f$ states and the conduction electrons, while $\bar{\chi}(Q)$ is the averaged (with respect to matrix elements) wave-vector-dependent susceptibility of the pure elements [the value of Q is the one which maximizes $\bar{\chi}(Q)$ and is nonzero for helical structures]. The A_R is the constant arising from the magnetic anisotropy of the rare-earth ions. The de Gennes factor, $(g_R-1)^2 J_R(J_R+1)$, is an atomic property and does not depend on alloy concentration. The j_R is also determined by atomic properties[7] and should not depend significantly on concentration. We see from this equation that if $\bar{\chi}_M(Q)\approx\bar{\chi}_R(Q)$ the transition temperature should drop linearly with concentration. The transition temperatures of Figs. 2 and 3 do decrease fairly linearly, albeit only over a very limited concentration range. More significantly the slopes show considerable variation which can only be explained with Eq. (1) as arising from differences in the generalized susceptibility functions. This was the assumption used by Lindgård,[3] who treated the $\bar{\chi}_M(Q)$ as parameters to fit the experimental results for a number of alloys.

Thus a possible approach for analyzing the present data is to take Lindgård's $\bar{\chi}_{\mathrm{Tb}}(Q)=2.06$ states/eV and then vary $\bar{\chi}_M(Q)$ in Eq. (1) to get the best fit for the initial ordering temperature of each alloy series. As Lindgård noted,[3] for some alloys (particularly those with Sc) this procedure leads to unrealistically low values of $\bar{\chi}_M(Q)$. Lindgård therefore suggested that the $\bar{\chi}(Q)$'s were not constant but rather one had to account for changes in the susceptibility caused by volume differences between the two metals making up the alloy. By making the reasonable assumption that these volume differences affect the susceptibility and the density of states at the Fermi level to the same extent, we can follow Lindgård and assume

$$[\bar{\chi}(Q)]_{\text{Tb,alloy}} = [\bar{\chi}(Q)]_{\text{Tb,metal}}[1 - c(V_{\text{Tb}} - V_M)/V_{\text{Tb}}] \ , \tag{2}$$

where V_{Tb} and V_M are the atomic volumes of Terbium and the diluent, respectively. A similar expression holds for the nonmagnetic diluent susceptibility. When these concentration-dependent susceptibilities are substituted into Eq. (1) one obtains

$$\begin{aligned} 3k_B(T_i - A) = {} & (1-c)J(J+1)(g-1)^2 j^2 \\ & \times \left[(1-c)\bar{\chi}_{\text{Tb}}(Q) \vphantom{\frac{V}{V}} \right. \\ & \quad + c\left\{ \bar{\chi}_M(Q)\frac{V_{Tb}}{V_M} - \frac{\Delta V}{V_{Tb}}\bar{\chi}_{Tb}(Q) \right\} \\ & \quad \left. + c^2\left\{ \frac{\Delta V}{V_{\text{Tb}}} \right\}\left\{ \bar{\chi}_{\text{Tb}}(Q) - \bar{\chi}_M(Q)\frac{V_{\text{Tb}}}{V_M} \right\} \right] \ , \end{aligned} \tag{3}$$

where $\Delta V = V_{\text{Tb}} - V_M$. This is a slightly revised version of the expression given by Lindgård[3] in his Eq. (9).

In his derivation of Eq. (1) Lindgård used arguments based on coherent potential approximation (CPA) theory justifying the use of an averaged $\chi(Q)$ only for alloys for which the bands of both constituent elements were similar.[3] For terbium this condition is satisfied by trivalent elements with similar chemical behavior. For this reason we only apply Eq. (3) to the alloys with Lu, Y, Sc, and La. We obtain very good fits to the data for these alloys using $\bar{\chi}_M(Q)$ values of 2.8, 3.0, 1.2, and 0.4 states/eV, respectively. Our values of $\bar{\chi}_M(Q)$ for Lu, Y, and Sc agree well with those derived by Lindgård (Lindgård did not consider alloys with La). The values for Lu and Y are also consistent with specific-heat measurements;[8] however, as found by Lindgård the $\bar{\chi}_{\text{Sc}}(Q)$ is unreasonably small, as is $\bar{\chi}_{\text{La}}(Q)$. This can be deduced from band-structure calculations[9] and specific-heat measurements[10] which both indicate the density of states at the Fermi level, $\rho(E_F)$, for Sc is about 2.5 states/eV. Since for elements which promote helical structures (as well as by direct calculation for Sc)[11] the following relation holds

$$\bar{\chi}(Q) > \bar{\chi}(Q=0) = \rho(E_F) \ ,$$

one expects $\bar{\chi}_{\text{Sc}}(Q)$ to be at least a factor of 2 larger than the 1.2 states/eV deduced using Eq. (3). We believe part of this discrepancy arises from other volume difference effects not included in Eq. (3). We discuss this situation below after commenting on the other alloys.

The Mg, Yb, and Th alloys cannot be analyzed using Eqs. (1) or (3) since they have a different valency than Tb and may cause substantial changes in the band structure. These alloys may in principle be treated by coherent-potential approximation (CPA) theory; however, an accurate calculation would be quite difficult. A model CPA calculation for the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction in rare-earth alloys[12] does provide some insight and suggests another mechanism which could account for the low values of $\bar{\chi}_M(Q)$ derived for some alloys. If the diluent atoms are incompatible with the host lattice because of either a large volume difference or valence difference the conduction-electron mean free path will be reduced. This in turn reduces the RKKY interaction between the local $4f$ spins a distance R apart by a factor $e^{-R/\lambda}$, where λ is the mean free path.[12] This mechanism has been discussed with respect to Gd alloys where a correlation between initial ordering temperatures and residual resistivities was noted.[13] The very large residual resistivity and the extremely low initial ordering temperatures for the Mg series of alloys (see Table I) suggests this mechanism may be particularly important for these samples. Some evidence of the diluent compatability with the host lattice is therefore advisable before Eq. (3) is adopted. For this purpose we list in Table I the residual resistivities and the lattice constants for some of the alloys. Further analysis, especially of our data for incompatible diluents, requires a more complete theory and we hope our results will motivate efforts in this direction.

The second ordering temperature to the ferromagnetic state is very interesting, but so little is known in the alloys about the driving mechanism for the transition that our discussion must be limited. Crystal-field and magnetoelastic effects are known to be strongly temperature dependent and to favor ferromagnetism [ferromagnetism is also favored by a peak in $\bar{\chi}(Q)$ for $Q=0$]. These effects are fairly well understood in the pure metals,[14] but their dependence on alloying is not as well characterized. For example, both the position of peaks in $\chi(q)$ and the crystal-field parameters can be affected by changes in lattice constants and some correlation between ordering temperatures and lattice constants does seem to exist. It can be seen in the figures that La, Th, and Yb promote ferromagnetism and that Sc, Lu, Mg, and Y favor the helical magnetic structure. Except in the case of Y this correlates well with the effect of alloying on the c-axis lattice constants for 10 at.% solutes as shown in Table I; i.e., alloys which expand the c parameter favor ferromagnetism while those which shrink the c parameter favor the helix. Clearly, a more extensive theory for alloys of rare-earth metals is needed before the data can be used to establish how the different microscopic mechanisms change with alloying and which ones are responsible for the relative changes in the ordering temperatures.

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