Influence of the f-d exchange interaction on the magnetic state of the itinerant d subsystem and field-induced magnetic phase transitions in the intermetallic compounds Y_{1-x}Gd_xCo_3

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The magnetization of the system Y_{1-x}Gd_xCo_3 (0<x<1) in pulsed magnetic fields up to 40 T was investigated. The dependence of the magnetic moment of the cobalt subsystem on the gadolinium concentration was determined experimentally. An anomalous increase of M_{Co}(t) was observed at t \approx 0.24 and possibly also at t \approx 0.1. For compounds with x<0.225 the magnetization undergoes a diffuse field-induced metamagnetic transition. The peculiarities of the concentration and field dependences of the magnetization can be explained on the basis of a model that takes into account the magnetic instability of the itinerant d subsystem of cobalt. They are determined by the transition of the cobalt subsystem in an external field (or the internal f-d exchange interaction field) from a weakly magnetic state into an intermediate and strongly magnetic state. The molecular-field f-d exchange interaction constants were determined. The H-versus-t magnetic phase diagrams of the systems Y_{1-x}Gd_xCo_3 and Y_{1-x}R_xCo_3 with heavy rare earths are constructed. © 1994 American Institute of Physics.

1. INTRODUCTION

The peculiarities of the band structure of magnetic materials based on 3d metals often result in magnetic instability—a transition from one magnetic state to another accompanying a change of the external parameters (external magnetic field, pressure, and temperature) and internal parameters (exchange field, stoichiometry, and so on). The most carefully studied manifestation of magnetic instability is itinerant metamagnetism—a transition in a magnetic field from a paramagnetic or weakly ferromagnetic state into a strongly ferromagnetic state in compounds based on YCo_3, LuCo_3, and also ThCo_3 (a review is given Ref. 1, where the original works are cited).

Magnetic instability was recently observed in the intermetallic YCo_3, which has a PuNi_3-type orthorhombic structure (space group R3m). The magnetic properties of the compound YCo_3 and the isostructural rare-earth compounds RCo_3 are summarized in Ref. 3. The compound YCo_3 is an itinerant ferromagnet, in which the f band is formed as a result of hybridization of the 3d electrons of cobalt with the 4d electrons of yttrium (or 5d electrons of the rare earth in the compounds RCo_3). According to data given in different works, the Curie temperature of this compound ranges from 264 to 320 K, and the total magnetic moment ranges from 1.2 \mu_B to 1.75 \mu_B per formula unit (FU). This large spread in the values of the basic magnetic characteristics could be caused by stoichiometric differences between the samples studied in different experiments.

Investigations of the magnetization of YCo_3 in strong magnetic fields of up to 110 T have revealed two metamagnetic transitions, as a result of which the magnetic moment M_{Co} of the d subsystem of cobalt increases to 3.69 \mu_B per FU, in fields of 60 T and 82 T. These magnetic transitions are interpreted as transitions, occurring in a magnetic field, of the magnetically unstable itinerant cobalt subsystem from a weakly magnetic state into an intermediate and then a strongly magnetic state. Band-structure calculations confirm the magnetic instability of the d subsystem in YCo_3.

There is another possibility for observing metamagnetic transitions in YCo_3-type compounds. This possibility is associated with the effect of the effective f-d exchange interaction, arising when a magnetic rare-earth R is substituted for nonmagnetic yttrium, on the itinerant magnetic d subsystem of the compounds Y_{1-x}R_xCo_3. In such compounds a second magnetic subsystem, formed by the localized 4f electrons of the rare earth, coexists with the itinerant magnetic d subsystem. The molecular field exerted on the d subsystem by the f subsystem is proportional to the concentration t of the rare earth:

$$H_{\text{m}}^f = \lambda_{f,d} \mu_B \mu_t,$$

where \mu_t is the magnetic moment of the rare earth and \lambda_{f,d} is the molecular-field f-d exchange interaction constant. Therefore, by varying the concentration t of the rare earth the itinerant subsystem can be transferred from a weakly magnetic state into a strongly magnetic state and anomalies re-
sulting from the metamagnetic character of the magnetization of this subsystem can be revealed in the concentration dependence of the magnetization of this subsystem. Substituting a rare earth for yttrium should also change the external fields \( H \) in which metamagnetic transitions occur, since the effective field acting on the \( d \) subsystem depends on the concentration of the rare earth:

\[
H_{\text{eff}} = |\mu_d H + H|.
\]  (2)

Anomalies appearing in the concentration dependence of the spontaneous magnetization of the system \( Y_{1-x}NdCo_3 \) as a result of a transition of cobalt from one magnetic state into another were observed in Ref. 6. The metamagnetic transition fields in this system also depend on the neodymium concentration.

In the present work we investigated the magnetic characteristics of intermetallides of the system \( Y_{1-x}GdCo_3 \). In \( GdCo_3 \) the magnetic moment of the cobalt subsystem is \( 4\mu_B \mu_0 \), i.e., it is considerably larger than in \( YCo_3 \), and it is greater than the magnetization of \( YCo_3 \), even in fields of 100 T. Hence it can be concluded that the cobalt subsystem in \( GdCo_3 \) is in a strongly ferromagnetic state.

Gadolinium was chosen as the substituent primarily because it is in a S state. Its orbital angular momentum is zero, and therefore the effect of the crystal field on the magnetic characteristics of the rare-earth subsystem can be ignored. In particular, the magnetic moment of this subsystem can be determined without any difficulty: \( \mu_{Gd} = 7\mu_B \) atom.

Our best present understanding is that the molecular-field \( f-d \) exchange interaction constant can be represented in the form

\[
\lambda_{f-d} = \frac{\mu_f}{\mu_d}.
\]  (3)

where \( \mu_f \) and \( \mu_d \) are, respectively, the spin moment and the total moment of the rare earth, and \( I_{f-d} \) is the \( f-d \) spin exchange constant, which, to a first approximation, is the same for all heavy rare earths. The effective field acting on the \( d \) subsystem is found to be strongest for gadolinium, i.e., by substituting gadolinium for yttrium it is possible to investigate the behavior of the cobalt subsystem in a much wider range of effective fields than in the previously studied system \( Y_{1-x}NdCo_3 \). This is the second reason for studying the system \( Y_{1-x}GdCo_3 \).

Finally, the third reason for choosing gadolinium is that, in contrast to the system \( Y_{1-x}NdCo_3 \), where the Nd and Co magnetic moments are parallel to one another, in \( Y_{1-x}GdCo_3 \) and Gd and Co magnetic moments are antiparallel \( (\lambda_{f-d} < 0) \), i.e., these compounds are ferrimagnetic, and a noncollinear magnetic structure should arise in them in fields \( H_{1} < H < H_{2} \). In the exchange approximation

\[
\begin{align*}
H_{1} &= \lambda_{f-d} M_{Co} + \mu_{Gd}, \\
H_{2} &= \lambda_{f-d} M_{Co} - \mu_{Gd},
\end{align*}
\]  (4)

and the magnetic susceptibility in the noncollinear phase is

\[
\chi = \frac{1}{\lambda_{f-d}}.
\]  (5)

Investigations of the field-induced noncollinear structure make it possible to determine independently the molecular-field \( f-d \) interaction constant \( \lambda_{f-d} \) and to compare its value to that obtained from measurements of the metamagnetic phase transitions in the \( d \) subsystem in the substituted compounds \( Y_{1-x}GdCo_3 \).
The figure also displays values of the magnetic-compensation temperature $T_{\text{comp}}$, at which the magnetization of the $d$ magnetic subsystem equals that of the $f$ magnetic subsystems. It is obvious that magnetic compensation is observed only over a comparatively narrow concentration range ($0.5 < t < 0.8$). Hence it follows that the temperature dependence of the magnetization of the $f$ magnetic subsystem is virtually identical to that of the magnetization of the $d$ magnetic subsystem.

Figures 2a and b display magnetization curves for some characteristic $Y_{1-x}Gd_{x}Co_{3}$ compounds at 4.2 K. In fields of up to approximately 150 kOe magnetization occurs in a nonlinear manner. This is explained by the large magnetic anisotropy of cobalt in these compounds, as shown previously on the basis of measurements of the magnetization of $YCo_{3}$ and $GdCo_{3}$ single crystals. The magnetization of most samples increases linearly in stronger fields and the increase is determined by the paraprocess.

It is interesting that anomalies are observed in magnetization curves of some of the mixed compounds in strong fields. For example, the magnetization of compounds with a low gadolinium concentration ($t < 0.225$) undergoes a diffuse metamagnetic transition (Fig. 2a). The metamagnetic transition field $H_{m2}$ as a function of the gadolinium concentration is displayed in Fig. 3. For compounds close to the concentration compensation point ($t_{\text{comp}} = 0.525$), the magnetization increases almost linearly in fields above a critical value (Fig. 2b). This is characteristic of a transition into a noncollinear ferrimagnetic phase.

Figure 4 (curve 1) displays the concentration dependence of the saturation magnetization $M_{s}$ of the system $Y_{1-x}Gd_{x}Co_{3}$ obtained at 4.2 K by linear extrapolation of the strong-field magnetization to zero field. This curve contains two features: a small magnetization anomaly near $t=0.10$ and a large, sharp increase at $t=0.24$. The features observed in the concentration dependences $M_{d}(t)$ at 4.2 K are also present at higher temperatures. This can be seen in Fig. 5, which displays the curve $M_{d}(t)$ at 83 K.

The magnetic susceptibility of the compounds studied at 4.2 K in fields above the magnetic saturation field (susceptibility of the paraprocess) is shown in Fig. 4b. The susceptibility is obviously a nonmonotonic function of the gadolinium concentration. Two peaks of the magnetic susceptibility are observed: one large and asymmetric peak at $t=0.225$ (this peak could be two peaks which have merged) and a second, wider but smaller peak, at $t=0.5$, i.e., near the compensation point.

4. DISCUSSION

In the collinear ferrimagnetic ordering model the spontaneous magnetization of the compounds $Y_{1-x}Gd_{x}Co_{3}$ can be represented in the form

$$M_t = \pm M_{Co} \mp \mu_{Gd},$$

where the upper signs refer to the concentration range $t < t_{\text{comp}}$ and the lower signs refer to the range $t > t_{\text{comp}}$. Since at 4.2 K $\mu_{Gd} = 7 \mu_{B}$, we constructed the concentration dependence of the $d$-subsystem magnetic moment $M_{Co}$ (Fig. 4a, curve 2). This curve shows that the total magnetic moment of the $d$ subsystem is a nonmonotonic function of the concentration and it increases near $t_1 \approx 0.1$ and $t_2 \approx 0.24$. Thus, our investigations show that the metamagnetic behavior observed in the itinerant $d$ subsystem of the compound $YCo_{3}$ in superstrong magnetic fields also remains when this subsystem is magnetized by the effective $f-d$ exchange interac-
observed in the concentration dependence $Y_{1-x}$Gd$\text{Co}_3$

**FIG. 4.** a) Concentration dependence of the saturation magnetization $M_s(t)$ (curve 1) and magnetic moment $M(t)$ of the $d$ subsystem (curve 2) at $Y_{1-x}$Gd$\text{Co}_3$ at 4.2 K. b) Susceptibility $\chi$ as a function of the gadolinium concentration $r$ in the system $Y_{1-x}$Gd$\text{Co}_3$, at 4.2 K. The arrows mark the critical concentrations $t_1$ and $t_2$ for which anomalies are observed in the concentration dependence $M_s(t)$ in the absence of a field.

The concentration range near the concentration compensation point $t_{comp}$ requires a separate analysis. According to Fig. 4, the anomalous increase of the spontaneous magnetic moment of cobalt in this region is small, if it exists at all, and it falls within the range of accuracy of the magnetization measurements. However, the large peak in susceptibility of the paraprocess near $t_{comp}$ confirms the anomalous magnetic behavior of the substituted compounds in this concentration region. It has not been ruled out that in $Y_{1-x}$Gd$\text{Co}_3$, a third transition occurs in the effective field at concentration $r=0.5$. It is also entirely possible that the observed anomalies are associated with other effects, in particular, the fact that phenomena caused by the appearance of a noncollinear magnetic structure in a field become important near the compensation point (see below). Although the experimental data were analyzed for fields below $H_{c1}$, in which a noncollinear magnetic structure arises, because of the random distribution of gadolinium the noncollinear phase can also contribute to the susceptibility in fields $H<H_{c1}$, giving rise to the peak near $t_{comp}$. Therefore, we can talk about a third metamagnetic transition only tentatively, and additional investigations are required to prove its existence unequivocally.

We now consider the behavior of the magnetization of the compounds $Y_{1-x}$Gd$\text{Co}_3$ in a magnetic field. As we have already noted, in some samples of the experimental system a metamagnetic transition is observed with gadolinium concentrations less than the critical concentration $t_1$ for the transition into the strongly magnetic state (see Fig. 2). Comparing the magnitudes of the magnetization jumps and the metamagnetic transition fields in the substituted compounds $Y_{1-x}$Gd$\text{Co}_3$ and Y$\text{Co}_3$ shows that this transition corresponds to a transition of cobalt in the field $H_{c1}$ from the intermediate into the strongly magnetic state. The molecular-field $f-d$ exchange interaction constant can be determined from the data on the concentration dependence of $H_{c1}$. The effective field acting on the itinerant $d$ subsystem is determined by Eq. (2), and since in the concentration range of the metamagnetic transition the magnetic moment of the itinerant $d$ subsystem is greater than the magnetic moment of the gadolinium subsystem, it is oriented parallel to the field.

FIG. 5. Concentration dependence of the $Y_{1-x}$Gd$\text{Co}_3$ saturation magnetization $M_s(t)$ at 83 K.

The concentration dependence of the saturation magnetization $M_s(t)$ (curve 1) and magnetic moment $M(t)$ of the $d$ subsystem (curve 2) at $Y_{1-x}$Gd$\text{Co}_3$ at 4.2 K.
The effective field can be represented in the form

\[ H_{\text{eff}}^{\lambda} = H + |\lambda_{\text{f-d}}|^2 g_\text{f-d} \mu_\text{B}. \]  

(7)

Therefore, the metamagnetic-transition field should decrease linearly with increasing gadolinium concentration:

\[ H_{\text{m1}}(t) = H_{\text{m1}}(0) - |\lambda_{\text{f-d}}|^2 g_\text{f-d} \mu_\text{B}. \]  

(8)

This agrees with the experimental data (Fig. 6), where we obtain \( \lambda_{\text{f-d}}^2 = 45 \) T/\( \mu_\text{B} \) per formula unit.

Although, as we have noted above, we were not able to observe metamagnetic transitions from the weakly ferrimagnetic state into an intermediate phase in the field \( H_{\text{m1}} \) (possibly because the change in the cobalt magnetic moment at this transition is small and the transition is spread over a large range of fields), we can estimate approximately the molecular-field constant also from the field of the rare-earth atoms in the first coordination sphere of the d atom at the ith position, and \( N_{d,i} \) is the number of such atoms per formula unit, and even if it is assumed that the f-d spin exchange parameters \( F_{\text{f-d}} \) are identical for the three nonequivalent positions, different values of \( \lambda_{\text{f-d}}^2 \) should be obtained because the number of nearest neighbors is different for different nonequivalent positions (three for the 3b positions, four for the 6c positions, and six for the 18h positions). Investigations of field-induced noncollinear magnetic structures yield, however, an average value \( \lambda_{\text{f-d}}^2 \) over the three nonequivalent positions.

5. MAGNETIC PHASE DIAGRAMS OF \( \text{Y}_{1-x} \text{Gd}_x \text{Co}_3 \)

The data obtained make it possible to construct the complete \( H \)-versus-\( t \) magnetic phase diagram for the system \( \text{Y}_{1-x} \text{Gd}_x \text{Co}_3 \). As we have already mentioned, two types of metamagnetic transitions are possible in this system and in the compounds \( \text{Y}_{1-x} \text{R}_x \text{Co}_3 \) with other heavy rare earths: metamagnetic transitions of the cobalt d system from a weakly magnetic into an intermediate state in a weakly magnetic field \( H_{\text{m1}} \) and from an intermediate state into a strongly magnetic state in an effective field \( H_{\text{m2}} \) as well as transitions from the ferrimagnetic phase into a noncollinear ferrimagnetic phase in the field \( H_{\text{m1}} \) and from the noncollinear phase into the ferrimagnetic phase in the field \( H_{\text{m2}} \) [see Eq. (4)].

According to the experimental data, \( H_{\text{m1}}, H_{\text{m2}} < H_{\text{c1}} \) in \( \text{Y}_{1-x} \text{Gd}_x \text{Co}_3 \) for all \( t \), and for this reason the transition into the noncollinear phase in the field \( H_{\text{c1}} \) occurs from the

![FIG. 6. Computed H-versus-t magnetic phase diagram for \( \text{Y}_{1-x} \text{Gd}_x \text{Co}_3 \). The circles and squares represent the experimental data. 1—Weakly ferrimagnetic collinear phase, 2—intermediate ferrimagnetic collinear phase, 3—strongly ferrimagnetic collinear phase, 4—noncollinear phase (cobalt in a strongly magnetic state), and 5—strongly ferromagnetic phase.](image-url)
The noncollinear phase occurs from the weakly ferrimagnetic state. The spontaneous intermediate and weakly ferrimagnetic states arise for \( t > t_{\text{comp}} \). Since in this case the cobalt subsystem is oriented antiparallel to the field, for \( t > t_{\text{comp}} \) demagnetization of the \( d \) subsystem should be observed: transitions from the strongly ferrimagnetic into the intermediate and weakly ferrimagnetic state. For fields \( H > H_2 \), when the magnetic moments of the \( d \) and \( f \) subsystems are parallel to one another (the system is ferromagnetic), the reverse transition of the \( d \) subsystem from a weakly magnetic state into an intermediate and strongly magnetic state occurs. Estimates made on the basis of Eqs. (2) and (4) under the assumption that the exchange parameter \( J_{d-f} \) is the same for all rare earths show that phase diagrams of this type should be observed for the mixed systems \( Y_{1-x}R_xCo_3 \), where \( R = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{and Tm} \). We note that in some cases the phase diagram could become much more complicated if the fact that \( J_{d-f} \) assumes different values in different non-equivalent positions is taken into account. Experimental investigations of the phase diagrams of some systems of this type are in progress.

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\[ H \]

**FIG. 7.** Qualitative \( H \)-versus-\( t \) magnetic phase diagram for \( Y_{1-x}R_xCo_3 \), \( R = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{and Tm} \). 1—Weakly ferrimagnetic collinear phase; 2—Intermediate ferrimagnetic collinear phase; 3—Strongly ferrimagnetic phase; 4—Noncollinear phase (cobalt in a weakly ferromagnetic state); 5—Strongly ferromagnetic phase, and 6—Intermediate ferromagnetic phase, and 7—Weakly ferromagnetic phase.

In the mixed compounds \( Y_{1-x}R_xCo_3 \) with other heavy rare earths, however, a different situation is possible when the metamagnetic-transition fields \( H_{a1} \) and \( H_{a2} \) are higher than the field \( H_{c1} \) of the transition into the noncollinear ferrimagnetic phase as \( t \rightarrow 0 \). In the simplest case, if it is assumed that \( \lambda_{d-f} \) has the same value in the nonequivalent cobalt positions, then the \( H \)-versus-\( t \) phase diagram for such compounds has the form shown in Fig. 7. The transition into the noncollinear phase occurs from the weakly ferrimagnetic state. The spontaneous intermediate and weakly ferrimagnetic states arise for \( t > t_{\text{comp}} \). Since in this case the cobalt subsystem is oriented antiparallel to the field, for \( t > t_{\text{comp}} \) demagnetization of the \( d \) subsystem should be observed: transitions from the strongly ferrimagnetic into the intermediate and weakly ferrimagnetic state. For fields \( H > H_2 \), when the magnetic moments of the \( d \) and \( f \) subsystems are parallel to one another (the system is ferromagnetic), the reverse transition of the \( d \) subsystem from a weakly magnetic state into an intermediate and strongly magnetic state occurs. Estimates made on the basis of Eqs. (2) and (4) under the assumption that the exchange parameter \( J_{d-f} \) is the same for all rare earths show that phase diagrams of this type should be observed for the mixed systems \( Y_{1-x}R_xCo_3 \), where \( R = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{and Tm} \). We note that in some cases the phase diagram could become much more complicated if the fact that \( J_{d-f} \) assumes different values in different non-equivalent positions is taken into account. Experimental investigations of the phase diagrams of some systems of this type are in progress.

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