Itinerant metamagnetism and ferromagnetism in the $M(Co_{1-x}Al_x)_2$ ($M \equiv Y$ and Lu) systems: The effect of unit cell volume

I. L. Gabelko, R. Z. Levitin, A. S. Markosyan, V. I. Silantiev, and V. V. Snegirev

Moscow State University

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The magnetic properties of the $(Y_{i-t}Lu_t)(Co_{1-x}Al_x)_2$ system, whose lattice parameter remains unchanged under substitutions, were investigated in the concentration range $0 \leqslant x \leqslant 0.22$. The concentration dependence of the metamagnetic transition fields from the paramagnetic to the ferromagnetic state was analyzed together with the features of the onset of ferromagnetic ordering; a magnetic (x–T) phase diagram of this system is also plotted. A comparison with the results from analogous studies of the $Y(Co_{1-x}Al_x)_2$ and $Lu(Co_{1-x}Al_x)_2$ systems in which the itinerant metamagnetism phenomenon was also observed experimentally suggests that the principal factor affecting the evolution of the magnetic properties of YCo_2 and $LuCo_2$ under Al substitution of Co is the change in d-electron concentration, and not the growth of the unit cell parameter.

INTRODUCTION

Interest in the intermetallides $M(Co_{1-x}Al_x)_2$, where $M = Y$, Lu ($C15$ cubic Laves phase for $x \leqslant 0.2$) can be attributed to the fact that these compounds are among the few systems in which experimental observations have been made of itinerant metamagnetism; the transition of the band electrons from the paramagnetic to the ferromagnetic state in an external magnetic field.[1-5] The itinerant metamagnetism phenomenon was initially predicted theoretically for the d-band paramagnets YCo_2 and $LuCo_2$ and is associated with anomalies in the density-of-states curve of the collectivized electrons near the Fermi level.[6-8] Itinerant metamagnetism was recently observed experimentally in them;[9,10] the critical metamagnetic transition field H_c was ~ 700 kOe for both of these intermetallides.

An important feature of $M(Co_{1-x}Al_x)_2$ compounds containing yttrium and lutetium is that their metamagnetic transition field decreases with increasing aluminum concentration, and compositions with $x \geqslant x_c$ ($x_c = 0.12$ for systems with yttrium and $x_c = 0.10$ for systems with lutetium) are itinerant ferromagnets.[2,3] It is believed that this evolution of the magnetic properties of the $M(Co_{1-x}Al_x)_2$ compounds derives from the fact that the density of states of the band d-electrons on the Fermi level $N(E_f)$ grows with increasing aluminum concentration, and this electron system approaches the Stoner criterion for the onset of band ferromagnetism $IN(E_f) \geqslant 1$ (I is the exchange interaction parameter).

However, other authors interpret the rise of $N(E_f)$ differently. A number of studies[3,4] have concluded that the increase in the density of states from Al-substitution of Co is due to narrowing of the d-band as a result of an increase in the lattice parameter (the metallic radius of aluminum, $r_{Al} = 1.432$ Å, is substantially greater than that of cobalt, $r_{Co} = 1.252$ Å [11]). The authors of Refs. 1, 2 believe that the principal cause of the change in properties of the $M(Co_{1-x}Al_x)_2$ systems as a function of x can be traced to the decreasing density of $3d$-electrons associated with Al substitution ($3d^0$ configuration) of Co ($3d^7$ configuration). Since the Fermi level lies on the descending section of the $N(E)$ relation in the YCo_2 and $LuCo_2$ compounds,[8] such a reduction in the d-electron concentration will cause $N(E_f)$ to rise.

In order to acquire a more complete understanding of the nature and features of the evolution of the magnetic properties of $M(Co_{1-x}Al_x)_2$ ($M = Y$, Lu) it is necessary to isolate the various factors affecting the band structure of these compounds under Al-substitution of Co. In the present paper we synthesized a $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system in which the crystal lattice parameter x was maintained at a constant level equal to the lattice parameter of pure YCo_2 as the aluminum concentration changed due to partial Lu-substitution of Y; the magnetic properties of this system were also investigated. Since the lattice parameter of YCo_2 ($a_{YCo_2} = 7.221$ Å), is substantially greater than that of $LuCo_2$ ($a_{LuCo_2} = 7.121$ Å), the condition $a_{(YLu)(CoAl)_2} = \text{const} = a_{YCo_2}$ will hold over a rather broad concentration range to $x = 0.22$ in the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system.

EXPERIMENTAL TECHNIQUE

Polycrystalline $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ samples were melted in a copper water-cooled crucible in an argon atmosphere within an induction furnace and annealed in a dynamic vacuum of 10^{-3} at 850 °C for 180 hours. The single-phase composition of the samples and their lattice parameter were monitored by x-ray analysis.

Samples with $0.06 \leqslant x \leqslant 0.22$ whose lattice parameter was within ± 0.009 Å of the lattice parameter of YCo_2 were synthesized (this deviation is more than an order of magnitude less than the variation of the lattice parameter of the $Y(Co_{1-x}Al_x)_2$ and $Lu(Co_{1-x}Al_x)_2$ systems over the same range of x). The table shows the compositions of the samples of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system together with their lattice parameters.

A $Lu(Co_{1-x}Al_x)_2$ system in which the lattice parameter went from 7.121 Å ($x = 0.0$) to 7.220 Å ($x = 0.2$) with increasing aluminum concentration was analyzed for comparison purposes.

The susceptibility in weak variable magnetic fields of ~ 3 Oe, magnetization in pulsed magnetic fields up to 270 kOe, and the temperature dependence of the crystal lattice parameter were measured by x-ray analysis. All measure-

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TABLE I. Lattice parameters a (Å), aluminum (x) and lutetium (t) concentrations of the synthesized compositions of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system.

N	x	t	a (±0,003)
1	0,060	0,294	7,211
2	0,070	0,341	7,220
3	0,075	0,364	7,216
4	0,085	0,410	7,222
5	0,090	0,432	7,221
6	0,095	0,455	7,219
7	0,100	0,477	7,220
8	0,125	0,586	7,223
9	0,150	0,692	7,224
10	0,200	0,893	7,229
11	0,220	0,970	7,225

ments were carried out over the temperature range 4.2–300 K.

EXPERIMENTAL RESULTS

Figure 1 shows the magnetic field dependence of the magnetization of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ compounds at 4.2 K. These compounds remain paramagnetic for $x \leqslant 0.06$ over this range of fields, and metamagnetic transitions from the para- to the magnetically-ordered phase are observed as the aluminum concentration increases. The fields H_c of these transitions decrease nearly linearly with increasing aluminum concentration (Fig. 2), while compositions with $x_c \geqslant 0.1$ are ferromagnetically ordered in zero field. There is a narrow range of $\Delta x \approx 0.01$ near x_c (compositions with $x = 0.09$ and 0.095) in which the compounds have a moderately large spontaneous ferromagnetic moment (~ 0.1–$0.2 \mu_B$/form. unit), while these samples have a metamagnetic transition in an external field.

The saturation magnetic moment as well as the magnetic moment of metamagnetic compounds immediately following the metamagnetic transition are shown in Fig. 3 as a function of aluminum concentration x. We note that not only does the spontaneous magnetization of these compounds decrease with increasing x, but the moment per cobalt atom also decays. This same figure shows the concentration dependence of the Curie temperature of the test system. It is clear that T_c is a maximum in the composition with $x = 0.15$ and drops precipitously near $x_c = 0.1$.

Ferromagnetic ordering of these compounds is accompanied by giant magnetovolumetric anomalies: $\omega_s = \Delta V/V \approx 10^{-3}$ comparable in magnitude to the magnetovolumetric anomalies in RCo_2 ($\approx 5.5 \cdot 10^{-3}$; cf. Ref. 12). Figure 4 shows the temperature dependence of the lattice parameter for compositions with $x = 0.15$ and 0.22 of the $(Y_{1-t}Lu_t) \times (Co_{1-x}Al_x)_2$ system which demonstrates this effect: Below T_c the experimental relation $a(T)$ deviates from the theoretical relation calculated in the Debye approximation based on the characteristics of pure YCo_2. At 6 K these values of ω_s are $1.6 \cdot 10^{-3}$ and $0.7 \cdot 10^{-3}$, respectively.

The existence of giant magnetovolumetric anomalies with ferromagnetic ordering confirms the itinerant nature of d-subsystem magnetism in $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$. The magnetovolumetric coupling coefficient $kC = \omega_s/M_s^2$ varies in the test system with increasing aluminum concentration over the range $(2\text{–}3) \cdot 10^{-3}$, remaining within an order of magnitude of the kC of other RCo_2 compounds: $1.4 \cdot 10^{-3}$ (Ref. 12) and of the $Lu(Co_{1-x}Al_x)_2$ system $(2\text{–}2.2) \cdot 10^{-3}$ (Ref. 2).

We note that if strongly ferromagnetic compositions near the critical composition $x_c = 0.1$ in $Lu(Co_{1-x}Al_x)_2$ undergo a first-order phase transition at the Curie temperature, they are second-order transitions in the

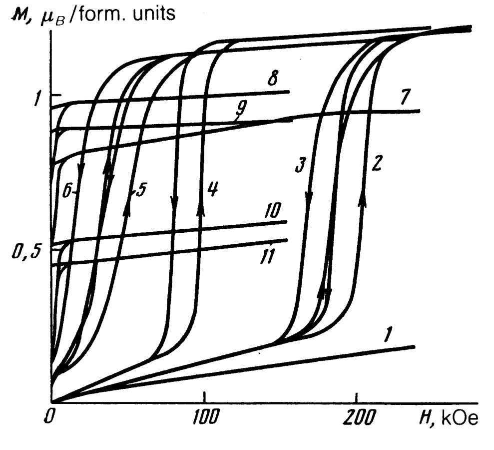

FIG. 1. Magnetization isotherms of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system at 4.2 K. $x = 0.06$ (1); 0.07 (2); 0.075 (3); 0.085 (4); 0.09 (5); 0.095 (6); 0.10 (7); 0.125 (8); 0.15 (9); 0.2 (10); 0.22 (11). Arrows indicate the direction of magnetic field variation.

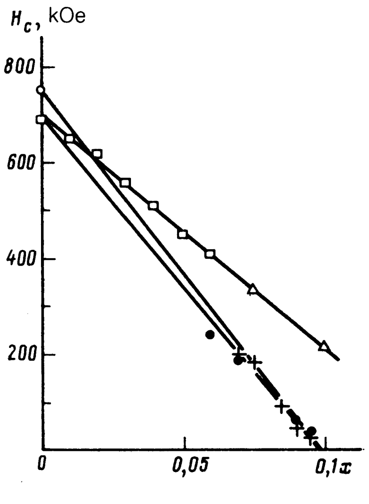

FIG. 2. Critical field of the metamagnetic transition (the mean of the values before and after application of the magnetic field) of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$—+, $Y(Co_{1-x}Al_x)_2$—△ (Ref. 1), □ (Ref. 10) and $Lu(Co_{1-x}Al_x)_2$—● systems plotted versus aluminum concentration x at 4.2 K; ○—Data from Ref. 9.

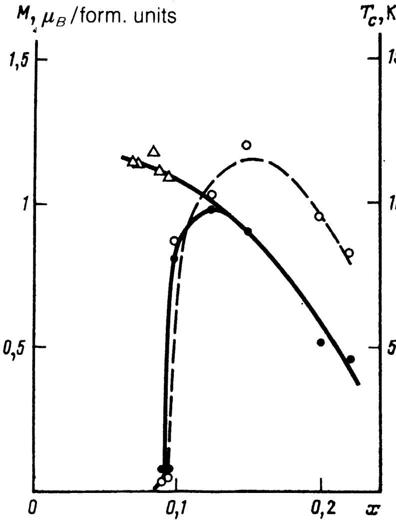

FIG. 3. Saturation magnetization (●), magnetization following the metamagnetic transition (△) at 4.2 K and the Curie temperature (○) of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system versus aluminum concentration x.

$(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ four-component system.

The metamagnetic character of magnetization is observed not only at 4.2 K but at higher temperatures as well in the paramagnetic compounds of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system. Figure 5 shows sample magnetization curves of a metamagnetic compound with $x = 0.085$ at various temperatures. The critical field of the metamagnetic transition rises with increasing temperature, while the transition itself is smeared out and is not observed above ~130 K. Here the hysteresis of the transition decreases and vanishes at ~100 K. Evidently this temperature corresponds to the tricritical point above which the metamagnetic transition becomes a second-order phase transition.

DISCUSSION OF RESULTS

The experimental data reported here show that the magnetic behavior of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system with a lattice parameter that remains constant with changing concentration is strongly dependent on the Al-substitution concentration. As we see from Fig. 2 the variation of H_c is $\approx$65–70 kOe with changing x in this system per 1 at.% Al in the d-subsystem and is very close to the $\Delta H/\Delta x$ of the other two systems $Y(Co_{1-x}Al_x)_2$ and $Lu(Co_{1-x}Al_x)_2$. Ferromagnetic ordering of all three systems also occur at approximately identical aluminum concentrations $x_c \approx 0.1$. Therefore a comparison of the experimental data for the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system with a fixed lattice parameter and the previously derived results for the $Y(Co_{1-x}Al_x)_2$ [1, 3] and $Lu(Co_{1-x}Al_x)_2$ systems[2,4,5] systems in which the lattice parameter rose with increasing x, shows that all three systems manifest qualitatively identical behavior. Consequently a change in the unit cell volume is not the dominant factor affecting the magnetic properties of the MCo_2 compounds with nonmagnetic rare earths upon d-metal atom substitutions and the primary cause of the onset of ferromagnetic ordering in these intermetallides upon partial Al-substitution of Co is the decreasing concentration of d-electrons, which in turn causes the density of states on the Fermi level to rise.

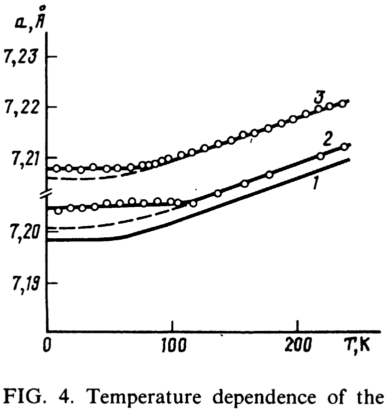

FIG. 4. Temperature dependence of the unit cell parameter of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ compounds, $x = 0.0$ (1), 0.15 (2), 0.22 (3). Dashed lines: Lattice contribution calculated at the Debye temperature $\Theta_D = 270$ K.

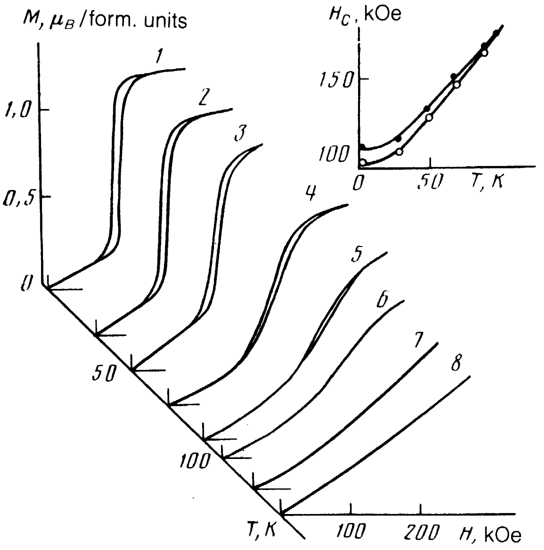

FIG. 5. Magnetization isotherms of the $(Y_{0.59}Lu_{0.41})(Co_{0.915}Al_{0.085})_2$ compound at various temperatures: 4.2 (1), 30 (2), 50 (3), 70 (4), 90 (5), 100 (6), 118 (7), 133 (8) K. The temperature dependence of the critical field H_c upon exposure to (●) and removal from (○) the magnetic field.

There are also, however, certain differences in the magnetic properties of these systems.

First, weakly ferromagnetic ordering alone rise in $Y(Co_{1-x}Al_x)_2$ under strong Al-substitution (the magnetic moment of cobalt is less than $0.3\mu_B$/form. unit), and a metamagnetic transition to the strongly ferromagnetic phase with a magnetic moment $\approx 1\mu_B$/form. unit occurs in this phase when it is exposed to a magnetic field. At the same time the weakly ferromagnetic region with the metamagnetic transition in the other two regions is narrow, and the weakly ferromagnetic phase at high aluminum concentrations appears even in zero field. Therefore the magnetic (x–T) phase diagram of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system is externally similar to the diagram of the $Lu(Co_{1-x}Al_x)_2$ system, while it is not analogous to the diagram of the $Y(Co_{1-x}Al_x)_2$ system, although the crystal lattice parameter of the $(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2$ system is equal to that of the YCo_2 compound.

Second, our comparison of the character of the metamagnetic transitions in the $\mathrm{Lu(Co_{1-x}Al_x)_2}$, $\mathrm{Y(Co_{1-x}Al_x)_2}$ (Refs. 1-4) and $\mathrm{(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2}$ systems reveals one additional difference in their magnetic behavior: The transitions occur much more rarely in the first of these two systems than in the last two. The "smearing out" of metamagnetic transitions in the $\mathrm{Lu(Co_{1-x}Al_x)_2}$ system has been related to statistical fluctuations of the compound in certain studies.[2,13] It was therefore determined that no weakly ferromagnetic phase existed in this system, while compositions in the aluminum concentration range $0.078 \leqslant x \leqslant 0.095$ having a low magnetization $\sim 0.3–0.7\mu_B$/form. unit, were magnetically heterogeneous and consist of a "mixture" of the paramagnetic and strongly-ferromagnetic phases. At the same time the weakly ferromagnetic phase in the $\mathrm{Y(Co_{1-x}Al_x)_2}$ system is homogeneous.[14]

In light of this evidence we consider in greater detail the weakly ferromagnetic phase in $\mathrm{(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2}$. It is clear from Fig. 1 that the magnetic state of our two weakly ferromagnetic compositions with $x = 0.09$ and 0.095 remain identical before and after magnetization (curves 5 and 6). This highlights the fundamental difference between the weakly ferromagnetic phase of the $\mathrm{(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2}$ system and the weakly ferromagnetic phase of the $\mathrm{Lu(Co_{1-x}Al_x)_2}$ system: The second magnetization cycle in the latter system is significantly different from the first cycle.[2,4]

We were not successful in modeling magnetization curves of weakly ferromagnetic compositions of the $\mathrm{(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2}$ system accounting for only a single inhomogeneity (assuming no weakly ferromagnetic phase in the homogeneous system). Consequently a homogeneous weakly ferromagnetic state arises in the test compositions of the $\mathrm{(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2}$ system, while the statistical variations of the composition in this system are substantially weaker than in a pure lutetium system. We can therefore conclude from this analysis that a sequential transition of magnetic phases from the paramagnetic phase to the strongly ferromagnetic phase through a homogeneous weakly ferromagnetic phase is observed in the $\mathrm{(Y_{1-t}Lu_t)(Co_{1-x}Al_x)_2}$ four-component system under Al-substitution of Co.

It is possible that a weakly ferromagnetic homogeneous phase also occurs in the $\mathrm{Lu(Co_{1-x}Al_x)_2}$ system, although it was not identified due to its significant degree of inhomogeneity. However the question, as discussed above, of why the variation is greater in the $\mathrm{Lu(Co_{1-x}Al_x)_2}$ compounds than in the $\mathrm{Y(Co_{1-x}Al_x)_2}$ compounds remains open. Moreover, as we see from a comparison of the results of the present study to those of Refs. 2, 4 for $\mathrm{Lu(Co_{1-x}Al_x)_2}$, the smearing of the metamagnetic transitions in four-component compounds and, consequently, the inhomogeneity, are lower than in the $\mathrm{Lu(Co_{1-x}Al_x)_2}$ three-component compounds. This issue requires further analysis.

In conclusion we note our belief that it is best to seek quantitative differences in the magnetic behavior of systems containing yttrium and lutetium in the fact that the *d*-band in a system containing yttrium is formed by the 3*d*-electrons of cobalt and the 4*d*-electrons of yttrium at the same time that in the lutetium system in addition to the 3*d*-electrons of cobalt the 5*d*-electrons of lutetium are involved in the formation of the *d*-band. The differences in the characteristics of the 4*d*- and 5*d*-electrons is in fact responsible for the differing behavior of compounds containing lutetium and yttrium.

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