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Metamagnetism of itinerant d-electrons in Laves phase compounds $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$

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Abstract. Representative first-order metamagnetic transitions with a large hysteresis have been observed for $x \leq 0.06$. The transition field H_c for $x = 0.06$ is 220 kOe at 4.2 K. Simple but strong ferromagnetism is found for $x > 0.12$. A mixing state of ferromagnetic and paramagnetic states of Co is assured for $0.06 \leq x \leq 0.12$. The paramagnetic component in the state also exhibits the metamagnetic transition.

By surveying the temperature dependence of metamagnetism, a boundary temperature of the first- and second-order metamagnetic transitions, and a first-order magnetic transition in thermomagnetic curves are found for the first time. In relation to the magnetic phase transitions the critical parameters T_1 and H_1 are introduced and discussed. Finally a magnetic phase diagram is presented.

1. Introduction

Since itinerant electron metamagnetism was first predicted by Wohlfarth and Rhodes (1962), many experimental and theoretical works have been made for strongly exchange-enhanced paramagnetic metals such as Pd (Jarlborg and Freeman 1981) and the Laves phase compounds TiBe_2 (Monod *et al* 1980), YCo_2 , ScCo_2 and LuCo_2 (Schinkel 1978, Yamada and Shimizu 1985). These metal and compounds have a characteristic peak in their temperature-dependent susceptibilities (Lemaire 1966, Bloch *et al* 1971, Ishiyama *et al* 1984). A theoretical energy band study for Pd showed that the metamagnetic transition fields H_c are of the order of 10^3 kOe. Yamada *et al* (1987) have estimated that the values of H_c are 890 kOe, 940 kOe and 1200 kOe for YCo_2 , LuCo_2 and ScCo_2 , respectively. Recently, the typical metamagnetic transition has been found in pseudo-binary Laves phase compounds such as $\text{Y}(\text{Co}_{1-x}\text{Al}_x)_2$ (Aleksandryan *et al* 1985, Sakakibara *et al* 1986) and $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ (Endo *et al* 1987, 1988a). The values of H_c determined by extrapolation were 1000 kOe and 1800 kOe for YCo_2 and LuCo_2 , respectively. Signs of the transition have been found also for $\text{Sc}(\text{Co}_{1-x}\text{Al}_x)_2$ (Ishiyama *et al* 1987). Quite recently, the metamagnetic transitions for YCo_2 and LuCo_2 have been observed directly at about 10 K by Goto *et al* (1989, 1990). The values of H_c were about 690 kOe and 740 kOe with a hysteresis 20 kOe and 60 kOe wide in its magnetization curves for YCo_2

and LuCo_2 , respectively. The values were consistent with the theoretical values. All these results were the values in the ground state for the compounds and the temperature dependence of the metamagnetism has not yet been clarified.

On the other hand, the magnetic properties of the Laves phase compounds RCo_2 and $\text{R}_x\text{Y}_{1-x}\text{Co}_2$ (Lemaire 1966, Bloch *et al* 1975, Steiner *et al* 1978, Franse *et al* 1983, Duc *et al* 1985, 1988, 1989, Inoue and Shimizu 1982, 1988), where R is a heavy rare-earth element, have been studied in detail. A first-order magnetic transition has been found for the compounds RCo_2 with $\text{R} \equiv \text{Dy}$, Ho and Er , and a second-order transition for $\text{R} \equiv \text{Gd}$ and Tb . It has been understood for these compounds that the moment of the Co atom antiparallel to those of R elements is induced by a molecular field from the R moments just like the metamagnetism for the Co atom in compounds. From an analysis for these compounds the value of H_c of the 'effective' metamagnetism has been estimated to be about 1500 kOe for YCo_2 (Bloch *et al* 1975, Duc *et al* 1988) but, in this metamagnetism, hysteresis was not able to be represented and the temperature dependence of the transition field was neglected.

A characteristic feature of the compounds $\text{Y}(\text{Co}_{1-x}\text{Al}_x)_2$ (Yoshimura and Nakamura 1985), $\text{Sc}(\text{Co}_{1-x}\text{Al}_x)_2$ (Ishiyama and Endo 1986) and $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ (Endo *et al* 1987) is that ferromagnetism appears in appropriate regions of x . In the three compounds, metamagnetism has been observed commonly for x regions just below the ferromagnetic regions. Recently, Gabelko *et al* (1987) also studied the ferromagnetic and metamagnetic properties of $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ and discussed electronic conditions for the formation of the Co moment on the basis of the Stoner criterion.

The purpose of this work is as follows.

(i) The relationship between the ferromagnetism and the metamagnetism for $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ is shown in section 3 in addition to our results reported previously.

(ii) In particular, the temperature dependence of the metamagnetic transition is studied by taking note of the hysteresis in magnetization and of the transition field.

(iii) The focus of this paper is the characteristic transition process in the present system, where the metamagnetic transition is first order at temperatures below 65 K, while the transition is second order above 65 K. We call this temperature T_1 a critical temperature.

In section 4, evidence of the first-order magnetic transition in $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ will be shown. From an analysis of the thermomagnetic curves at a constant field a new critical field H_1 is introduced corresponding to T_1 . In this section a magnetic phase diagram is determined from all the results as a summary. A relation between H_c and T_{max} , which is the temperature where the susceptibility is a maximum, will be discussed in relation to H_c for LuCo_2 . Consideration of T_1 and H_1 , which are important parameters for determining the types of magnetic phase transition in the present system, will be given in the final paragraph of the section.

2. Experimental procedure

2.1. Preparation of samples

The purities of the starting metals were 99.99% for Co and Al, and 99.9% for Lu. Appropriate amounts of these metals for the samples were melted three times repeatedly in an argon arc furnace. The ingots thus obtained were homogenized at 850 °C in vacuum-sealed quartz tubes for 100 h. Portions of the ingots were crushed into powder through

Table 1. Values of the lattice constant a , the spontaneous magnetic moment μ (μ_{H} and μ_{L}), the Curie temperature T_{C} , the effective Bohr magneton number P_{eff} and the moment carrier number P_{c} defined as $P_{\text{eff}}^2 = P_{\text{c}}(P_{\text{c}} + 2)$. Two kinds of P_{eff} and P_{c} are obtained from the Curie constants at high and low temperatures.

x	a (Å)	μ (μ_{B}/Co)		$T \approx 7 T_{\text{C}}$		$T \approx 2 T_{\text{C}}$		T_{C} (K)
		μ_{H}	μ_{L}	P_{eff}	P_{c}	P_{eff}	P_{c}	
0.00	7.110			(3.55	2.50)			
0.04	7.124			3.03	2.19			
0.06	7.130	0.63	0.05	3.03	2.19	3.86	2.99	143
0.07	7.137		0.16	2.96	2.12	3.20	2.35	143
0.08	7.143	0.62	0.27	3.02	2.18	2.92	2.08	143
0.11	7.162	0.66	0.58	2.89	2.06	2.59	1.77	143
0.12	7.168		0.65	3.03	2.19	2.41	1.61	143
0.17	7.186		0.50	2.98	2.14	2.14	1.36	145
0.20	7.194		0.36					136
0.24	7.224		0.21					80

a 325 mesh sieve and annealed at 850 °C for a few minutes so that they were free from mechanical strain. The powder samples were used for x-ray analysis, magnetization measurements in a pulsed high field and NMR experiments (Shinogi *et al* 1987). For the magnetization measurements, nearly spherical samples of about 4.8 mm diameter were prepared to correct the demagnetizing field. In order to prevent the samples from contamination by some ferromagnetic phases, the Co component was kept slightly lower than the stoichiometric composition, e.g. $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_{1.95}$ for all samples.

A C15-type crystal structure was assured for all samples by x-ray powder diffraction using Fe $K\alpha$ radiation, although faint extra lines were detected for the samples with large x . The lattice constant linearly increases with increasing x as shown in figure 1 and in table 1, taking an intermediate course between the Y (Yoshimura and Nakamura 1985) and the Sc compound systems (Ishiyama and Endo 1986).

2.2. Magnetization measurements

The values of magnetization and susceptibility were determined in the following three ways.

(i) A vibrating-sample magnetometer was used for the spherically polished samples at constant temperatures from 4.2 to 300 K with a sweeping field of up to 56 kOe. The temperatures were controlled to within 0.5 K. The induced voltage in a search coil of the magnetometer was integrated and fed to a lock-in amplifier. The output signals were accumulated in a computer together with field current data. A nickel sphere was used for calibration of the apparatus.

(ii) The high-field magnetization was measured by an induction method for the powder samples at temperatures from 4.2 to 150 K by using the pulse magnets of the Institute for Solid State Physics, University of Tokyo. The duration time of the pulse field was about 20 ms. The maximum field was 400 kOe at 4.2 K, and 320 kOe at temperatures above 4.2 K.

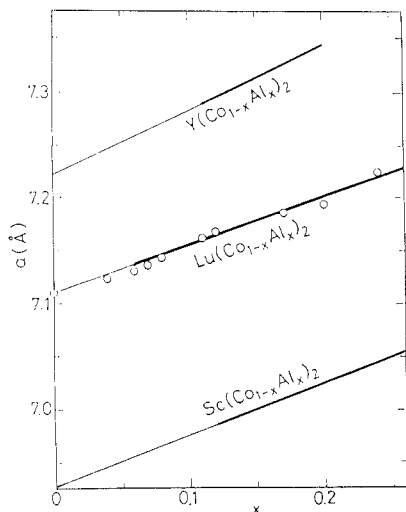


Figure 1. Lattice constant a of $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ at room temperature as a function of Al concentration x , and the lines above and below that for $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ represent the lattice constants of $\text{Y}(\text{Co}_{1-x}\text{Al}_x)_2$ and $\text{Sc}(\text{Co}_{1-x}\text{Al}_x)_2$, respectively; —, the ferromagnetic region for each compound.

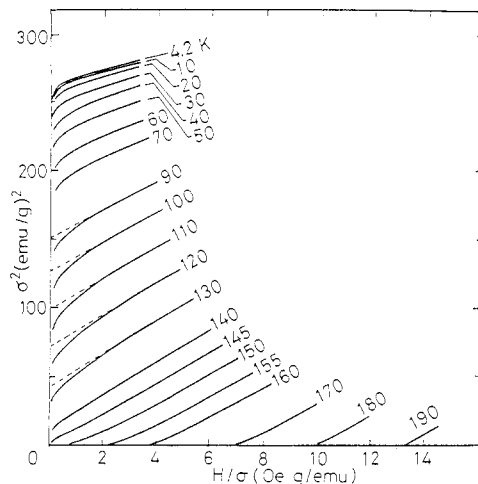


Figure 2. Magnetic isotherms represented in the form of σ^2 versus H/σ (Arrott plot) for the sample with $x = 0.17$. The spontaneous magnetization σ_0 is determined by extrapolation to $H/\sigma = 0$ along the broken lines.

(iii) The magnetic susceptibility was determined by the Faraday method using a balance and an electromagnet in fields up to 10 kOe from 4.2 to 1050 K. During the measurements the samples were sealed in evacuated quartz tubes in order to prevent oxidation at high temperatures.

3. Experimental results

3.1. Ferromagnetic region

The ferromagnetism was observed in the x -range from 0.06 to 0.24. As an example of a representative ferromagnet, the magnetization σ for $x = 0.17$ are presented in a σ^2 versus H/σ plot as shown in figure 2. Spontaneous magnetizations $\sigma_0(T)$ are determined from the nearly parallel broken lines. The temperature dependence of $\sigma_0(T)$ is given by the following formula:

$$[\sigma_0(T)/\sigma_0(0)]^2 = 1 - (T/T_C)^{11/6}$$

as shown in figure 3. We obtain the moment $\mu = 0.50 \mu_B$ per Co atom and the Curie temperature $T_C = 145$ K. It should be noted that the power of T/T_C in the formula is between 2 and $\frac{3}{2}$. The former is expected from the Stoner theory for weak itinerant-electron ferromagnetism (Edwards and Wohlfarth 1968) and the latter is from the self-consistent renormalization theory of spin fluctuation (Moriya 1985).

The σ^2 versus H/σ plots for the sample with $0.06 \leq x \leq 0.12$ showed an anomalous behaviour relating to the metamagnetism in the present system. For the sample with $x =$

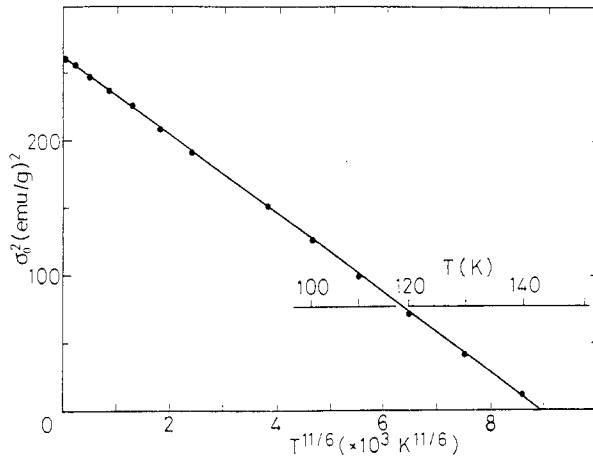


Figure 3. Plot of σ_0^2 against $T^{11/6}$ for the sample with $x = 0.17$.

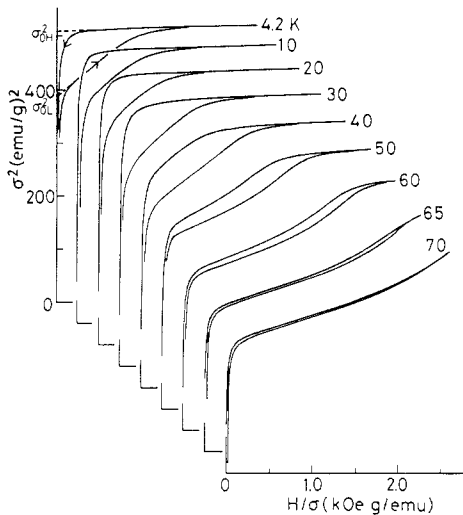


Figure 4. Plot of σ^2 versus H/σ for the sample with $x = 0.11$ with a hysteresis loop. Two kinds of the spontaneous magnetization (σ_{0H} and σ_{0L}) at 4.2 K are evaluated from the broken lines.

0.11, as an example, the values of σ^2 are shown against H/σ in figure 4, where the characteristic hysteresis in the magnetizations indicated by arrows is observed. The same anomalies as this were shown previously for $x = 0.08$ and 0.12 (Endo *et al* 1987). In order to determine the spontaneous magnetization in this case we take two values: σ_{0L} is from the initial magnetizations and the other, σ_{0H} , is determined by extrapolation from a high field as shown by the broken lines in figure 4.

The temperature dependences of σ_0 (σ_{0L} and σ_{0H}) thus obtained are shown in figure 5(a) for $0.06 \leq x \leq 0.12$ and in figure 5(b) for $x > 0.12$. Unusual forms of the σ_0 - T curves related closely to the metamagnetism are shown in figure 5(a), where the open and full symbols correspond to σ_{0H} and σ_{0L} , respectively, while the curves of σ_0 for $x > 0.12$ in figure 5(b) are rather simple for an itinerant ferromagnet. It is to be noted that the apparent Curie temperatures T_C for $0.06 \leq x \leq 0.12$ is almost the same as that for $x = 0.12$ ($T_C = 143$ K).

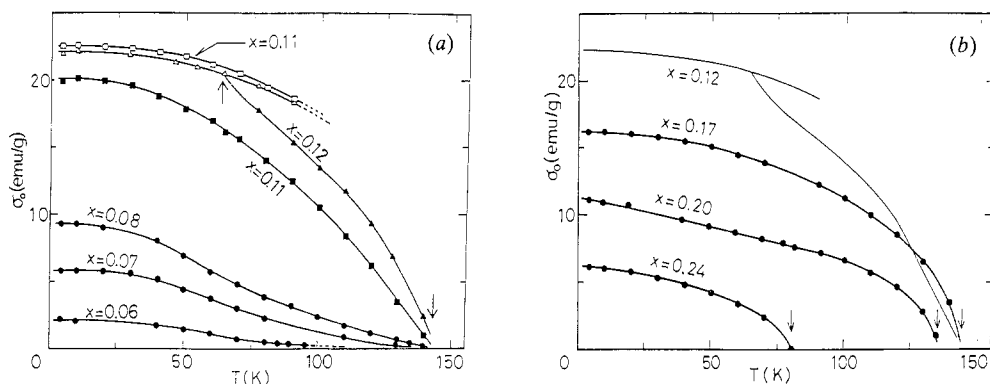


Figure 5. Temperature dependence of the spontaneous magnetization σ_0 for the ranges (a) $x > 0.12$: $\square, \triangle, \sigma_{0H}$ (see text); $\blacksquare, \blacktriangle, \bullet, \sigma_{0L}$ (see text); \uparrow, T_1 (see text); \downarrow, T_C and (b) $0.06 \leq x \leq 0.12$.

In relation to the magnetization results, NMR studies previously reported (Shinogi *et al* 1987, 1988) showed very important results for interpretation from a microscopic point of view. The results were for compounds with $0.06 \leq x \leq 0.12$ and showed that

- (i) the ferromagnetic and paramagnetic states of the Co atoms coexist at 4.2 K,
- (ii) the NMR intensity of the ferromagnetic Co increases with increasing magnetization and
- (iii) the values of hyperfine fields of ^{59}Co for the compounds with $x = 0.06$ and 0.08 are almost the same as that with $x = 0.12$.

From the NMR results it can be demonstrated that the Co atoms in this concentration range are in either a ferromagnetic state with a moment of $0.65 \mu_B$ or non-magnetic state, and that nearly the same values as T_C for $0.06 \leq x \leq 0.12$ correspond to the existence of the same ferromagnetic state of the Co atoms in the compounds.

The composition dependence of the magnetic moment μ per Co atom is shown by the open circles in figure 6 together with the data (open squares) obtained by Gabelko *et al* (1987). The maximum moment is $0.66 \mu_B$ at $x = 0.11$. The values of μ for $0.06 \leq x \leq 0.11$ corresponding to μ_L which is evaluated from σ_{0L} mean the average moments of the ferromagnetic and paramagnetic states of the Co atoms. The values indicated by crosses in the figure are the ferromagnetic moments estimated from the NMR hyperfine fields of ^{59}Co as mentioned previously (Shinogi *et al* 1987). They seem to be constant at $0.65 \mu_B$ in the region $0.06 \leq x \leq 0.12$. The data indicated by the full circles are obtained from the high-field measurements of magnetization shown in the next section.

On the other hand, our study of forced magnetostrictions for the compounds with $0.06 \leq x \leq 0.12$ reported previously (Iijima *et al* 1989) can be reasonably explained from the two states of Co mentioned above. In this study we can show that the magnetostrictions $\omega(H)$ at 4.2 K for $x = 0.06$ and 0.08 are proportional to $\mu(H)$ but not μ^2 below the saturation moment. Since the values of $\mu(H)$ mean the average Co moments which consist of $0.65 \mu_B$ and $0 \mu_B$ at a field H , the increase in $\mu(H)$ with increasing H corresponds to the increase in the number of the ferromagnetic Co with $0.65 \mu_B$, to which

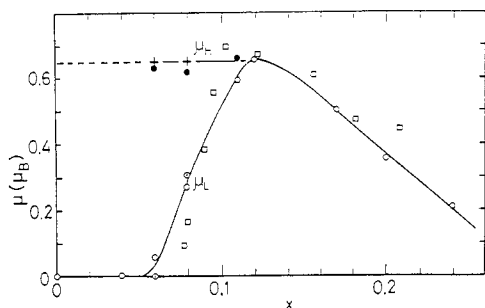


Figure 6. Al concentration dependence of the magnetic moment μ per Co atom at 4.2 K: \circ , μ_L (average moment determined at low fields) for bulk samples; \odot , μ_L for powder samples; \bullet , data from the pulsed high-field measurements; +, data from the NMR hyperfine field; \square , after Gabelko *et al* (1987).

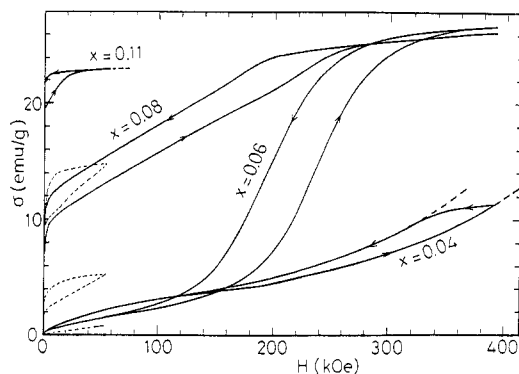


Figure 7. Magnetization curves with hysteresis for $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ at 4.2 K: ---, our previous results; the arrows on the curves indicate the directions of the field sweep.

ω is thus proportional. From all the results it can be said that the compounds with $0.06 \leq x \leq 0.12$ are in a magnetically inhomogeneous state.

3.2. Metamagnetic transition

As was reported previously (Endo *et al* 1988a, b), the metamagnetic transition was observed for the powder samples with $x = 0.04, 0.06$ and 0.08 by the magnetization measurements in pulsed high fields up to 400 kOe at 4.2 K as shown in figure 7. A typical metamagnetic transition is observed for $x = 0.06$ with a large hysteresis in the magnetization curve. The transition is incomplete for $x = 0.04$ because the transition field H_c is too high to be observed. For the ferromagnetic sample with $x = 0.08$, it can be considered that the transition takes place for the paramagnetic component in the sample. The transition is observed also for the bulk sample with $x = 0.11$ as shown in figure 4. The previous results observed for the bulk samples (Endo *et al* 1987) are also shown by the broken curves in the figure. The remarkable difference between the magnetization curves of the bulk and powdered states of the sample with $x = 0.06$ may be due to large magnetovolume effects in the present compounds (Iijima *et al* 1989). The values of σ_{0H} are determined by extrapolation of the magnetization at a high field through the σ^2 versus H/σ plots. The Co moments μ_H evaluated from σ_{0H} are shown in figure 6 by the full circles and listed in table 1. It should be emphasized that the values are very close to the moment for $x = 0.12$.

In order to make the present metamagnetism clearer, the magnetizations for $x = 0.06$ and 0.08 were measured at the various temperatures in fields up to 290 kOe. The results for $x = 0.06$ are shown in figure 8. The transition field H_c and the width ΔH of the hysteresis are determined at the centre of the hysteresis as shown by the broken vertical and horizontal lines in the figure. It is to be noted that the metamagnetic behaviours are still retained at temperatures above 65 K although not hysteresis. The behaviours are consistent with the results of the forced magnetostrictions reported

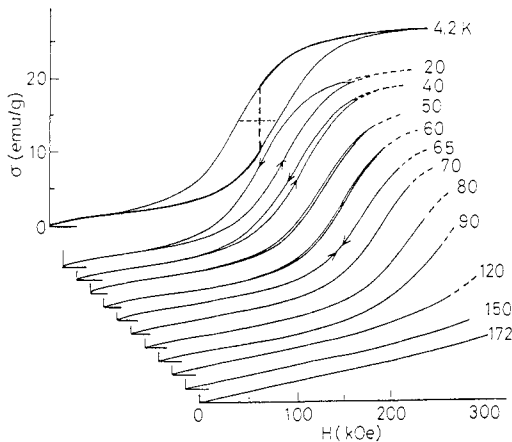


Figure 8. Magnetization curves for $x = 0.06$ at various temperatures in a pulsed high field: —, stable magnetization curve; broken vertical line of the centre on the hysteresis loop at 4.2 K indicates the critical field H_c . The width ΔH of the hysteresis is determined at H_c .

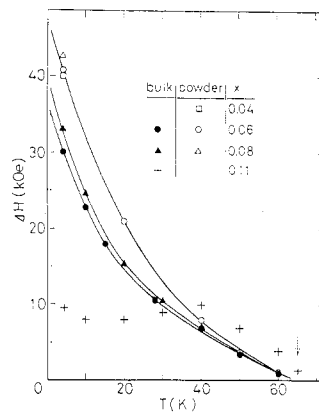


Figure 9. Temperature dependence of the width ΔH of the hysteresis. T_1 is denoted by the arrow. The concentrations x corresponding to each symbol are listed in the table in the figure.

previously (Iijima *et al* 1989), i.e. the hysteresis in the magnetizations disappears completely at 77 K. From these results it can be said that the metamagnetic transitions are of first and second order below and above 65 K, respectively.

The values of ΔH decrease rapidly with increasing temperature and disappear at about 65 K for all samples, as shown in figure 9. The full circles and full triangles in the figure are the data determined for bulk samples reported already (Endo *et al* 1987). It seems that the unusual data indicated by the crosses for the bulk sample with $x = 0.11$ are due to ambiguous determination of ΔH because of the too low value of H_c . As mentioned above, the magnetizations for $x \leq 0.12$ decrease rapidly with increasing temperature at about 65 K, as shown in figure 5(a). This temperature is consistent with the temperature at which the hysteresis disappears. Therefore, we consider the temperature, denoted by T_1 , as a kind of a critical temperature.

The temperature dependence of H_c is obtained for various x as shown in figure 10, where the critical temperature T_1 is shown by the broken vertical line. We define H_1 , indicated by the arrows in the figure, as another critical field at T_1 for a reason mentioned later. This figure means that the upper left and lower right sides of each curve correspond to the ferromagnetic and paramagnetic states, respectively. Thus, crossing the full and broken curves in any direction corresponds to the first- and second-order phase transition, respectively. The type of the metamagnetic transition changes from first order to second order at T_1 . This is supported also by our previous work on the forced magnetostriction (Iijima *et al* 1989). At a constant field between H_c at 0 K and H_1 for each composition, the magnetic first-order transition takes place inevitably on the thermomagnetic curves as shown in the next section. Consequently, both H_1 and T_1 are the critical parameters for the magnetic phase transition in the present system.

3.3. Magnetic susceptibility

The temperature dependence of the magnetic susceptibilities $\chi(T)$ for $x = 0$ and 0.04 show broad maximum values around 450 K and 230 K, respectively, as shown in figure

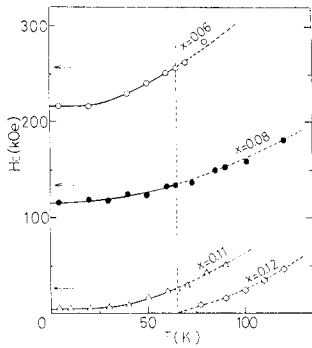


Figure 10. Temperature dependence of the transition field H_c : —, first-order metamagnetic transition at H_c ; ---, second-order metamagnetic transitions at H_c ; the vertical broken line is drawn at T_1 ; ← (for each concentration), H_1 which corresponds to H_c at T_1 .

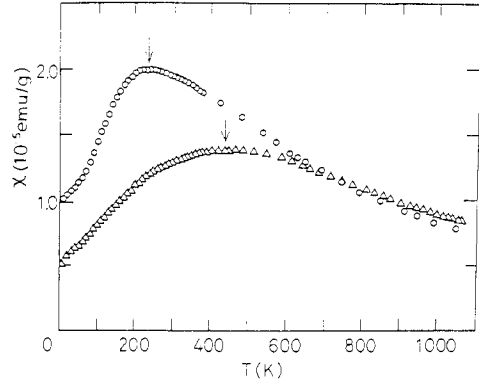


Figure 11. Temperature dependence of the magnetic susceptibility χ for the $x = 0$ (Δ) and $x = 0.04$ (\circ): ↓, temperature T_{max} where χ is a maximum.

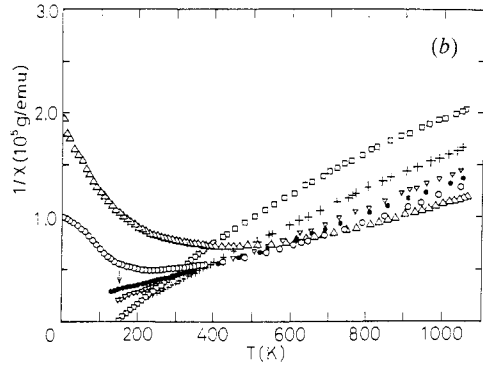
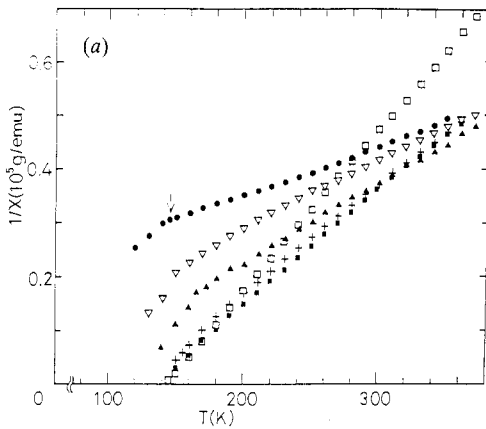


Figure 12. Temperature dependences of the inverse susceptibility χ^{-1} for $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ at temperatures (a) below 370 K and (b) below 1050 K: Δ , $x = 0$, \circ , $x = 0.04$; \bullet , $x = 0.06$; ∇ , $x = 0.07$; \blacktriangle , $x = 0.08$; $+$, $x = 0.11$; \blacksquare , $x = 0.12$; \square , $x = 0.17$; the arrows indicate T_C .

11. The maximum temperature T_{max} , where χ has a peak, shifts towards low temperatures with increasing x . The temperature variations in the inverse susceptibilities $\chi(T)^{-1}$ for the ferromagnetic compounds are shown in figure 12(a) ($T_C < T < 380$ K) and for all samples in figure 12(b) ($T < 1100$ K). Figure 12(a) shows that $\chi(T)$ for each compound obeys the Curie–Weiss law in this temperature range, whereas figure 12(b) shows that $\chi(T)$ deviates remarkably from the law. It seems that the values of χ^{-1} for all compounds run parallel to each other increasing temperature. Although the curves are remarkably convex for $x = 0.17$ and 0.11 , no proof of ferrimagnetism was found for them.

From the experimental results, we evaluated the values of the effective Bohr magneton numbers P_{eff} and the moment carrier numbers P_c defined as $P_{eff}^2 = P_c(P_c + 2)$ at

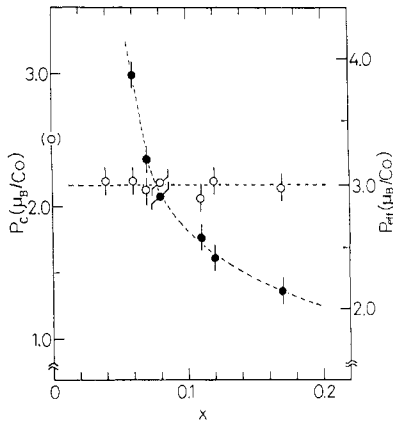


Figure 13. Al concentration dependence of the moment carrier number P_c and the effective Bohr magneton number P_{eff} per Co atom: \circ , P_c at a high temperature ($T \approx 7 T_C$), \bullet , P_c at a low temperature ($T \approx 2 T_C$).

high ($T \approx 7 T_C$) and low ($T \approx 2 T_C$) temperatures. The results are shown in figure 13 and listed in table 1. The values of P_c obtained at low temperatures (full circles) depend strongly on the concentration x as seen in figure 13. This seems to be related to the occurrence of the ferromagnetism. On the contrary, the values of P_c at high temperatures (open circles) have an almost constant value of 2.2 ($P_{\text{eff}} = 3.0$) except for the value at $x = 0$. At higher temperatures the latter may be close to the constant value. Therefore the values of P_c take nearly the same values at sufficiently high temperatures irrespective of x . Moreover figure 13 shows that the value of P_c at high temperatures agrees with that at low temperatures near $x = 0.07$. This means that the Curie–Weiss law for $x = 0.07$ will hold over a wide temperature range with the nearly zero Weiss temperature as shown in the figure. The value of $x = 0.07$ is interestingly close to the concentration at which ferromagnetism occurs in this system.

4. Discussion

4.1. Evidence of first-order magnetic transition

In relation to metamagnetism, one stable magnetization curve can be defined as that at increasing field up to H_c and another at decreasing field down to H_c as shown by the bold lines in figure 8. Taking account of the first-order metamagnetic transition shown in the previous section, we can expect the first-order transition in the thermomagnetic curve to exist at a certain temperature. In order to make this clear, the results of the stable magnetizations are reconstructed with temperature T and field H as variables as shown in figure 14. The horizontal and vertical arrows in the figure indicate T_1 and H_1 , respectively.

In the figure the dotted shading instead of hysteresis corresponds to a discontinuous change in the magnetization. At a constant field in the range $220 \text{ kOe} < H < 260 \text{ kOe}$ (H_1) the first-order transition in the thermomagnetic curve can be deduced at a temperature below T_1 as shown by the bold broken curve, whereas for $H > H_1$ the transition is second order at a temperature above T_1 . From a similar consideration we can see the first- and second-order transitions in the thermomagnetic curves at other concentrations in figure 10, where the full curves correspond to the walls. Therefore the

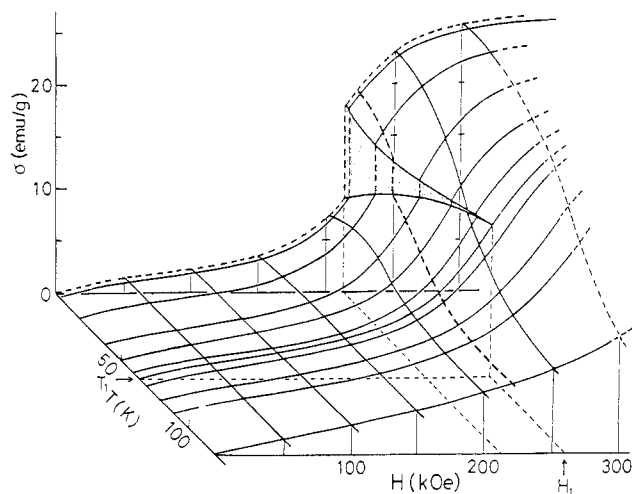


Figure 14. Stable magnetizations for $\text{Lu}(\text{Co}_{0.94}\text{Al}_{0.06})_2$ with temperatures T and fields H as variables: ---, thermomagnetic curve where the first-order magnetic transition exists; \square , first-order magnetic phase transition; \rightarrow , T_1 ; \uparrow , H_1 .

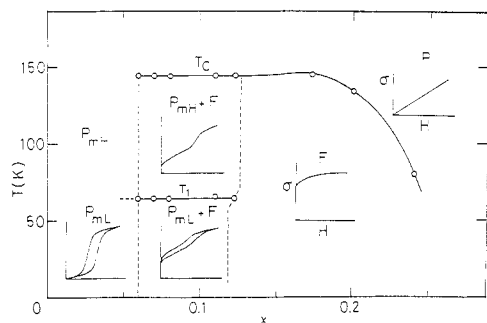


Figure 15. Magnetic phase diagram for $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$. The insets show the representative magnetization curves in each phase. The critical temperature T_1 is the boundary between the metamagnetic transitions of first and second order.

anomaly in the thermomagnetic curve (see figure 5(a)) for $x = 0.12$ at 65 K can be explained from the second-order transition because $H_1 = 0$ kOe (see figure 10).

4.2. Magnetic phase diagram for $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$

As a summary of the experimental results, the magnetic phase diagram for $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ is made as shown in figure 15. F, P and T_C in the figure correspond to the ferromagnetic and paramagnetic states and the Curie temperature, respectively. P_{mL} and P_{mH} correspond to the paramagnetic states at temperatures below and above T_1 , respectively. The insets show the characteristic magnetization curves for each region.

The compounds with $0.12 < x \leq 0.24$ are characteristic of the itinerant ferromagnetism which can be seen in the temperature dependence of the magnetizations and ratios of P_c to P_s .

For $0.06 \leq x \leq 0.12$ the compounds are in the mixed state of ferromagnet and exchange-enhanced paramagnet. It seems to be unreasonable that the samples in this region are chemically homogeneous at room temperature but magnetically inhomogeneous at 4.2 K. The proof of the chemical homogeneity is based on the x-ray diffraction results that the large-angle diffraction line with the index (551) for $x = 0.08$, for example,

lies between those for $x = 0.06$ and 0.12 without overlapping. On the other hand the magnetic inhomogeneity at 4.2 K for samples with the same compositions is clear from the results of the NMR spectra (Shinogi *et al* 1987) and magnetic measurements. As mentioned previously, the NMR experiments have already proved that the Co atoms are in either the non-magnetic or the magnetic state with $0.65 \mu_B$ in this concentration range. Therefore we can expect that the diffraction lines at 4.2 K for $x = 0.08$ split into two groups: one belongs to the ferromagnetic part and the other to the non-magnetic part of the sample, because of the large magnetovolume effect in the present system (Iijima *et al* 1989). In any case, a detailed x-ray analysis at low temperatures is important for the samples with $x = 0.06$ – 0.12 . The reason why the broken line at around $x = 0.12$ in figure 15 is twisted is that all the Co atoms in the compound are in the magnetic state with a unified moment of nearly $0.65 \mu_B$ below T_1 , but above T_1 a portion of the Co atoms change to the non-magnetic state.

For $0 \leq x \leq 0.06$ the present system exhibits the itinerant-electron metamagnetism with hysteresis at low temperatures. This hysteresis disappears at T_1 , although it is still in question whether T_1 is just 65 K or not over this region. The compounds in this region are exchange-enhanced Pauli paramagnets in a low external field which show maxima in the temperature dependence of χ .

4.3. The relation between H_c and T_{max}

In our previous work (Endo *et al* 1988a) we estimated the value of H_c for LuCo_2 from extrapolation by means of a logarithmic plot of H_c against x , giving a roughly linear line. The value of H_c was 1800 kOe, which is twice as large as the theoretical value of 940 kOe (Yamada *et al* 1987).

On the other hand it should be pointed out that there is a correlation between the value of H_c and T_{max} . The relation gives another way of estimating H_c for LuCo_2 (Endo *et al* 1988b). In order to attempt this, the temperature dependence of the Knight shifts K for the paramagnetic component in the compounds with $x = 0.06$ and 0.08 was measured to obtain the temperature dependence of χ , because the values of χ were difficult to measure directly (Shinogi *et al* 1988). They obtained broad peaks around 200 K in χ for both samples, i.e. the values of T_{max} were 200 K for those. Moreover, $T_C (= 143$ K) for $x = 0.12$ should be adopted as the minimum of T_{max} in $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$. Because the ferromagnetic components for $x = 0.06$ and 0.08 have the same values of T_C as that for $x = 0.12$ (see figure 5(a)), and the rest of the components are strongly paramagnetic and are just below the ferromagnetic state, T_{max} cannot take a lower value than 143 K (T_C for $x = 0.12$).

Consequently, from the nearly linear relation between H_c and T_{max} , we conclude that H_c of LuCo_2 is almost 1000 kOe, which is very near the theoretical value by Yamada *et al* (1987). Quite recently, the metamagnetic transition for LuCo_2 was directly measured in pulsed fields up to 1000 kOe by Goto *et al* (1990) and H_c was about 740 kOe at 8 K. Thus it is considered that the relation between H_c and T_{max} is more reliable than the relation between H_c and x for the estimation of H_c for LuCo_2 by extrapolation.

4.4. A consideration of T_1 and H_1

In the previous section we showed that the type of the metamagnetic transition changed from first order to second order at T_1 . We should point out that T_1 corresponds to a characteristic temperature T^* which is introduced to explain the types of magnetic

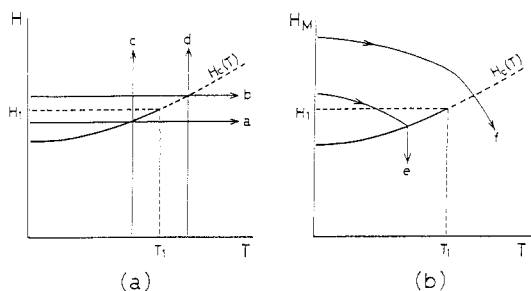


Figure 16. (a) Schematic illustration of the magnetic phase transition for $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ in constant external fields (lines a and b) and at constant temperatures (lines c and d). (b) Illustration of the transition for RCo_2 with the molecular fields acting on the Co atoms. The lines e and f correspond to the first- and second-order transitions, respectively.

transition at T_C in RCo_2 ($\text{R} \equiv$ heavy rare-earth) obtained by Inoue and Shimizu (1982, 1988). They discussed, on the basis of a study by Bloch *et al* (1975), that the type of magnetic transition at T_C in RCo_2 changes from the first to second order at T^* . This means that the sign of C_3 changes at T^* . This C_3 is the coefficient of M^4 in the expansion formula of the magnetic free energy in terms of the total magnetization $M = M_{\text{RE}} + M_d$, where M_{RE} and M_d are the magnetizations of the localized 4f and itinerant 3d electrons, respectively.

From the results in figure 14 we can show that the thermomagnetic curve for $x = 0.06$ shows a first-order magnetic transition if the external field is in the range $H_1 > H > 220$ kOe (H_c at 0 K), whereas it is second order if $H > H_1$. On the basis of the H_c versus T curves (see figure 10) the above processes are shown schematically in figure 16(a) indicated by the lines a and b. As the temperature T_1 is the boundary corresponding to H_1 , then the lines c and d result in the first- and second-order metamagnetic transitions, respectively. On the other hand the Co atoms in RCo_2 and $\text{Y}_{1-x}\text{R}_x\text{Co}_2$ have the molecular fields $H_M(T)$ instead of the external field. If $H_M(0) > H_c$, the compounds are in a ferrimagnetic state at the starting points of lines e and f as shown in figure 16(b). The two lines have to cross the $H_c(T)$ curve with increasing temperature. If the crossing point (H_c, T) is inside the critical point (H_1, T_1), the magnetic transition is of first order as shown by the line e. Then the line f is of second order when $H_M(0)$ is fully large. Thus it can be considered that T_1 in the present study, equivalent to T^* introduced by Inoue and Shimizu, and H_1 are simultaneously important in the magnetic phase transition. The value of H_1 depends on x from 260 kOe for $x = 0.06$ to null for $x = 0.12$, while T_1 is independent of x . The value of H_1 for LuCo_2 can be estimated to be about 800 kOe from the value of H_c for LuCo_2 if $T_1 = 65$ K. From the above considerations it can be said that the compounds RCo_2 with low and high T_C should exhibit the first- and second-order transitions at T_C , respectively. Moreover, the lower T_C , the sharper the transition of first order is. In fact the above behaviours are found in RCo_2 (Bloch *et al* 1975), $\text{Ho}_x\text{Y}_{1-x}\text{Co}_2$ (Steiner *et al* 1978), $\text{Er}_x\text{Y}_{1-x}\text{Co}_2$ (Duc *et al* 1988) and $\text{Tb}_x\text{Y}_{1-x}\text{Co}_2$ (Duc *et al* 1989).

According to Bloch *et al* (1975) the temperature T^* in RCo_2 should be 250 K corresponding to the T_{max} for YCo_2 , while Inoue and Shimizu (1988) assumed that $T^* = 150$ K for $\text{R}_x\text{Y}_{1-x}\text{Co}_2$ and Duc *et al* (1988, 1989) estimated experimentally that $T^* = 178$ K. However, the above temperatures T^* are three or four times larger than $T_1 = 65$ K for the present system. For $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ there seems to be no relation between T^* and T_{max} contrary to the suggestion by Bloch *et al* (1975), because the value of T_{max} lies between 450 K for $x = 0$ (LuCo_2) at a maximum and 143 K for $x = 0.12$ at a minimum. On the other hand there is a possibility that T_1 for LuCo_2 may not take the

same value as 65 K in this work. In order to make clear experimentally the relation between T^* , T_{\max} and T_1 it is necessary for the analysis of T^* to study $R_x\text{Lu}_{1-x}\text{Co}_2$.

5. Concluding remarks

From all the experimental results, the conclusions in this study on $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ compounds can be summarized as follows.

(i) The first-order magnetic transition for $\text{Lu}(\text{Co}_{0.94}\text{Al}_{0.06})_2$ is found for the first time on the thermomagnetic curve. The type of transition is characterized by the critical temperature T_1 and field H_1 defined for the present compounds.

(ii) The temperature T_1 , which is constant at 65 K, is phenomenologically equivalent to T^* introduced in the studies of RCO_2 . The value of H_1 depends strongly on the concentration x .

(iii) For $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ there is a nearly proportional relation between H_c and T_{\max} , from which the value of H_c for LuCo_2 is somewhat larger than the recent result measured directly.

(iv) The magnetic phase diagram for $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ is determined as shown in figure 15.

Finally, in comparison with the magnetic properties of $\text{Y}(\text{Co}_{1-x}\text{Al}_x)_2$ and $\text{Sc}(\text{Co}_{1-x}\text{Al}_x)_2$, the magnetic states of the Co atoms in $\text{Lu}(\text{Co}_{1-x}\text{Al}_x)_2$ are clearly distinguished between, i.e. the moment is either magnetic and $0.65 \mu_B$ or non-magnetic. There is no intermediate state with very small moments as observed for the Y and Sc compounds. In the metamagnetic transition the hysteresis width in the magnetization curve, which is roughly independent of x , is much larger than that for $\text{Y}(\text{Co}_{1-x}\text{Al}_x)_2$. The most characteristic property of the present compounds is the coexistent state which consists of the magnetic and non-magnetic states of the Co atoms. This results in a chemically homogeneous but magnetically inhomogeneous state which has never been found.

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