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The temperature dependence of the itinerant-electron metamagnetic transition in Laves-phase $Lu(Co_{1-x}Ga_x)_2$ compounds

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Abstract. The high-field magnetization and temperature dependence of the critical field have been investigated for Laves-phase $Lu(Co_{1-x}Ga_x)_2$ compounds. A clear itinerant-electron metamagnetic transition is observed and its critical field increases with increasing temperature for $x = 0.09$. The results are discussed on the basis of the Clausius–Clapeyron equation for the magnetic phase transition. This reveals that the magnetic entropy of these compounds decreases above the critical field, suggesting the suppression of the spin fluctuations due to the metamagnetic transition. This is consistent with the recent results on the field dependence of the electronic specific-heat coefficient of these compounds. The Arrott plots for the specimen with $x = 0.12$, which has a very low critical field, have also been investigated. The squared hypothetical spontaneous magnetization M_h^2 decreases linearly with increasing T^2 and the reduced M_h versus T plot for $Lu(Co_{0.88}Ga_{0.12})_2$ is very similar to the reduced magnetization for an Invar-type ferromagnetic $Lu(Cu_{0.83}Al_{0.17})_2$ compound. This results suggests that $Lu(Co_{0.88}Ga_{0.12})_2$ in the ferromagnetic state is expected to exhibit marked magnetovolume effects.

1. Introduction

In the ground state, itinerant-electron metamagnetism has been mainly discussed in terms of the characteristic feature of band structure (Wohlfarth and Rhodes 1962). Several band calculations have been carried out for Co-based Laves-phase compounds such as YCo_2 and $LuCo_2$ and the occurrence of the itinerant metamagnetic transition in these compounds discussed (Shimizu 1982, Cyrot and Lavagna 1979, Jarlborg and Freeman 1981, Yamada and Shimizu 1985). Recently, such an itinerant-electron metamagnetic transition has been confirmed by applying ultra-high magnetic fields to the cubic Laves-phase compounds YCo_2 and $LuCo_2$ (Goto *et al* 1989, 1990, Sakakibara *et al* 1990b).

At finite temperatures, many itinerant-electron metamagnets exhibit a maximum in the temperature dependence of magnetic susceptibility $\chi(T)$ (Lemaire 1966, Givord and Lemaire 1971). However, this behaviour is not explained in terms of the self-consistent renormalization (SCR) theory for spin fluctuation, which can qualitatively explain many physical properties of weak ferromagnets (Lonzarich and Taillefer 1985, Moriya 1985). Up to the present stage, the thermodynamic properties of itinerant-electron metamagnets are not well known, especially for the Co-based Laves-phase compounds (Yoshimura *et al* 1988, Sakakibara *et al* 1990a, b, Yamada 1991) which have a high critical field H_c in

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the range 600–800 kOe (Goto *et al* 1989, 1990). A marked reduction in the critical field of the metamagnetic transition has been confirmed by partial replacement of Co by other non-magnetic elements such as Al, Sn and Ga (Aleksandryan *et al* 1985, Sakakibara *et al* 1986, Murata *et al* 1991, 1992). Depending on the substitutional elements, no spontaneous magnetization appears in $Lu(Co_{1-x}Ga_x)_2$ compounds (Murata *et al* 1992), in contrast with $Y(Co_{1-x}Al_x)_2$ (Yoshimura and Nakamura 1985) and $Lu(Co_{1-x}Al_x)_2$ compounds (Endo *et al* 1988). Since $Lu(Co_{1-x}Ga_x)_2$ compounds exhibit a low metamagnetic transition (Murata *et al* 1992), they are good candidates in which to investigate the temperature dependence of the critical field. In the present paper, attention will be paid to the thermodynamic properties of the metamagnetic transition in $Lu(Co_{1-x}Ga_x)_2$ compounds.

2. Experimental details

Alloying of $Lu(Co_{1-x}Ga_x)_2$ was carried out by arc melting in an argon gas atmosphere. To avoid precipitation of the ferromagnetic phase, the Lu content was kept slightly higher than in the stoichiometric composition. Annealing of $Lu(Co_{1-x}Ga_x)_2$ to ensure homogenization was carried out at 1073 K for a week in a vacuum quartz tube. X-ray powder diffraction confirmed that the samples were of single phase. All the specimens were powdered for the magnetization measurements. The magnetization in a low field up to 55 kOe was measured with a SQUID magnetometer. To discuss the temperature dependence of the metamagnetic transition, the high-field magnetization was measured using an induction method in pulsed fields in the temperature range 4.2–200 K. High magnetic fields up to 360 kOe were produced using a wire-wound pulse magnet cooled in liquid N_2. The detailed experimental procedures in pulsed high fields have been described elsewhere (Yamada *et al* 1986).

3. Results and discussion

Figure 1 shows the representative magnetization curves of powdered $Lu(Co_{0.91}Ga_{0.09})_2$ in pulsed fields up to 360 kOe at various temperatures. A clear metamagnetic transition for 4.2 K takes place at 60 kOe. At higher temperatures the transition becomes broader, resulting in a smaller magnetization jump. The critical transition field H_c is obtained from the average of the values at the peaks of the differential susceptibility in increasing and decreasing fields. The value of H_c increases with increasing temperature, being consistent with the results for $Co(S_{1-x}Se_x)_2$ (Adachi *et al* 1972) and $Lu(Co_{1-x}Al_x)_2$ (Iijima *et al* 1990). Magnetization measurements in static fields up to 150 kOe were also carried out and the results obtained are in good agreement with those in pulsed fields.

Figure 2 shows the temperature dependence of $H_c(T)$ in the form of $H_c(T)$ versus T^2. In this figure, the plots of $H_c(T)$ against T^2 for $Lu(Co_{0.91}Ga_{0.09})_2$ show a nearly straight line in the low-temperature regions. The temperature dependence of the critical fields $H_c(T)$ obeys the following expression:

$$H_c(T) = H_c(0) + \alpha T^2 \tag{1}$$

where $H_c(0)$ and α are the H_c-value at 0 K and the constant, respectively. In the present study, the values obtained for $H_c(0)$ and α for $Lu(Co_{0.91}Ga_{0.09})_2$ are 56.9 kOe and 0.0135 kOe K^{-2}, respectively. According to a recent theoretical consideration, the temperature dependence of the critical field is expressed by

$$H_c(T) = A + B\xi(T)^2 \tag{2}$$

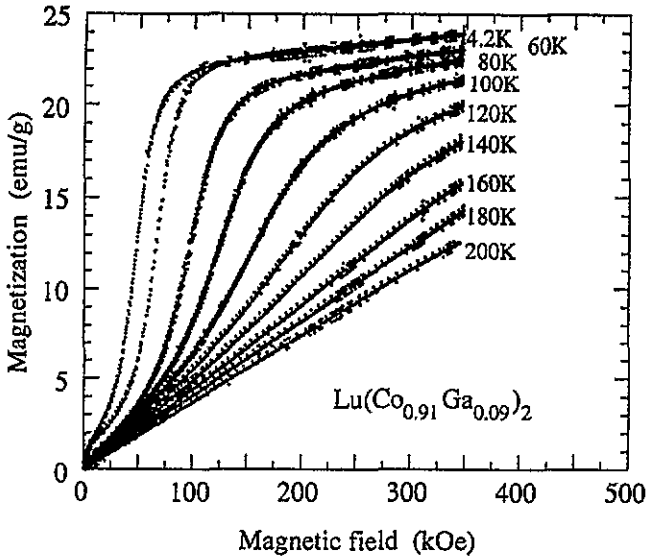

Figure 1. High-field magnetization curves for $Lu(Co_{0.91}Ga_{0.09})_2$ at various temperatures.

where A and B are constants, which can be obtained from the band structure in the ground state (Yamada 1992), and $\xi(T)^2$ is the mean square of the local amplitude of thermal spin fluctuation, being an increasing function of T for nearly ferromagnetic materials (Moriya 1985). Since the value of $H_c(T)$ is proportional to T^2 as shown in equation (1), $\xi(T)^2$ for the present compound is considered to be proportional to T^2 in low-temperature regions. In high-temperature regions, the plot slightly deviates downwards from the linear full line. A similar deviation has also been reported for $Y(Co_{0.9}Al_{0.1})_2$ (Sakakibara *et al* 1992). When the longitudinal stiffness constant of spin fluctuation is sufficiently small, $\xi(T)^2$ markedly increases with increasing temperature and saturates at high temperatures (Moriya 1985); such a behaviour has been observed for $Co(S_xSe_{1-x})_2$ with $x < 0.88$ (Adachi *et al* 1972). Therefore, the reason for the behaviour mentioned above would be correlated to the saturation of $\xi(T)^2$ at high temperatures. The metamagnetic transition smears out gradually and is no longer visible at about 180 K as shown in figure 1. At the same time, the hysteresis of transition becomes narrow and vanishes at about 80 K. In the case of a typical spin-flop-type metamagnetic transition in the antiferromagnet, the critical field of the transition decreases with increasing temperature because the value of H_c is equal to that of the exchange field. Thus the critical field is interrelated to the Néel temperature T_N and it becomes zero at T_N. The positive temperature dependence of the critical field observed in the present study is a characteristic feature of the itinerant-electron magnetization.

Since the width ΔH_c of hysteresis rapidly decreases with increasing temperature as shown in figure 1, the temperature dependence of ΔH_c is shown in figure 3 in the form of $\log(\Delta H_c)$ versus T. The width of hysteresis is obtained from the peaks of the differential susceptibility of the magnetization curves. The logarithmic plot of ΔH_c linearly decreases with increasing temperature for the specimen with $x = 0.09$. The observed temperature dependence of ΔH_c can be fitted by the following expression, suggesting some contribution from the thermal excitation process:

$$\Delta H_c\,(\mathrm{kOe}) = 31.1\ \exp(-0.106T). \tag{3}$$

A similar temperature dependence of the coercive force was observed in various pseudo-binary compounds containing a rare-earth element (RE) such as $RE(Co_{1-x}Cu_x)_5$,

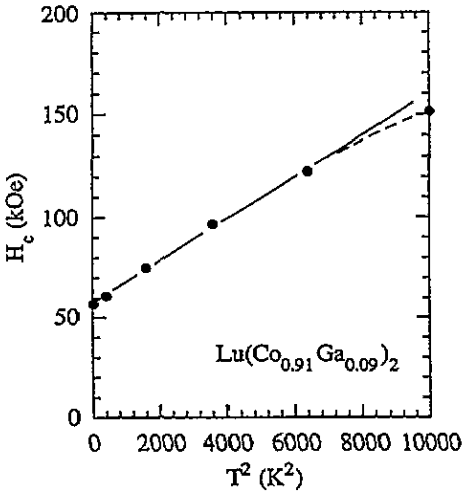

Figure 2. Temperature dependence of the critical fields H_c for $Lu(Co_{0.91}Ga_{0.09})_2$ in the form of H_c versus T^2.

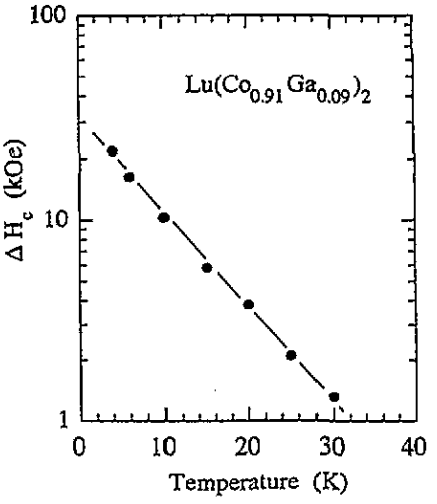

Figure 3. The logarithmic plot of the width ΔH_c of hysteresis at the critical field against temperature T for $Lu(Co_{0.91}Ga_{0.09})_2$.

RE$(Co_{1-x}Ni_x)_5$ (Yermolenko *et al* 1976) and amorphous RE–Fe alloys (Buschow and Kraan 1981).

The Arrott plots for $Lu(Co_{0.88}Ga_{0.12})_2$ at various temperatures are shown in figure 4. The plot of $T = 4.2$ K rapidly increases in the low-H/M regions and the extrapolations to $H/M = 0$ gives a negative M^2-value, suggesting the absence of spontaneous magnetization. On the other hand, it could be concluded that the metamagnetic transition occurs at a low field for the specimen with $x = 0.12$, because a positive M^2-value is given in high fields. Furthermore, the plots in high magnetic fields below 110 K are almost parallel to one another and the situation is similar to the case of weakly itinerant ferromagnets such as $ZrZn_2$ (Ogawa and Sakamoto 1967, Ogawa 1976), Sc_3In (Hioki and Masuda 1977), and Ni_3Al (Umemura and Masuda 1983, Sasakura *et al* 1984). As is well known, the magnetic free energy G in the Landau–Belov expansion is expressed by the following equation:

$$G = c_1M^2 + c_2M^4 + c_3M^6 \tag{4}$$

where c_1, c_2 and c_3 are constants. The coefficient c_2 of the M^4-term is inversely proportional to the slope of the Arrott plot and the condition $c_2 < 0$ is necessary for the occurrence of metamagnetism (Shimizu 1982), implying a negative slope of the Arrott plot. The sign of c_2 of the present compound with $x = 0.12$ is positive. This would come from an extremely large initial susceptibility following a small metamagnetic jump and from some local magnetic inhomogeneity due to the arrangement of Ga atoms accompanying a broader transition.

Since the metamagnetic transition in $Lu(Co_{0.88}Ga_{0.12})_2$ occurs in a very low field, we can estimate the hypothetical spontaneous magnetization M_h, assuming that the ferromagnetic state is stable even in zero field. Figure 5 shows the temperature dependence of magnetization in the ferromagnetic state for $Lu(Co_{0.88}Ga_{0.12})_2$ in the form of M_h^2 versus T^2. This plot is a straight line below 110 K. The value of M_h extrapolated to $H/M = 0$ along the full line in figure 4 decreases with increasing temperature and disappears at around 105 K, giving a hypothetical Curie temperature T_C. It is noteworthy that the slope

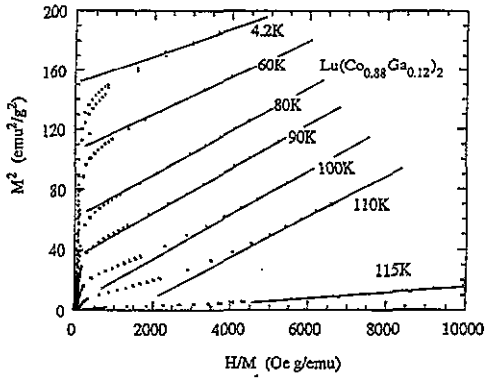

Figure 4. The Arrott plots for $Lu(Co_{0.88}Ga_{0.12})_2$ at various temperatures.

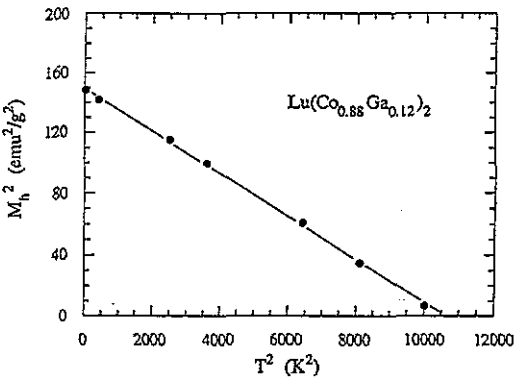

Figure 5. Temperature dependence of the hypothetical spontaneous magnetization for $Lu(Co_{0.88}Ga_{0.12})_2$ in the form of M_h^2 against T^2.

of the Arrott plot in high fields at 115 K is markedly different from that below 100 K as shown in figure 4. A strong temperature dependence of the calculated value of c_2 has been reported for YCo_2 and the value changes sign from negative to positive, suggesting that the metamagnetic transition will not occur in YCo_2 above a certain temperature where c_2 becomes positive (Yamada and Shimizu 1990). In the present study, the value of 105 K seems to be the critical temperature above which the metamagnetic transition will not occur in $Lu(Co_{0.88}Ga_{0.12})_2$. Consequently, the higher the temperature, the smaller the hysteresis width becomes, resulting in the second-order transition above 80 K. It should be noted that no metamagnetic transition occurs above this hypothetical Curie temperature.

For weak ferromagnets the temperature dependence of the magnetization is given by

$$M(T)^2 = M(0)^2\left[1 - \left(T/T_C\right)^2\right]. \tag{5}$$

Such behaviour has been reported in many weak ferromagnets such as Y–Ni amorphous alloy (Liénard and Rebouillat 1978) and Ni_3Al (Schrieffer 1969). In the vicinity of T_C, $M(T)^2$ is expected to show a $T^{4/3}$-dependence from the SCR theory (Moriya and Kawabata 1973a, b). However, the present results show not a $T^{4/3}$ but a T^2-dependence in almost the whole temperature range. On the other hand, a similar expression to equation (5) is also obtained in terms of the spin fluctuation theory for the intermediate case (Lonzarich and Taillefer 1985). Since the hypothetical Curie temperature is about 105 K, much higher than those of many typical weak ferromagnets such as $ZrZn_2$ (Ogawa and Sakamoto 1967, Ogawa 1976), the spin fluctuation would not be so marked. This is correlated to the fact that the γ-value of $Lu(Co_{1-x}Ga_x)_2$ after the metamagnetic transition becomes small (Murata *et al* 1992), suggesting that the enhancement of spin fluctuation is not so marked.

When the observed behaviour is taken into account, the temperature dependence of the critical field is discussed using the thermodynamic relations. The metamagnetic transition of the present compounds is considered to be of first order in the ground state, because the magnetization is accompanied by hysteresis. Therefore, the magnetic transition behaviour is considered to obey the following Clausius–Clapeyron equation:

$$\Delta Q = -\Delta M\ T(\partial H/\partial T)_M \tag{6}$$

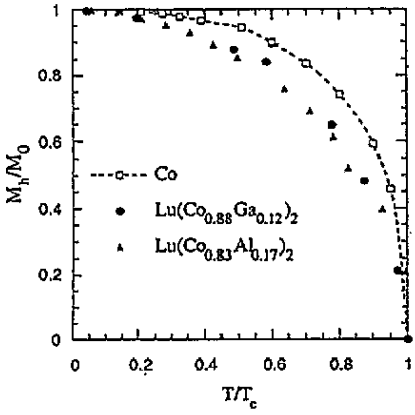

Figure 6. Reduced thermomagnetization curve of $Lu(Co_{0.88}Ga_{0.12})_2$, together with that of $Lu(Co_{0.83}Al_{0.17})_2$ (Iijima *et al* 1990) and Co (Myers and Sucksmith 1951), for comparison.

where ΔQ and ΔM are the enthalpy change and the magnetization jump due to the transition, respectively. On the other hand, the change ΔC in the low-temperature specific heat due to the transition is given by

$$\Delta C/T = \Delta\gamma + \Delta\beta\, T^2 + \ldots \tag{7}$$

where $\Delta\gamma$ and $\Delta\beta$ are the changes in the electronic and lattice specific heat coefficients, respectively. Extrapolating to $T \to 0$, $\Delta\gamma$ is given by

$$\Delta\gamma = (\Delta C/T)_{T\to 0}. \tag{8}$$

Rewriting equation (8), we obtain

$$\Delta\gamma = (1/T)(\partial/\partial T)\Big[(\partial H/\partial T)_M T\ \Delta M\Big]_{T\to 0} \simeq -\Big[(\Delta M/T)\big(\partial H_c/\partial T\big)\Big]_{T\to 0}. \tag{9}$$

Since the critical field $H_c(T)$ is proportional to T^2 as mentioned before, the insertion of equation (1) in equation (9) yields

$$\Delta\gamma = 2\alpha\ \Delta M \tag{10}$$

where α is the coefficient of T^2 in the temperature dependence of critical field. From figure 2, the coefficient α is positive, and the sign of $\Delta\gamma$ becomes negative, i.e. the value of γ is reduced by the metamagnetic transition. The magnetizations at the critical field are estimated to be 3.0 emu g^{-1} and 21.5 emu g^{-1} in the paramagnetic and ferromagnetic phases, respectively, resulting in ΔM = 18.5 emu g^{-1} at 4.2 K. From the observed data, the value of $\Delta\gamma$ is estimated to be -14.1 mJ K^{-2} mol^{-1}. The magnetic field dependence of the electronic specific-heat coefficient γ has been observed (Murata *et al* 1992). The γ-value of the specimen with x = 0.12, which is about 36 mJ K^{-2} mol^{-1} at 0 kOe, is reduced markedly in the magnetic field because of the metamagnetic transition and remains constant at about 20 mJ K^{-2} mol^{-1} above H = 60 kOe. For the specimen with x = 0.09, the γ-value of about 35.5 mJ K^{-2} mol^{-1} in the paramagnetic state decreases with increasing magnetic field and reaches 25 mJ K^{-2} mol^{-1} at 146 kOe. Considering that the reduced γ-value for x = 0.09 is not saturated, further reduction is expected by applying much higher fields. The γ-value after the metamagnetic transition would also become almost the same value of 20 mJ K^{-2} mol^{-1} for x = 0.12, implying that $\Delta\gamma$ for x = 0.09 estimated from the specific-heat measurement is -15.5 mJ K^{-2} mol^{-1} which is comparable with the value of -14.1 mJ K^{-2} mol^{-1} evaluated from the present method.

The reduced hypothetical spontaneous magnetization M_h/M_0 versus reduced temperature T/T_C for $Lu(Co_{0.88}Ga_{0.12})_2$ is shown in figure 6 together with the reduced spontaneous magnetization M_s/M_0 for $Lu(Co_{0.83}Al_{0.17})_2$ (Iijima *et al* 1990) and that for typical ferromagnet Co (Myers and Sucksmith 1951). The variation in the present compound is quite similar to that of $Lu(Co_{0.83}Al_{0.17})_2$. The Invar behaviour in the thermal expansion has been observed in $Lu(Co_{1-x}Al_x)_2$ with $x = 0.1$ and 0.156 (Gabelko *et al* 1987). It should be noted that the temperature dependence of the magnetization in both Laves-phase compounds decreases more rapidly with increasing temperature than it does for Co. This means that the ferromagnetic state of the present compound is unstable in a similar manner to that of $Lu(Co_{1-x}Al_x)_2$ Invar alloys, and large magnetovolume effects are expected.

4. Conclusions

The high-field magnetizations M and the temperature dependence of the critical field $H_c(T)$ have been investigated for Laves-phase itinerant-electron metamagnets $Lu(Co_{1-x}Ga_x)_2$. The main results are summarized as follows.

(1) The critical field $H_c(T)$ for the transition linearly increases with increasing T^2. This positive temperature dependence of the critical field is a characteristic feature of the itinerant-electron metamagnetic transition, in contrast with the transition for localized-moment systems.

(2) The width ΔH_c of hysteresis of the metamagnetic transition decreases with increasing temperature, following an exponential expression of the form $\Delta H_c = 31.1 \exp(-0.106T)$ kOe.

(3) The decrease in γ-value is estimated from the Clausius–Clapeyron equation at the metamagnetic transition and is comparable with the value of the low-temperature specific-heat measurement in magnetic fields.

(4) The plot of hypothetical spontaneous magnetization for $Lu(Co_{0.88}Ga_{0.12})_2$ in the form of M_h^2 versus T^2 is a straight line.

(5) The reduced hypothetical magnetization for $Lu(Co_{0.88}Ga_{0.12})_2$ decreases more rapidly than the reduced spontaneous magnetization of Co, suggesting that the ferromagnetic state of the present compound is unstable.

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