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The lattice constant and itinerant electron metamagnetic transition in Laves-phase pseudo-binary $Lu(Co_{1-x}Si_x)_2$ compounds

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Abstract. The lattice constant, low-temperature specific heat and high-field magnetization of the Laves-phase itinerant electron metamagnets $Lu(Co_{1-x}Si_x)_2$ have been investigated. By partial substitution of Co by Si, the critical field H_c of the metamagnetic transition decreases and the temperature T_{max} of the magnetization maximum shifts to lower temperatures with increasing x regardless of the decrease in the lattice constant. Both the electronic specific heat coefficient γ and the magnetic susceptibility χ increase with increasing x up to $x = 0.09$ and decrease above this concentration. The present results suggest that the decrease in the critical field is not due to the increase in the lattice constant but is due to the hybridization between 3d electrons of Co and 3p electrons of Si.

1. Introduction

The itinerant electron metamagnetic transition was first discussed for the exchange-enhanced Pauli paramagnets having a maximum in the temperature dependence of susceptibility (Wohlfarth and Rhodes 1962). It is well known that Co-based Laves-phase compounds such as YCo_2 and $LuCo_2$ exhibit strongly exchange-enhanced paramagnetic properties and have a broad maximum in the temperature dependence of their magnetic susceptibility (Lemaire 1966, Bloch *et al* 1971). Recently, the metamagnetic transitions in YCo_2 and $LuCo_2$ have been confirmed at 8 K and their critical fields are 69 T and 74 T, respectively (Goto *et al* 1990).

The substitution of other elements in the compounds causes a change in both the d electron density and the lattice constant. It has been confirmed that the Laves-phase pseudo-binary $Y(Co_{1-x}Al_x)_2$ compounds are magnetically enhanced with increasing x and become weak ferromagnets in the concentration range $0.12 < x < 0.19$ (Yoshimura and Nakamura 1985). For these pseudo-binary compounds, low-temperature magnetization measurements in high magnetic fields up to 40 T have been performed and a clear itinerant electron metamagnetic transition has been observed (Aleksandryan *et al* 1985, Sakakibara *et al* 1986, 1987). More recently, we have reported that the magnetic susceptibility of $LuCo_2$ is also increased by partial substitution of Co by other elements such as Ga and Sn, and the transition occurs in relatively low fields (Murata *et al* 1991, 1993a, b). A broad peak in the temperature dependence of the susceptibility, centred on T_{max}, shifts to lower

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temperatures with increasing x, resulting in a linear relationship to H_c (Endo *et al* 1988, Sakakibara *et al* 1990a, b, Murata *et al* 1991, 1993b). However, these studies have been mainly carried out only for compounds with a larger substitutional element than Co and the magnetic enhancement is often interpreted by the chemical pressure effect. For example, the lattice expansion between YCo_2 and $Y(Co_{0.85}Al_{0.15})_2$ is equivalent to a chemical pressure of -40 kbar (Armitage *et al* 1990). Recent results on the pressure dependence of the magnetic properties for weak ferromagnetic $Y(Co_{1-x}Al_x)_2$ compounds have revealed that the ferromagnetic state is unstable when no lattice constant expansion is caused by chemical pressure (Armitage *et al* 1990). On the other hand, it has been confirmed that ferromagnetic states are established in $(Y_{1-x}Lu_x)(Co_{1-y}Al_y)_2$ compounds, although their lattice constants are scarcely changed (Gabelko *et al* 1991). We are interested in studying the case of a decrease in the lattice constant for pseudo-binary Laves-phase compounds. In the present paper, attention will be paid to the effect of substitution on the lattice constant and the metamagnetic transition in $Lu(Co_{1-x}Si_x)_2$.

2. Experimental details

$Lu(Co_{1-x}Si_x)_2$ compounds were made by arc melting in an argon gas atmosphere. The samples were remelted several times. The Lu content was slightly higher than the stoichiometric composition to compensate some loss due to vaporization and oxidation. Annealing of $Lu(Co_{1-x}Si_x)_2$ to ensure homogenization was carried out at 1073 K for a week in a vacuum quartz tube. The room-temperature lattice constant was obtained by x-ray powder diffraction. The samples were powdered for the magnetization measurements. High magnetic fields up to 40 T were generated with a long pulse magnet at 4.2 K. Ultra-high magnetic fields up to 100 T at 8 K were generated by means of a fast capacitor discharge into a copper single-turn coil with a 100 kJ capacitor bank (Nakao *et al* 1985). The magnetization was measured by an induction method with well balanced pick-up coils. Details of these experimental procedures have already been described elsewhere (Nakao *et al* 1985, Sakakibara *et al* 1990a). The magnetic susceptibility was measured with a SQUID magnetometer. The electronic specific heat coefficient was calculated from the low-temperature specific heat measured by a conventional heat pulse method.

3. Results and discussion

Figure 1 shows the concentration dependence of the room-temperature lattice constant of $Lu(Co_{1-x}Si_x)_2$, together with that of $Lu(Co_{1-x}Ga_x)_2$, for comparison. Since the atomic radius of the Si atom is smaller than that of the Co atom, the lattice constant of $Lu(Co_{1-x}Si_x)_2$ compounds is expected to be reduced. In fact, the lattice constants of $Lu(Co_{1-x}Si_x)_2$ compounds decrease linearly with increasing x. These results are comparable with the results for $Y(Co_{1-x}Si_x)_2$ and $Sc(Co_{1-x}Si_x)_2$ (Michels *et al* 1990). On the other hand, the value for $Lu(Co_{1-x}Ga_x)_2$ increases with increasing x and the behaviour is similar to the results for $Y(Co_{1-x}Al_x)_2$ (Yoshimura and Nakamura 1985) and $Lu(Co_{1-x}Al_x)_2$ (Iijima *et al* 1990).

Figure 2 shows the magnetization curves of $Lu(Co_{1-x}Si_x)_2$ compounds at 4.2 K. The magnetic susceptibility increases with increasing x up to $x = 0.09$ and subsequently decreases. It should be noted that the magnetic susceptibility of $LuCo_2$ at 4.2 K is enhanced by substitution of Co by Si.

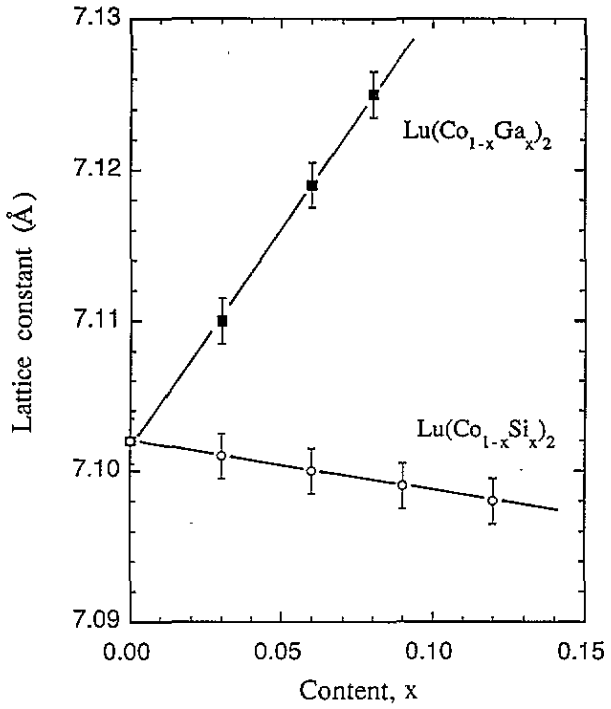

Figure 1. The concentration dependence of the lattice constant of $Lu(Co_{1-x}Si_x)_2$ compounds, together with that of $Lu(Co_{1-x}Ga_x)_2$ compounds (Murata *et al* 1993b).

The temperature dependence of susceptibility for $Lu(Co_{1-x}Si_x)_2$ compounds is shown in figure 3. The susceptibility in low-temperature regions increases with increasing x below $x = 0.09$; however, no magnetic ordering is observed. The maximum temperature T_{max} determined from the $d\chi/dT$ curve shifts to lower temperatures and it becomes obscure, resulting in its disappearance above $x = 0.09$ in the present experimental temperature range above 4.2 K.

The concentration dependences of the electronic specific heat coefficient γ and initial susceptibility χ of $Lu(Co_{1-x}Si_x)_2$ are shown in figure 4. The χ-value increases with increasing x and decreases above $x = 0.09$ and a similar tendency is expected for the γ-value. In many itinerant electron systems, Wilson's (1975) relation

$$R_W = \frac{\chi}{\gamma} \tag{1}$$

is observed. The γ-value for $x = 0.12$ is about 37 mJ K^{-2} mol^{-1} at $x = 0.12$, being comparable with the value of 37.8 mJ K^{-2} mol^{-1} for $Lu(Co_{1-x}Ga_x)_2$ (Matura *et al* 1993a). As is well known, both the magnetic susceptibility and the electronic specific heat coefficient are proportional to the density of states (DOS) at the Fermi level. For $Y(Co_{1-x}Al_x)_2$ and $Lu(Co_{1-x}Al_x)_2$ compounds, the initial susceptibility χ and the electronic specific heat coefficient γ are increased (Wada *et al* 1990), and then a ferromagnetic state is established beyond $x = 0.12$ for $Y(Co_{1-x}Al_x)_2$ and $x = 0.08$ for $Lu(Co_{1-x}Al_x)_2$ (Yoshimura and Nakamura 1985, Gabelko *et al* 1987). It has been considered that the magnetic enhancement comes from the increase in the lattice constant (Yoshimura and Nakamura 1985, Gabelko *et*

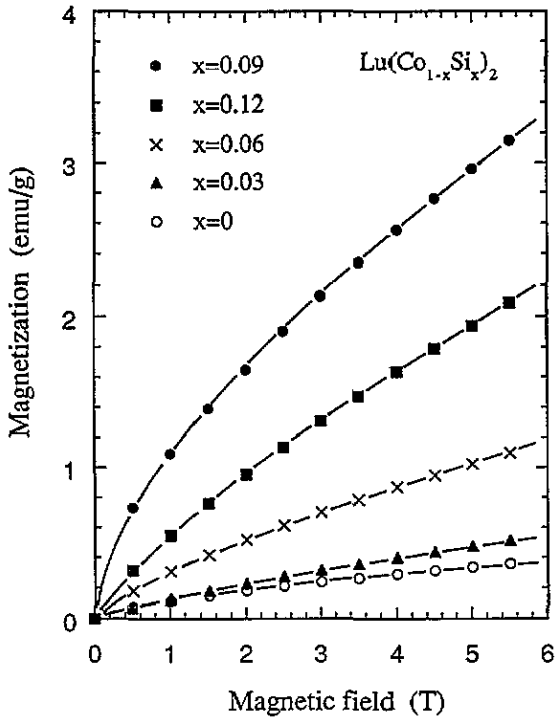

Figure 2. The magnetization curves of $Lu(Co_{1-x}Si_x)_2$ compounds at 4.2 K.

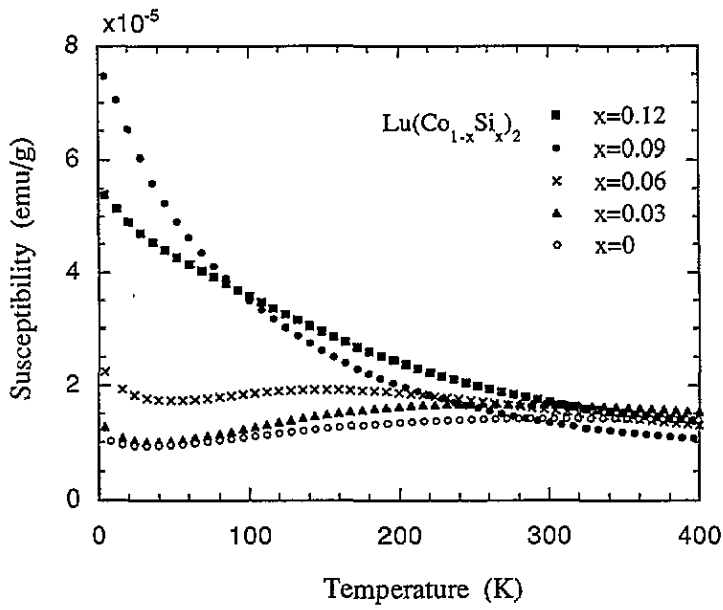

Figure 3. The temperature dependence of magnetization for $Lu(Co_{1-x}Si_x)_2$ compounds.

al 1987), because the d bandwidth becomes narrower with the lattice expansion. However, both the magnetic susceptibility and the electronic specific heat coefficient are enhanced by

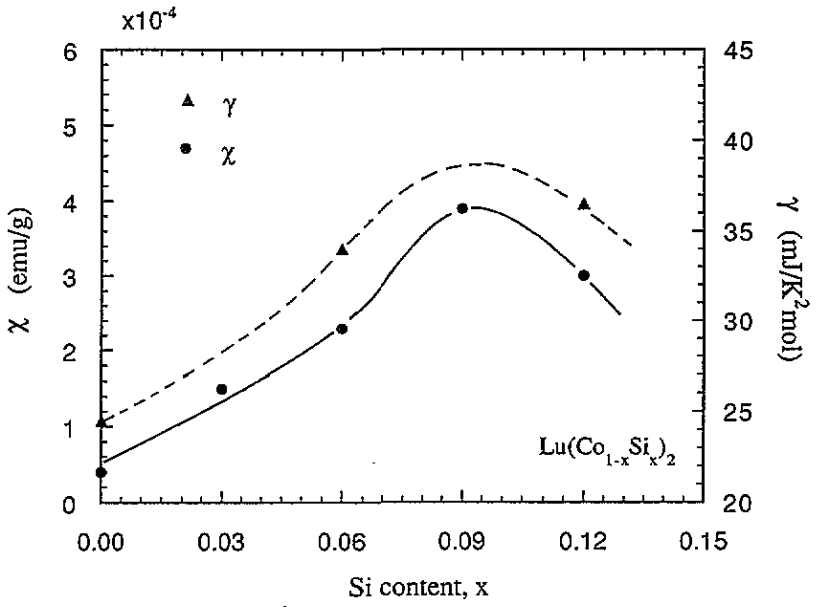

Figure 4. The concentration dependences of the electronic specific heat coefficient γ and the magnetic susceptibility χ for $Lu(Co_{1-x}Si_x)_2$ compounds.

the substitution of Si, although the lattice constant decreases with increasing x as shown in figure 1. From these results, the magnetic enhancement is not due to the chemical pressure. It has been calculated that the Fermi level of Co-based Laves-phase compounds lies just above a sharp peak of the DOS (Cyrot and Lavagna 1979, Yamada *et al* 1984). From their results, it is expected that the higher DOS is formed by partial substitution of Si atoms which has no 3d electrons. In higher-concentration regions, however, a hybridization effect would be important. Further discussion will be given later in the present discussion.

For many compounds, a linear relationship between the peak T_{max} in the temperature dependence of susceptibility and the critical field H_c for the metamagnetic transition has been confirmed (Endo *et al* 1988, Sakakibara *et al* 1990a, b). Since T_{max} for $Lu(Co_{1-x}Si_x)_2$ compounds is lower than that for $LuCo_2$, the metamagnetic transition is expected to occur in relatively low magnetic fields. Figure 5 shows the high-field magnetizations obtained at 4.2 K ($B < 40$ T) and 10 K ($B > 40$ T) for $Lu(Co_{1-x}Si_x)_2$. As reported previously, the metamagnetic transition in $LuCo_2$ has been observed at 74 T (Goto *et al* 1990). With increasing x, the critical field decreases and the partial substitution of Co by Si is effective in reducing H_c. A very sharp transition takes place in the samples with $x \leqslant 0.06$. In high-x regions, however, the magnetization jump at the transition becomes smaller and eventually vanishes above $x = 0.12$. These features are in accord with the fact that the broad maximum fades away at such a high x as shown in figure 3, suggesting a strong correlation between T_{max} and H_c. Both the maximum and the critical field have been considered to arise from a peculiar band structure (Yamada *et al* 1984).

Figure 6 shows the metamagnetic transition field H_c versus the susceptibility maximum temperature T_{max} for $Lu(Co_{1-x}Si_x)_2$. H_c is obtained from the average of the values at the peaks of the differential susceptibility in increasing and decreasing fields. In this figure, the data for $Y(Co_{1-x}Al_x)_2$ (Sakakibara *et al* 1990a) and $Lu(Co_{1-x}Ga_x)_2$ (Murata *et al* 1993b) are also given, for comparison. A linear relationship between H_c and T_{max} is also observed for $Lu(Co_{1-x}Si_x)_2$. Similar results have been reported not only for 3d compounds (Endo *et*

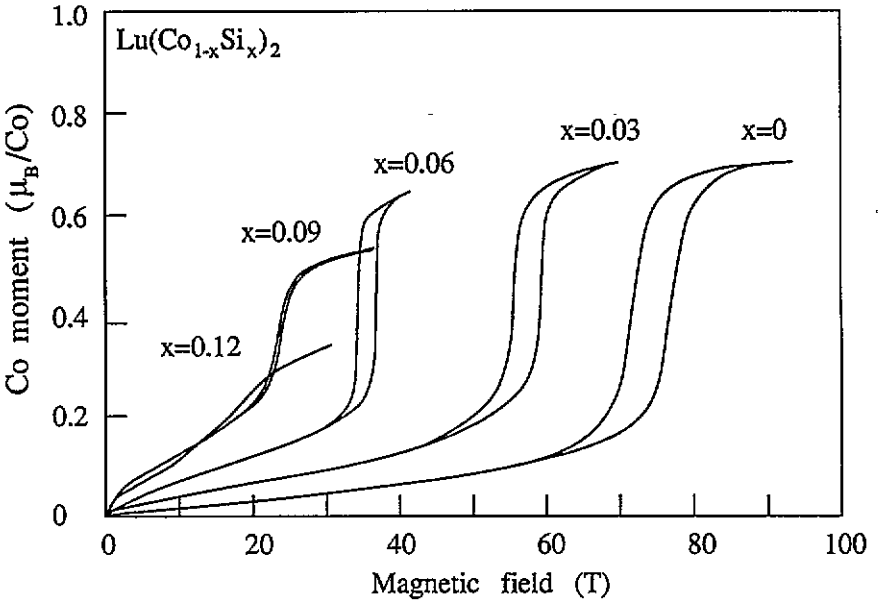

Figure 5. High-field magnetizations, obtained at 4.2 K ($B < 40$ T) and 10 K ($B > 40$ T) for $Lu(Co_{1-x}Si_x)_2$.

al 1988, Sakakibara *et al* 1990a) but also for heavy-fermion-type compounds (Sakakibara *et al* 1990b). According to the Landau–Berov expansion, the magnetic free energy F can be expressed as

$$F = \tfrac{1}{2}AM^2 + \tfrac{1}{4}BM^4 + \tfrac{1}{6}CM^6 - MH \tag{2}$$

where A, B and C are the expansion coefficients and H the magnetic fields (Wohlfarth and Rhodes 1962). The critical field for the metamagnetic transition can be expressed as (Shimizu 1962)

$$H_c = \frac{1}{2}\sqrt{\frac{|B|}{3C}}\left(A - \frac{3}{16}\frac{B^2}{C}\right) \tag{3}$$

with $A = 1/\chi$. Therefore, the increase in χ directly reflects on the reduction in the critical fields. According to a recent theoretical consideration which takes into account the spin fluctuation effect on the Landau–Ginzburg theory, the paramagnetic susceptibility always shows a maximum when the metamagnetic transition is induced by the external magnetic field (Yamada 1993). That is, the metamagnetism is associated with a negative sign of B in equation (2) and the positive temperature dependence of the susceptibility at low temperatures would come from the same origin.

A pressure dependence of the magnetic properties for weakly ferromagnetic $Y(Co_{1-x}Al_x)_2$ compounds has been reported (Armitage *et al* 1990). The critical pressure for the collapse of ferromagnetism is about 9 kbar for $Y(Co_{1-x}Al_x)_2$ with $0.14 < x < 0.18$ and the chemical pressure due to the Al substitution corresponds to -40 kbar for $x = 0.15$ (Armitage *et al* 1990). It has been suggested that ferromagnetism is not stabilized in $Y(Co_{1-x}Al_x)_2$ compounds if the lattice constant were the same as the value of YCo_2.

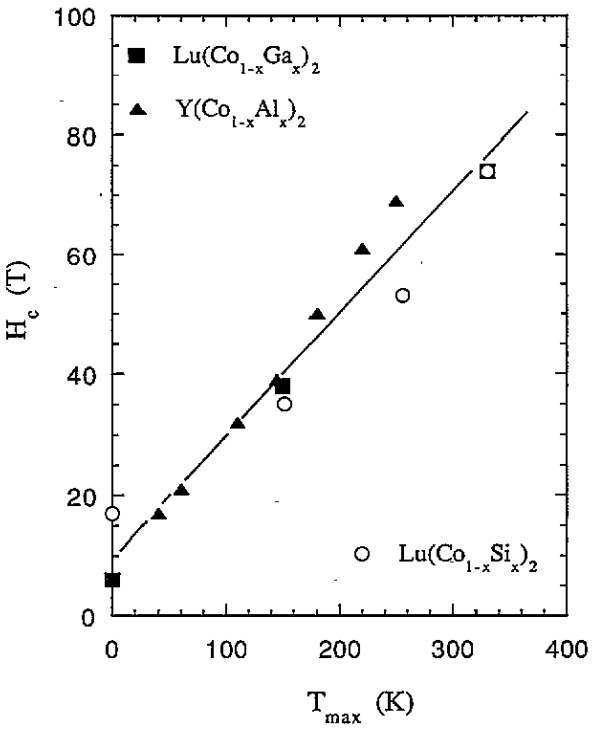

Figure 6. Metamagnetic transition field versus susceptbility maximum temperature for $Lu(Co_{1-x}Si_x)_2$ (○). The data for $Y(Co_{1-x}Al_x)_2$ (▲) (Sakakibara *et al* 1990a) and $Lu(Co_{1-x}Ga_x)_2$ (■) (Murata *et al* 1993b) are also given, for comparison.

On the other hand, detailed band calculations using the self-consistent augmented-plane-wave (APW) method have been made for the ordered pseudo-binary $Y(Co_{1-x}Si_x)_2$ and $Y(Co_{1-x}Al_x)_2$ compounds with $x = 0, 0.25, 0.5$ and 0.75 (Aoki and Yamada 1992). The DOS for YCo_2 is characterized by the two sharp peaks near the Fermi level. By partially replacing Co atoms with Al atoms, the 3d orbits of Co atoms are broken and the hybridized orbits are constructed, resulting in a significant change in the DOS, i.e. the sharp peak at a high energy is rapidly reduced and the Fermi level shifts to a lower energy. The Fermi level would go across the reduced peak which is relatively high and then the ferromagnetic state would be established at a certain concentration. In the case of Si, however, the sharp peak at a high energy has already disappeared at $x = 0.25$ and furthermore the shift in the Fermi energy is smaller than for Al (Aoki and Yamada 1992). Therefore, the present concentration dependences of χ and γ would arise from a significant change in the sharp peak and this change would bring about the broadening of the metamagnetic transition at such a high Si concentration.

4. Conclusion

To study the negative volume effects due to the partial substitution for Co by Si, the lattice constant, low-temperature specific heat and magnetization of the itinerant electron metamagnetic pseudo-binary Laves-phase $Lu(Co_{1-x}Si_x)_2$ compounds have been investigated. The main results are summarized as follows.

(1) The lattice constant of $Lu(Co_{1-x}Si_x)_2$ compounds decreases linearly with increasing x.

(2) The magnetic susceptibility of $Lu(Co_{1-x}Si_x)_2$ increases with increasing x up to $x = 0.09$ and decreases above $x = 0.12$ without the appearance of ferromagnetism.

(3) The temperature T_{max} of the magnetization maximum of $Lu(Co_{1-x}Si_x)_2$ shifts to lower temperatures with increasing Si concentration and then fades away above $x = 0.09$.

(4) The critical field H_c for the metamagnetic transition decreases with increasing x. A linear relationship between H_c and T_{max} is observed.

(5) The present results strongly suggest that the decrease in the critical field is not due to the increase in the lattice constant but is due to the hybridization effect between 3d electrons of Co and 3p electrons of Si, because H_c decreases regardless of the decrease in the lattice constant with increasing Si content.

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