PHYSICAL REVIEW B **66**, 024112 (2002)

Effect of pressure and substitution for Yb on the first-order valence transition in YbInCu_4

W. Zhang,[1] N. Sato,[1] K. Yoshimura,[1] A. Mitsuda[2,*] T. Goto,[2] and K. Kosuge[1]
[1]*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*
[2]*Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

(Received 12 July 2001; revised manuscript received 5 March 2002; published 15 July 2002)

Single-crystalline samples of YbInCu_4 and its partially substituted compounds by Y and Lu were synthesized by the flux method. The temperature dependence of the magnetic susceptibility from 2 to 320 K in the magnetic field of 0.5 T and the high-field magnetization up to 41 T under various fixed pressures were measured in order to investigate the effect of substitution, inherent chemical pressure, and external pressure on the first-order valence transition of YbInCu_4. Substitution of Yb by Y or Lu results in a small increase or decrease of the lattice parameter, while both systems show a steep decrease of transition temperature (T_v) and transition magnetic field (H_v) with substitution, resulting in suppression of the valence transition around $x=0.30$ for $\mathrm{Yb}_{1-x}\mathrm{Y}_x\mathrm{InCu}_4$ $(0\leqslant x\leqslant 0.3)$ and $x=0.15$ for $\mathrm{Yb}_{1-x}\mathrm{Lu}_x\mathrm{InCu}_4$ $(0\leqslant x\leqslant 0.15)$. The effect of pressure on H_v of the pure and Y-substituted YbInCu_4 is reported by $dH_v/dP\approx -1$ T/kbar, with a suppression of the valence transition of $\mathrm{Yb}_{0.8}\mathrm{Y}_{0.2}\mathrm{InCu}_4$ at the pressure of 8 kbar. The effect of inherent chemical pressure is very small compared with the intrinsic effect of substitution. The decreasing of Kondo temperature T_K $(\propto 1/\chi_0)$ below T_v resulting from the substitution for the Yb lattice is discussed as an important factor affecting the valence transition of YbInCu_4.

DOI: 10.1103/PhysRevB.66.024112 PACS number(s): 75.30.Mb, 75.20.Hr, 71.27.+a, 71.28.+d

I. INTRODUCTION

The large variations in physical properties have drawn much attention among the cubic $C15b$-type $\mathrm{Yb}X\mathrm{Cu}_4$ compounds with $X=$ Ag, Au, Cd, Cu, In, Mg, Pd, Tl, and Zn.[1] The physics in these systems are associated with valence fluctuations of Yb derived from hybridization between localized $4f$ and ligand electrons. YbAgCu_4 forms a dense Kondo lattice with no magnetic order observed to the lowest temperatures measured.[2–4] In contrast, YbAuCu_4 and YbPdCu_4 order magnetically below 1 K.[2,5] Among $\mathrm{Yb}X\mathrm{Cu}_4$ compounds, YbInCu_4 has been rather intensively studied and represents the most extreme limit of mixed-valence behavior: a first-order isostructural valence transition in ambient pressure near 42 K.[3,6–11] The cubic YbCu_5 that was recently synthesized under high pressure of 15 kbar is discovered to be a heavily correlated dense Kondo compound.[12–14] The $\mathrm{Yb}X\mathrm{Cu}_4$ compounds for $X=$ Cd, Mg, Tl, and Zn are relatively less studied and each displays properties intermediate to those for $X=$ Ag, Au, Cu, and In.[1,15]

YbInCu_4 has a face-centered-cubic $C15b$-type structure with space symmetry of $F43m$.[9] The magnetic susceptibility follows the Curie-Weiss law at high temperatures with an effective magnetic moment close to the Yb^{3+} ($4f^{13}$, $J=7/2$, $g_J=8/7$) free ion value ($\mu_{\mathrm{eff}}=4.54\mu_{\mathrm{B}}$). The magnetic susceptibility drops suddenly at transition temperature (T_v) of 42 K and shows nearly temperature-independent Pauli paramagnetic behavior at low temperatures. The Kondo temperature estimated from $\chi(T)$ is $T_K^H=25$ K for the high-temperature (HT) phase and $T_K^L=400$ K for the low-temperature (LT) phase,[16,17] within the single-impurity Kondo model.[18] The Yb valence change is only 0.1 derived from volume thermal-expansion measurements and L_{III} x-ray-absorption spectra: Yb^{3+} in the HT phase changes to $\mathrm{Yb}^{2.9+}$ in the LT phase with a consequent increase in lattice volume of 0.5%.[7] The intermediate valence state in the LT phase is an exchange enhanced Pauli paramagnetic Fermi-liquid state.[6,8,19] Microscopic measurements such as neutron diffraction, ^{171}Yb NMR, ^{115}In NMR, and ^{63,65}Cu nuclear quadrupole resonance (NQR) also demonstrated that the LT phase below T_v is a Fermi-liquid state without magnetic ordering.[20–23] The first-order valence transition can be induced by an applied magnetic field as well as by temperature.[3,24] It was shown that the magnetic-field-induced transition at $T<T_v$ is a valence transition with the same mechanism as observed in the magnetic susceptibility as a function of temperature at low magnetic field below transition magnetic field (H_v).[3]

The valence transition in YbInCu_4 accompanied with lattice volume expansion of 0.5% should be susceptible to the ambient pressure and the inherent chemical pressure by substitution. It has been reported that applying pressure can affect T_v by $dT_v/dP\approx -2$ K/kbar.[25–28] In this work we report studies of the pressure effect on H_v for the pure and Y-substituted YbInCu_4. Negative chemical pressure obtained by substituting Yb by La increases the valence transition temperature,[25] but substituting Yb by Y or Lu depresses the valence transition temperature.[26,29,30] The YInCu_4 and LuInCu_4 are isostructures with YbInCu_4 and are all nonmagnetic compounds. $\mathrm{Y}^{3+}(1.015\ \text{Å})$ has an ionic radius larger than that of $\mathrm{Yb}^{3+}(0.98\ \text{Å})$, but $\mathrm{Lu}^{3+}(0.97\ \text{Å})$ has an ionic radius smaller than that of Yb^{3+};[31] substituting Yb with Y or Lu can make the lattice parameter increase or decrease to produce the negative or positive chemical pressure, but the T_v and H_v are all decreased.[26,29,30] In this paper we investigate the effect of Yb substitution with Y or Lu on the first-order valence transition, and compare T_v and H_v of the two substitution systems by measurements of magnetic susceptibility and high-field magnetization.

The magnitude and sharpness of the transition of YbInCu_4 as a function of temperature is extremely sensitive to small variations in stoichiometry and site disorder.[11] Thus a YbInCu_4 sample including YbIn site disorder showed a broad peak in the $\chi(T)$ curve around $T=80$ K.[27] The compound probably forms peritectically.[32] The single crystals of YbInCu_4 synthesized by the InCu flux-grown method possess the smallest amount of site disorder.[32] The properties of YbInCu_4 can be self-consistently characterized by the physical measurements on these crystals and their substituted variants. In our recent research, the single-crystalline samples of pure and Yb-site substituted YbInCu_4 by Y or Lu synthesized by the flux method[26] were used for measurements.

II. EXPERIMENTAL DETAILS

Single crystals of pure and substituted YbInCu_4 were grown from an In-Cu flux as reported previously by Sarrao *et al.*[16,26] Polycrystal samples were first prepared by combining stoichiometric ratios of the constituent elements (minimum 99.9% purity for Yb, Lu, Y, and 99.99% for Cu, In) in a 1:1 ratio with InCu_2 by arc method in argon atmosphere. The arc-melted mixture was crashed and placed in an alumina crucible, then sealed in an evacuated quartz tube. Subsequently the samples were heated to 1000 °C and cooled very slowly to 800 °C, at which point the flux was separated from single crystals. X-ray diffraction (XRD) measurement was performed by the Debye-Scherrer method using $\mathrm{Cu}K_\alpha$ radiation for the structural investigation on the samples. Lattice parameters were determined from XRD data by measns of the Wilson-Pike deviation function calculating method.

Magnetic susceptibility was measured by using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design Magnetic Property Measurement System) in a magnetic field of 0.5 T in the temperature range from 2 to 320 K. The high-field magnetization measurement under fixed high pressure was performed at the Institute for Solid State Physics, the University of Tokyo. High-field magnetization was measured using an induction method in pulse magnetic fields up to 41 T with a pulse duration time of about 20 ms.[33] High magnetic field was generated by a wire wound pulse magnet, cooled in liquid nitrogen, with a 200-kJ capacitor bank. The sample was set inside a small coaxial-type pick-up coil for measuring the magnetization. This assembly was compressed in a Teflon capsule filled with a liquid pressure medium of Fomblin in a CuBe clamp cylinder. The applied pressure and magnetic fields in the pressure cell were calibrated as described in Ref. 34. Magnetization for $\mathrm{Yb}_{0.8}\mathrm{Y}_{0.2}\mathrm{InCu}_4$ under pressure was measured by an extraction technique using a Ti-Cu clamp cylinder and mixture of two types of Fluorinert (CF70:CF77=1:1) as a pressure medium in a static magnetic field up to 9 T genetated by a superconduction magnet.[35] In order to reduce eddy current in the material of a high-pressure clamp cell, a metal-ceramic hybrid clamp cylinder was used.[33]

III. EXPERIMENTAL RESULTS

A. Effect of Y or Lu partial substitution on Yb site

X-ray-diffraction analysis showed that the samples crystallize in a single phase of the cubic $C15b$-type structure in good agreement with a previous report.[9] The lattice parameters estimated from XRD data are shown in Fig. 1, where the value of the lattice constant of YbInCu_4 is 7.155 Å. In the case of the substituted system, the value of the lattice constant increases with the Y substitution for Yb, while that decreases with the Lu substitution because of the different ionic size of Yb, Y, and Lu.

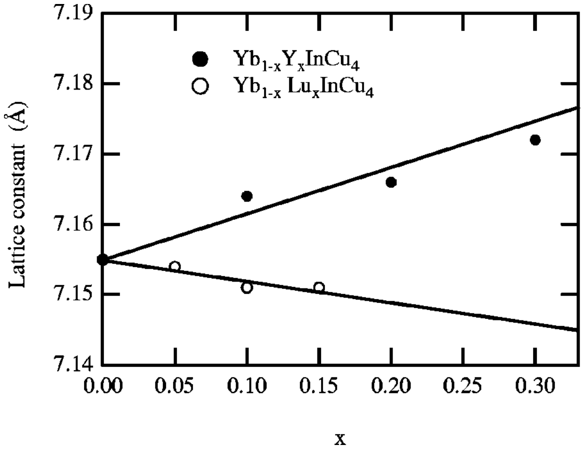

FIG. 1. The lattice parameter of a (Å) vs x of the cubic $\mathrm{Yb}_{1-x}\mathrm{Y}_x\mathrm{InCu}_4$ ($0 \leqslant x \leqslant 0.3$) and $\mathrm{Yb}_{1-x}\mathrm{Lu}_x\mathrm{InCu}_4$ ($0 \leqslant x \leqslant 0.15$) with $C15b$ (AuBe_5-type) structure. The solid lines are to guide the eye.

The temperature dependence of the magnetic susceptibility $\chi(T)$ measured for pure and substituted YbInCu_4 at the magnetic field of 0.5 T are shown in Figs. 2(a) and 3(a). The temperature dependence of the reciprocal susceptibility $1/\chi$ is also shown in Figs. 2(b) and 3(b). The χ(T) for pure and substituted YbInCu_4 is consistent with previous reports.[3,6,7,11,26,29,30] The effect of atomic disorder in YbInCu_4 is obviously observed in the magnetic susceptibility. I. V. Svechkarev *et al.* have discussed this mechanism quantitatively with a distribution function $W(T)$ for T_v^i (just as in the ideal crystal).[27] For perfect single-crystalline YbInCu_4, χ(T) shows the characteristic behavior as follows with $W(T)$ as a switching value between 0 and 1 at T_v:[16,27]

$$\chi(T)=\chi_0+\left(\frac{C}{T-\Theta}-\chi_0\right)W(T), \tag{1}$$

where C is the Curie constant and Θ the Weiss temperature.

(i) At $T<T_v$, $W(T)=0$, a low-temperature plateau χ_0 (the temperature-independent Fermi-liquid susceptibility) can be measured. At this region, Yb ions fluctuate between trivalence ($4f^{13}$) and divalence ($4f^{14}$) to form intermediate-valence state. The small upturn tails of susceptibility at the lowest temperature may arise from impurities in the samples such as $\mathrm{Yb}_2\mathrm{O}_3$. According to this measurement, we found that χ_0 increases with the substitution of Y and Lu for Yb [shown in the insets of Figs. 2(b) and 3(b)].

(ii) At $T=T_v$, the first-order valence transition occurs. Magnetic susceptibility is at its maximum around T_v. Here the sharpness of the transition depends on the sample quality with the smallest site disorder.

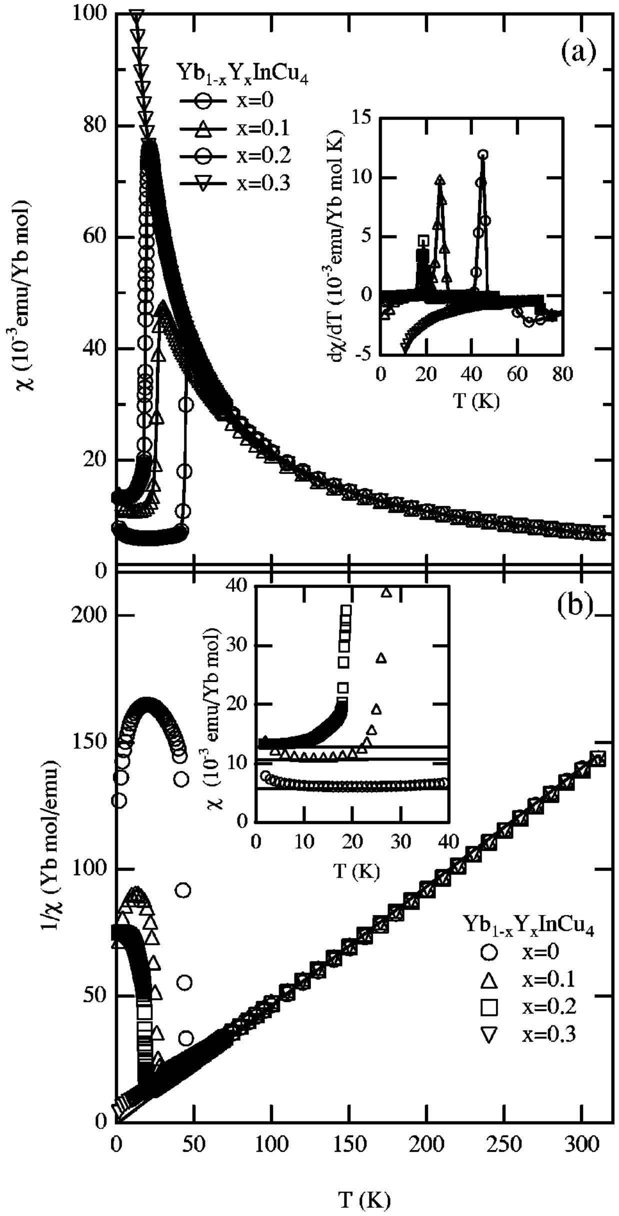

FIG. 2. Temperature dependence of magnetic susceptibility χ (a) and reciprocal susceptibility $1/\chi$ (b) of $\mathrm{Yb}_{1-x}\mathrm{Y}_x\mathrm{InCu}_4$ $(0 \leqslant x \leqslant 0.3)$ at the field of 0.5 T. The inset of (a) is the curves of $d\chi/dT$ vs temperature of $\mathrm{Yb}_{1-x}\mathrm{Y}_x\mathrm{InCu}_4$ $(0 \leqslant x \leqslant 0.3)$ and the inset of (b) is the enlarged magnetic susceptibility plotted against temperature below T_v. The solid lines in (b) are to guide the eye.

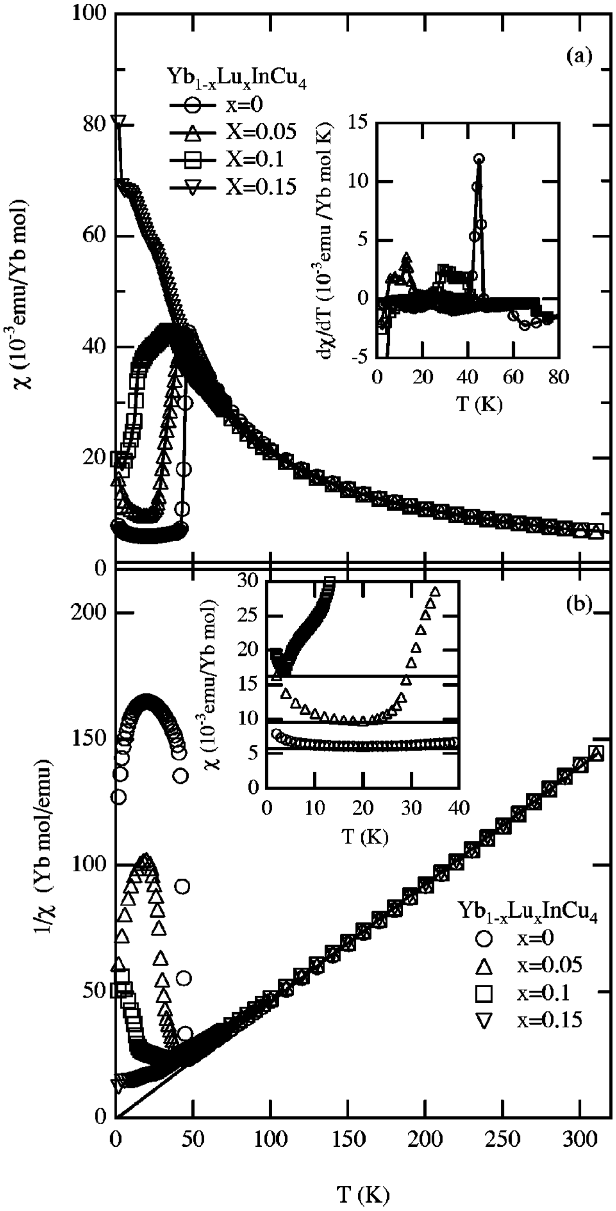

FIG. 3. Temperature dependence of magnetic susceptiblity χ (a) and reciprocal susceptibility $1/\chi$ (b) of $\mathrm{Yb}_{1-x}\mathrm{Lu}_x\mathrm{InCu}_4$ $(0 \leqslant x \leqslant 0.15)$ at the field of 0.5 T. The inset of (a) is the curves of $d\chi/dT$ vs temperature of $\mathrm{Yb}_{1-x}\mathrm{Lu}_x\mathrm{InCu}_4$ $(0 \leqslant x \leqslant 0.15)$ and inset of (b) is the enlarged magnetic susceptibility plotted against temperature below T_v. The solid lines in (b) are to guide the eye.

(iii) At $T > T_v$, $W(T) = 1$, the magnetic susceptibility follows a Curie-Weiss law. By fitting high-temperature (above 100 K) susceptiblity to the Curie-Weiss law [as shown in Figs. 2(b) and 3(b)], the effective magnetic moments for all samples are very close to $4.54\mu_B$ of free Yb^{3+} ion $(J = 7/2,\ g_J = 8/7)$ indicating that Yb exists in a stable trivalent state in the high-temperature region above T_v.

Both the low-temperature plateau $(1/\chi_0)$ and the transition temperature (T_v) decrease in the $\mathrm{Yb}_{1-x}\mathrm{Y}_x\mathrm{InCu}_4$ $(0 \leqslant x \leqslant 0.3)$ and $\mathrm{Yb}_{1-x}\mathrm{Lu}_x\mathrm{InCu}_4$ $(0 \leqslant x \leqslant 0.15)$ systems as x increases. For the Y-substitution system, T_v shifts to lower temperature with almost the same sharpness of transition as the pure one [see the derivative of $\chi(T)$ shown in the inset of Fig. 2(a)]. When 30% Y is substituted we have not observed any valence transition in $\mathrm{Yb}_{0.7}\mathrm{Y}_{0.3}\mathrm{InCu}_4$ down to 2 K. For the Lu substitution, no transition has been found in $\mathrm{Yb}_{0.85}\mathrm{Lu}_{0.15}\mathrm{InCu}_4$ in our research. The transition becomes broader while substituting Lu for Yb [see the inset of Fig. 3(a)]. This may be attributed to more site disorder in the Lu substituted samples. Their paramagnetic state at high temperature with small positive Weiss temperature obtained from Curie-Weiss fitting implies that the ground state may be weak ferromagnetic, which has recently been observed in $\mathrm{Yb}_{0.8}\mathrm{Y}_{0.2}\mathrm{InCu}_4$ during magnetization measurements under high pressures at the temperaure of 0.6 K.[36]

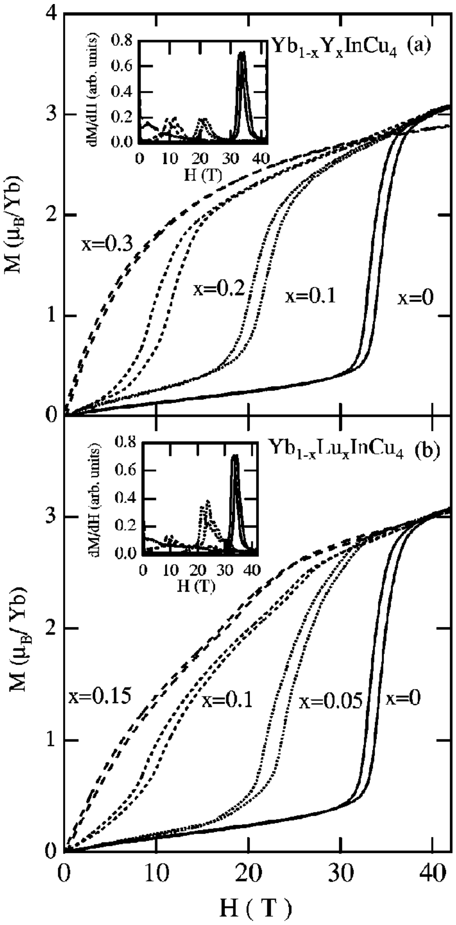

FIG. 4. High-field magnetization curves of $Yb_{1-x}Y_xInCu_4$ ($0 \leqslant x \leqslant 0.3$) (a) and $Yb_{1-x}Lu_xInCu_4$ ($0 \leqslant x \leqslant 0.15$) (b) at 4.2 K. The insets are the curves of dM/dH vs H for $Yb_{1-x}Y_xInCu_4$ ($0 \leqslant x \leqslant 0.3$) (a) and $Yb_{1-x}Lu_xInCu_4$ ($0 \leqslant x \leqslant 0.15$) (b) at 4.2 K.

The existence of two Yb valance states in $YbInCu_4$ (one being of trivalence and the other of mixed valence) indicates that these states are very close in energy below T_v. It is possible to revert the valence state from the mixed valence to trivalence by applying high enough magnetic field that can overcome a critical field, that is transition from the nonmagnetic (large volume) state towards the magnetic (small volume) state below the transition temperature.[3] This can be considered as a magnetic-field-induced first-order valence transition below T_v, from the Pauli paramagnetic Kondo coherent state toward the Yb^{3+} localized moment state ($\mu_{eff} \sim 4.0 \mu_B$) at H_v with increasing H. In Fig. 4 we show plots of magnetization as a function of magnetic field for both positive and negative field sweeps for the samples of pure and substituted $YbInCu_4$ at 4.2 K under the ambient pressure. A clear metamagnetic transition was observed in the high-field magnetization curves of $Yb_{1-x}Y_xInCu_4$ ($0 \leqslant x \leqslant 0.3$) and $Yb_{1-x}Lu_xInCu_4$ ($0 \leqslant x \leqslant 0.15$) in agreement with previous reports.[3,30] This effect is consistent with what is observed in the temperature-dependent magnetic susceptibility at 0.5 T as shown in Figs. 2 and 3. The transition occurs at higher fields for increasing-field sweeps as compared to decreasing-field sweeps. The hysteresis is about 1 T for $YbInCu_4$ and becomes larger for substituted $YbInCu_4$.

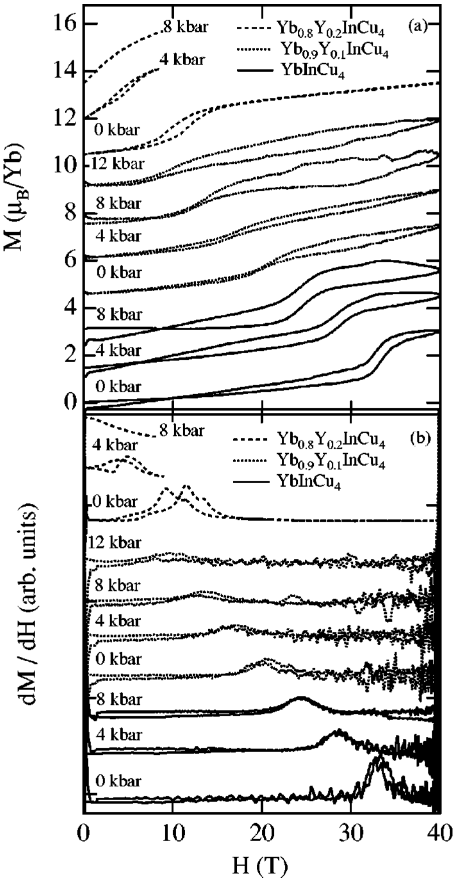

FIG. 5. High-field magnetization curves (a) and dM/dH vs H curves (b) of $Yb_{1-x}Y_xInCu_4$ ($0 \leqslant x \leqslant 0.2$) under various fixed pressures at 4.2 K.

Just like the temperature dependence of susceptibility, both Y and Lu substitutions make the transition magnetic field (H_v) of $YbInCu_4$ shift to lower magnetic field. The H_v decreases in the $Yb_{1-x}Y_xInCu_4$ ($0 \leqslant x \leqslant 0.3$) and $Yb_{1-x}Lu_xInCu_4$ ($0 \leqslant x \leqslant 0.15$) systems as x increases, while the transition becomes broader especially in the Lu-substituted system, which may be due to more site disorder of the Yb lattice suffered from the substitution.

B. Effect of pressure on H_v

The pressure dependence of the first-order phase-transition temperture (T_v) have been studied by many groups.[25–28] In this research we have studied the effect of pressure on the first-order phase-transition magnetic field (H_v) of pure and Y-substituted $YbInCu_4$. The high-field magnetization measurements of $Yb_{1-x}Y_xInCu_4$ ($0 \leqslant x \leqslant 0.2$) under various fixed pressures have been performed at 4.2 K. The experimental results are shown in Fig. 5. Here, the Y-substituted system is preferable to the Lu-substituted one because it displays a sharp transition at magnetic susceptibility and magnetization measurements. The change of the valence transition magnetic field as a function of pressure is evident.

In Fig. 6 the pressure dependence of H_v for $Yb_{1-x}Y_xInCu_4$ ($0 \leqslant x \leqslant 0.2$) is displayed. In the whole in-

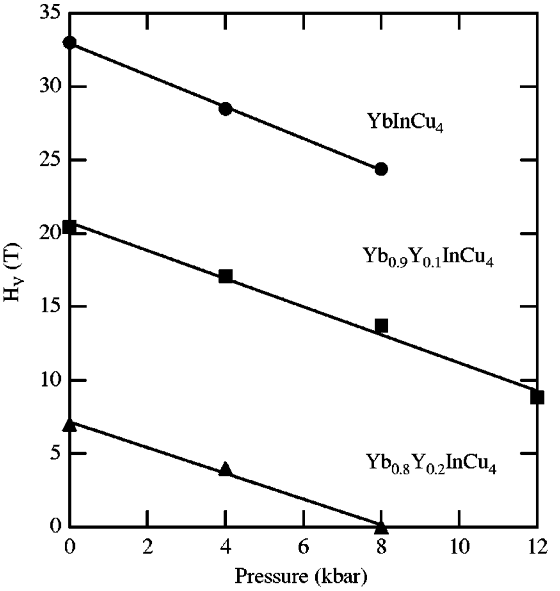

FIG. 6. Pressure dependence of transition magnetic field (H_v) of Yb$_{1-x}$Y$_x$InCu$_4$ ($0 \leqslant x \leqslant 0.2$) at 4.2 K.

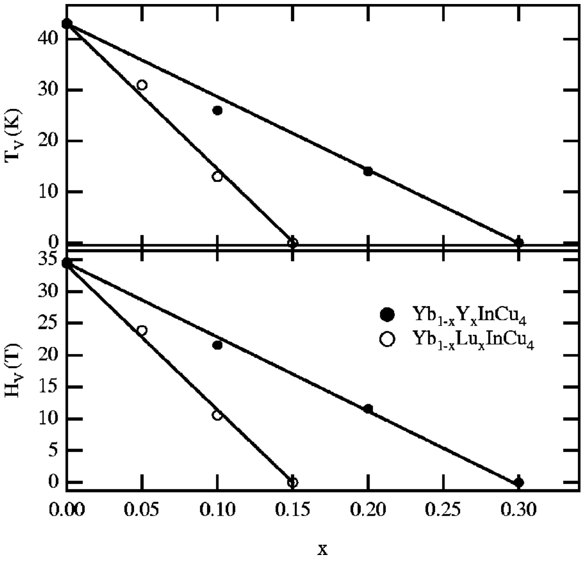

FIG. 7. Transition temperaure (T_v) at the magnetic field of 0.5 T (above) and transition magnetic field (H_v) at 4.2 K (below) of Yb$_{1-x}$Y$_x$InCu$_4$ ($0 \leqslant x \leqslant 0.3$) and Yb$_{1-x}Lu_x$InCu$_4$ ($0 \leqslant x \leqslant 0.15$) determined from the data of Figs. 2, 3, and 4, plotted vs alloy concentration *x*.

vestigated pressure range, the curves in Fig. 6 are quite linear, with the average slope of $dH_v/dP \approx -1.0$ T/kbar. The fact that H_v decreases with pressure is consistent with favoring the smaller trivalent state of Yb; the rate of suppression is almost the same ($dH_v/dP \approx -1.0$ T/kbar) whether or not the sample is substituted by Y for Yb, corresponding to the rate of suppression to T_v under pressure, in which $dT_v/dP = -2.1$ K/kbar,[25] or $dT_v/dP = -2.0$ K/kbar.[27]

IV. DISCUSSION

Studies of the valence phase transition in systems where the Yb was substituted by other rare earths have been reported extensively so far.[7,25,26,29,30] The first-order valence-phase transition is strongly volume dependent, and changes drastically under substitution of the Yb by other elements. The results of measurements of magnetic susceptibility and high-field magnetization in this research show that T_v and H_v are driven to lower points by the Y or Lu substitution in the Yb site until the critical point ($H_v = 0$ and $T_v = 0$). This indicates that the local-moment state is stabilized down to lower temperatures by the substitution. The phase boundaries of the first-order valence transition are shown in Fig. 7. The critical point is around $x_c = 0.3$ for the Y-substituted system and is around $x_c = 0.15$ for the Lu-substituted system. We have calculated the thermal energy ($k_B T_v$) and Zeeman energy ($\mu_B H_v$) at the transition point for each sample, both of which are of the same order with each other. In particular, by equating $k_B T_v = a \mu_B H_v$ as reported in Refs. 3 and 26, we also find $a = 1.8 \pm 0.1$ for each of the samples in Fig. 7.

We show the concentration (x) derivatives of T_v and H_v for Yb$_{1-x}$Y$_x$InCu$_4$ ($0 \leqslant x \leqslant 0.3$) and Yb$_{1-x}Lu_x$InCu$_4$ ($0 \leqslant x \leqslant 0.15$) in Table I, and we can find $d \ln T_v/dx = d \ln H_v/dx$ for both the Y-substituted system and the Lu-substituted system. These derived numbers also can be calculated as

$$\frac{\partial \ln T_v}{\partial x} = \frac{\partial \ln H_v}{\partial x} = \left.\frac{\partial \ln T_v}{\partial \ln a}\right|_x \frac{\partial \ln a}{\partial x} + \left.\frac{\partial \ln T_v}{\partial x}\right|_a .$$

In the Y-substituted system Yb$_{1-x}$Y$_x$InCu$_4$ for $x > x_c$ (critical point) samples, magnetic susceptibility at ambient pressure is the same as the $x = 0.3$ sample, the local moment state (Yb^{3+}) is stabilized down to low temperatures (data not shown), and no valence transition can be observed.[29,30] For $x = 1$, YInCu$_4$ is a semimetal and the susceptibility is diamagnetic.[29,37] In the Lu-substituted system Yb$_{1-x}$Lu$_x$InCu$_4$, for $x > x_c$, magnetic susceptibility under the ambient pressure is the same as the $x = 0.15$ sample (data not shown), the local moment state (Yb^{3+}) is stabilized down to low temperatures, and no valence transition can be observed.[30] For $x = 1$, LuInCu$_4$ is normally a metallic and nonmagnetic compound.[8]

We show the derived dependences of the lattice parameter on concentration (x) for Yb$_{1-x}$Y$_x$InCu$_4$ ($0 \leqslant x \leqslant 0.3$) and Yb$_{1-x}Lu_x$InCu$_4$ ($0 \leqslant x \leqslant 0.15$) in Table I which is obtained from Fig. 1. We know that substitution by Lu has the effect of positive chemical pressure; on the other hand, substitution

TABLE I. Concentration (x) derivatives of transition point (T_v and H_v) and lattice constants (a) for Yb$_{1-x}$Y$_x$InCu$_4$ ($0 \leqslant x \leqslant 0.3$) and Yb$_{1-x}Lu_x$InCu$_4$ ($0 \leqslant x \leqslant 0.15$).

System	$\frac{dT_v}{dx}$	$\frac{d \ln T_v}{dx}$	$\frac{dH_v}{dx}$	$\frac{d \ln H_v}{dx}$	$\frac{da}{dx}$	$\frac{d \ln a}{dx}$	$\left.\frac{\partial \ln T_v}{\partial x}\right\|_a$
Y- [a]	−143	−3.3	−115	−3.3	0.063	0.0088	−4.1
Lu- [b]	−287	−6.7	−230	−6.7			−6.2
					−0.033	−0.0047	

[a] Yb$_{1-x}$Y$_x$InCu$_4$ ($0 \leqslant x \leqslant 0.3$).

[b] Yb$_{1-x}$Lu$_x$InCu$_4$ ($0 \leqslant x \leqslant 0.15$).

by Y has the effect of negative chemical pressure. However, both the magnetic susceptibility and high-field magnetization measurements indicate that the transition point of $\mathrm{YbInCu_4}$ is driven down to lower temperatures and lower magnetic fields by the substitution of Y and Lu for Yb.

In order to discuss the effect of substitution by Y and Lu, comparison between the effect of chemical pressure $d\ln T_v/d\ln V$ (variation of the lattice parameter by Y, Lu substitution) and the intrinsic effect of substitution $\partial ln T_v/\partial x|_a$ (variation of T_v and H_v by the effect of substitution without a change of the lattice parameter) is necessary. An analysis of $\chi(T)$ by means of a theory for the Kondo system with $J=7/2$ qualifies the $\mathrm{YbInCu_4}$ as a heavy fermion (HF) compound.[16,27,38] The Grüneisen parameter for the Kondo energy Ω_K in the HF state is calculated as[27]

$$\Omega_K^{HF} \equiv -\frac{d\ln T_K}{d\ln V} = \frac{1}{T_K}\frac{d\Theta}{d\ln V} \simeq -32. \tag{2}$$

From Eq. (2) we can see that the pressure can decrease the T_K as $d\ln T_K/d\ln V=32$ or $d\ln T_K/d\ln a=96$. The Kondo volume collapse model suggests that the valence transition in $\gamma-\alpha$ Ce occurs near the Kondo temperature.[39] This also appears to be true in $\mathrm{YbInCu_4}$, $T_v \simeq T_K$,[26] which means $d\ln T_v/d\ln a \simeq d\ln T_K/d\ln a=96$. Then, we can get that the value of $\partial\ln T_v/\partial x|_a$ for the Y-substituted system is -4.1 and for Lu-substituted system is -6.2 (shown in the last column of Table I).

From these values we can see that the effect of variation of lattice parameter is very small and the effect of substitution of the Yb lattice is large to the first-order valence transition of $\mathrm{YbInCu_4}$. This means that the $4f$ electronic state in Yb is strongly affected by the substitution of Y and Lu and the chemical pressure is not the dominant effect to the valence transition of Yb in the substituted $\mathrm{YbInCu_4}$ systems. The change in the electronic, magnetic, and/or thermodynamic properties of the system by substitution on the Yb site and their impact on the first-order valence transition is the main reason for this phenomenon. From the value of $\partial ln T_v/\partial x|_a$ we find that the Lu substitution seems to be more effective than Y substitution because of the differences between Y and Lu, probably the Lu $5d$-band electrons interact more strongly with Yb $5d$-band electrons than the $4d$-band electrons of Y. This phenomenon also can be explained by the electronic band calculation: the electronic band structure of $\mathrm{YbInCu_4}$ in the HT phase is very similar to $\mathrm{LuInCu_4}$,[40] but the band structure of $\mathrm{YInCu_4}$ is different than $\mathrm{YbInCu_4}$, because $\mathrm{YInCu_4}$ has a lattice constant larger than that of $\mathrm{YbInCu_4}$.[37] The dimensions of the Fermi surface of these compounds are sensitive to the lattice constants.

Within the Bethe-ansatz solution of the Coqblin-Schrieffer impurity model[38] the thermodynamical properties of a dense Kondo system are described by the single energy scale (T_0). Therefore χ_0 is directly proportional to $1/T_0$ as

$$\chi_0 = \frac{N_A \upsilon(\upsilon^2-1) g_J^2 \mu_B^2}{24\pi k_B T_0}, \tag{3}$$

where N_A is the Avogadro number, υ the degeneracy of the ground state, g_J the Landé g factor, μ_B the Bohr magneton, and k_B the Boltzmann constant. The χ_0 is evaluated from the low-temperature data by subtracting the small Curie term possibly originating from magnetic impurities. T_0 that can be calculated by the Eq. (3) is in proportion to the Kondo temperature T_K,[1,4,38] i.e., $T_0 = mT_K$ (m is constant). From Figs. 2 and 3 we have found that the χ_0 is increased by the substitution in the $\mathrm{Yb_{1-x}Y_xInCu_4}$ $(0 \leqslant x \leqslant 0.3)$ and $\mathrm{Yb_{1-x}Lu_xInCu_4}$ $(0 \leqslant x \leqslant 0.15)$ systems. That means that the T_0 will decrease with the substitution through Eq. (3). The decrease of T_0 with the substitution of Yb by the Y and Lu implies that it would become unstable in the Kondo coherent state at low temperatures; meanwhile the trivalent state could be stabilized to lower temperatures, so as to lead T_v and H_v to lower points. In Fig. 8 we have plotted the T_v and H_v in response to $1/\chi_0$ as well as T_0 for the pure and substituted samples. The T_v and H_v decrease linearly toward the origin with decreasing $1/\chi_0$ and T_0. The decrease of Kondo temperature in the mixed-valence state should be the main reason for driving T_v and H_v to lower points.

This phenomenon is also elucidated in the dilute system $\mathrm{Yb_{1-x}Y_xInCu_4}$ with $0 \leqslant x \leqslant 1$ by nuclear quadrupole resonance (NQR) measurments.[29] The resonance frequency ${}^{63}\nu_Q = e^2qQ/2h$, for ^{63}Cu (where eq is the maximum component of electric-field gradient at Cu sites and Q the quadrupole moment of ^{63}Cu) below T_v increases rapidly with increasing x. The $\Delta\nu_Q = \nu_Q$ (local moment) $-\nu_Q$ (Fermi liquid), has the similar concentration dependence to that of T_v, suggesting that the coherent Fermi-liquid state in $\mathrm{YbInCu_4}$ becomes unstable by the substitution of Y into the Yb sites.

The valence transition also can be tuned with applied pressure, which means an external pressure stabilizes the trivalent state with the local moment. The studies under external pressure show strong changes in T_v.[25–28] Here we present the magnetization measurements under pressure up to 12 kbar to investigate the pressure dependence of H_v corresponding to the pressure dependence of T_v. From Fig. 6 we can find that 10% Y substituted in $\mathrm{YbInCu_4}$ is equivalent to a 12-kbar pressure effect on $\mathrm{YbInCu_4}$ $(\mathrm{Y}_{x=0.1} \sim 12\ \mathrm{kbar})$. In this study we get $dH_v/dP = -1.1$ T/kbar for $\mathrm{YbInCu_4}$, in correspondence with $dT_v/dP = -2.1$ K/kbar at low pressure (up to 6 kbar) and $dT_v/dP = -1.1$ K/kbar at higher pressures for $\mathrm{YbInCu_4}$.[25]

According to the phase diagram as functions of T and P of $\mathrm{YbInCu_4}$ proposed by I. V. Svechkarev *et al.*,[27] above 20 kbar T_v may be suppressed to zero and the appearance of a ferromagnetic phase caused by the latent positive interaction Θ_L was predicted. The H_v has not been suppressed to zero up to the pressure of 12 kbar for pure and $\mathrm{Yb_{0.9}Y_{0.1}InCu_4}$, while it can be annihilated for $\mathrm{Yb_{0.8}Y_{0.2}InCu_4}$ by the pressure above 8 kbar in magnetization measurements at 4.2 K. Furthermore, magnetization versus magnetic-field curves for $\mathrm{Yb_{0.8}Y_{0.2}InCu_4}$ measured at 0.6 K under 8 kbar exhibit spontaneous magnetization and a hysteretic loop, demonstrating that the ground state is weakly ferromagnetic under high pressure which will be reported elsewhere.[36]

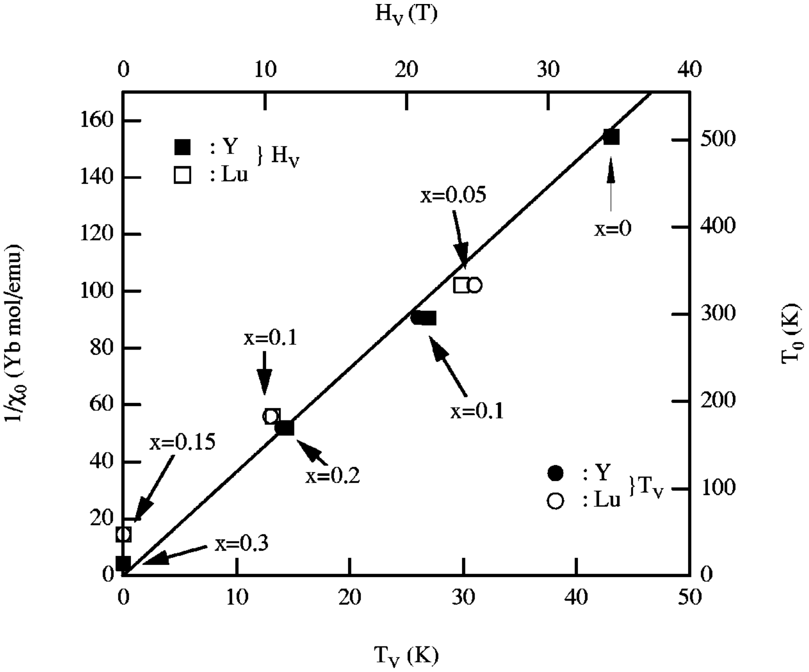

FIG. 8. The plots of transition temperature (T_v) and transition magnetic field (H_v) vs the zero-temperature inverse magnetic susceptibility ($1/\chi_0$) and the scaling temperature (T_0) of the dense Kondo system. The solid line is to guide the eye.

V. CONCLUSION

The effect of substitution by Y and Lu for Yb on the first-order valence transition of $\mathrm{YbInCu_4}$ has been investigated by studying the magnetic susceptibility and high-field magnetization which accompany this transition. The first-order valence transition of $\mathrm{YbInCu_4}$ is strikingly affected by the substitution of Y and Lu. Despite that the lattice parameter of $\mathrm{YbInCu_4}$ is increased with Y substitution and decreased with Lu substitution, the transition temperature (T_v) and transition magnetic field (H_v) are all changed to lower temperature and lower magnetic field. Consequently, the inherent chemical pressure effect is very small on the first-order valence transition in $\mathrm{YbInCu_4}$, compared with the substitution effect. The Lu substitution is more effective than Y substitution. The Kondo temperature T_K obtained from χ_0 below T_v is decreased as x increases in both $\mathrm{Yb_{1-x}Y_xInCu_4}$ ($0 \leqslant x \leqslant 0.3$) and $\mathrm{Yb_{1-x}Lu_xInCu_4}$ ($0 \leqslant x \leqslant 0.15$) systems. It is suggested that the stability of the Kondo lattice below T_v in the substituted $\mathrm{YbInCu_4}$ systems would be reduced by the substitution of Y or Lu for Yb, which implies that the $\mathrm{Yb^{3+}}$ state will be stable to lower temperatures and lower magnetic fields. This indicates that the T_v and H_v decrease as x increases in both $\mathrm{Yb_{1-x}Y_xInCu_4}$ ($0 \leqslant x \leqslant 0.3$) and $\mathrm{Yb_{1-x}Lu_xInCu_4}$ ($0 \leqslant x \leqslant 0.15$) systems until the critical point ($T_v = 0$, $H_v = 0$).

Furthermore, the effect of pressure on the first-order valence transition of pure and Y-substitued $\mathrm{YbInCu_4}$ has been investigated. The magnetization measurements up to 41 T under various fixed pressures up to 12 kbar have shown that the valence transition is strongly affected by external pressure. The transition magnetic field of H_v is driven towards lower magnetic field as pressure increases at the rate of ≈ -1 T/kbar for pure and Y-substituted $\mathrm{YbInCu_4}$. As expected, the small volume state ($\mathrm{Yb^{3+}}$ state) is favored by the application of high pressure which eventually leads to suppression of the first-order valence transition by the high external pressure.

ACKNOWLEDGMENTS

We are very grateful to Dr. Masaki Kato for valuable discussions. This work was performed under the auspices of the Ministry of Education, Science and Culture of Japan and was supported from the Japan Society for Promotion of Science (JSPS) through Grant Nos. 11440195, 12440195, and 12874038. One of the authors (A.M.) also gratefully acknowledges support from JSPS.

---

*Present address: Department of Physics, Toyama University, 3190 Gofuku, Toyama 930-8555, Japan.

[1] J. L. Sarrao, C. D. Immer, Z. Fisk, C. H. Booth, E. Figueroa, J. M. Lawrence, R. Modler, A. L. Cornelius, M. F. Hundley, G. H. Kwei, and J. D. Thompson, Phys. Rev. B **59**, 6855 (1999), and references therein.

[2] C. Rossel, K. N. Yang, M. B. Maple, Z. Fisk, E. Zirngieble, and J. D. Thompson, Phys. Rev. B **35**, 1914 (1987).

[3] K. Yoshimura, T. Nitta, M. Mekata, T. Shimizu, T. Sakakibara, T. Goto, and G. Kido, Phys. Rev. Lett. **60**, 851 (1988).

[4] N. Tsujii, J. He, K. Yoshimura, K. Kosuge, H. Michor, K. Kreiner, and G. Hilscher, Phys. Rev. B **55**, 1032 (1997).

[5] E. Bauer, P. Fischer, F. Marabelli, M. Ellerby, K. A. McEwen, B. Roessli, and M. T. Fernandes-Dias, Physica B **234-236**, 676 (1997).

[6] I. Felner and I. Nowik, Phys. Rev. B **33**, 617 (1986).

[7] I. Felner, I. Nowik, D. Vaknin, U. Potzel, J. Moser, G. M. Kalvius, G. Wortmann, G. Schmiester, G. Hilscher, E. Gratz, C. Schmiester, N. Pillmayr, K. G. Prasad, H. de Waard, and H. Pinto, Phys. Rev. B **35**, 6956 (1987).

[8] H. Müller, E. Bauer, G. E. K. Yoshimura, T. Nitta, and M. Mekata, J. Magn. Magn. Mater. **76&77**, 159 (1988).

[9] K. Kojima, H. Hayashi, A. Minami, Y. Kasamatsu, and T. Hihara, J. Magn. Magn. Mater. **81**, 267 (1989).

[10] A. Severing, E. Gratz, B. D. Rainfold, and K. Yoshimura, Physica B **163**, 409 (1990).

[11] J. L. Sarrao, Physica B **259-261**, 128 (1999).

[12] K. Yoshimura, N. Tsujii, J. He, M. Kato, K. Kosuge, H. Michor, K. Kreiner, G. Hilscher, and T. Goto, J. Alloys Compd. **262&263**, 118 (1997).

[13] J. He, N. Tsujii, M. Nakanishi, K. Yoshimura, and K. Kosuge, J. Alloys Compd. **240**, 261 (1996).

[14] N. Tsujii, J. He, F. Amita, K. Yoshimura, K. Kosuge, H. Michor, G. Hilscher, and T. Goto, Phys. Rev. B **56**, 8103 (1997).

[15] K. Hiraoka, K. Kojima, T. Hihara, and T. Shinohara, J. Magn. Magn. Mater. **140-144**, 1243 (1995).

[16] J. L. Sarrao, C. D. Immer, C. L. Benton, Z. Fisk, J. M. Lawrence, D. Mandrus, and J. D. Thompson, Phys. Rev. B **54**, 12 207 (1996).

[17] A. L. Cornelius, J. M. Lawrence, J. L. Sarrao, Z. Fisk, M. F. Hundley, G. H. Kwei, J. D. Thompson, C. H. Booth, and F. Bridges, Phys. Rev. B **56**, 7993 (1997).

[18] B. Coqblin and J. R. Schrieffer, Phys. Rev. **185**, 847 (1969).

[19] S. Ogawa, S. Suga, M. Taniguchi, M. Fujisawa, A. Fujimori, T. Shimizu, H. Yasuoka, and K. Yoshimura, Solid State Commun. **67**, 1093 (1988).

[20] K. Yoshimura, T. Nitta, T. Shimizu, M. Mekata, H. Yasuoka, and K. Kosuge, J. Magn. Magn. Mater. **90&91**, 466 (1990).

[21] H. Nakamura, K. Nakajima, Y. Kitaoka, K. Asayama, K. Yoshimura, and T. Ntta, J. Phys. Soc. Jpn. **59**, 28 (1990).

[22] K. Nakajima, H. Nakamura, Y. Kitaoka, K. Asayama, K. Yoshimura, and T. Nitta, J. Magn. Magn. Mater. **90&91**, 581 (1990).

[23] T. Koyama, M. Matsumoto, S. Wada, and J. L. Sarrao, Phys. Rev. B **63**, 172410 (2001).

[24] K. Yoshimura, T. Nitta, M. Mekata, T. Shimizu, T. Sakakibara, T. Goto, and G. Kido, J. Phys. (Paris), Colloq. **49**, C8-731 (1988).

[25] I. Nowik, I. Felner, J. Voiron, J. Beille, A. Najib, E. du Tremolet de Lacheisserie, and G. Gratz, Phys. Rev. B **37**, 5633 (1988).

[26] C. D. Immer, J. L. Sarrao, Z. Fisk, A. Lacerda, C. Mielke, and J. D. Thompson, Phys. Rev. B **56**, 71 (1997).

[27] I. V. Svechkarev, A. S. Panfilov, S. N. Dolja, H. Nakamura, and M. Shiga, J. Phys.: Condens. Matter **11**, 4381 (1999).

[28] J. M. De Teresa, Z. Arnold, A. del Moral, M. R. Ibarra, J. Kamarád, D. T. Adroja, and B. Rainford, Solid State Commun. **99**, 911 (1996).

[29] H. Nakamura and M. Shiga, Physica B **206&207**, 364 (1995).

[30] K. Yoshimura, N. Tsujii, K. Sorada, T. Kawabata, H. Mitamura, T. Goto, and K. Kosuge, Physica B **281&282**, 141 (2000).

[31] D. R. Lide, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, 2001-2002).

[32] J. M. Lawrence, G. H. Kwei, J. L. Sarrao, Z. Fisk, D. Mandrus, and J. D. Thompson, Phys. Rev. B **54**, 6011 (1996).

[33] N. V. Mushnikov and T. Goto, J. Phys.: Condens. Matter **11**, 8095 (1999).

[34] A. Mitsuda, T. Goto, H. Wada, and M. Shiga, J. Magn. Magn. Mater. **226-230**, 167 (2001).

[35] K. Koyama, S. Hane, K. Kamishima, and T. Goto, Rev. Sci. Instrum. **69**, 3009 (1998).

[36] A. Mitsuda, T. Goto, K. Yoshimura, W. Zhang, N. Sato, K. Kosuge, and H. Wada, Phys. Rev. Lett. **88**, 137204 (2002).

[37] H. Nakamura, K. Ito, A. Uenishi, H. Wada, and M. Shiga, J. Phys. Soc. Jpn. **62**, 1446 (1993).

[38] V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).

[39] J. W. Allen and R. M. Martin, Phys. Rev. Lett. **49**, 1106 (1982).

[40] K. Takegahara and T. Kasuya, J. Phys. Soc. Jpn. **59**, 3299 (1990).