# Anomalous High-Field Magnetization and Negative Forced Volume Magnetostriction in $Yb_{1-x}M_xCu_2$ ($M$ = In and Ag) — Evidence for Valence Change in High Magnetic Fields

K. Yoshimura, T. Nitta, and M. Mekata
*Department of Applied Physics, Fukui University, Bunkyo, Fukui 910, Japan*

T. Shimizu, T. Sakakibara, and T. Goto
*Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo 106, Japan*

and

G. Kido
*Institute for Materials Research, Tohoku University, Katahira, Sendai 980, Japan*
(Received 3 November 1987)

The magnetization and the volume magnetostriction were measured up to 39 T at low temperatures in the mixed-valence compound $Yb_{0.38}In_{0.62}Cu_2$ and the dense Kondo compound $Yb_{0.50}Ag_{0.50}Cu_2$. $Yb_{0.38}In_{0.62}Cu_2$ shows a distinct metamagnetic transition at 33 T. A remarkable negative volume magnetostriction was observed at the transition, giving evidence of an abrupt increase in Yb valence from the mixed-valence state to the trivalent state. $Yb_{0.50}Ag_{0.50}Cu_2$ shows an appreciable upturn of magnetization and a gradual volume shrinkage, corresponding to a gradual Yb valence change toward the trivalent state also in the dense Kondo system.

PACS numbers: 75.30.Mb, 71.28.+d, 72.15.Qm, 75.20.Hr

Anomalous electric and magnetic properties associated with unstable $4f$ and $5f$ electron states have been investigated extensively in rare-earth and actinide intermetallic compounds. This work has proceeded from the points of view of mixed- (fluctuating- or intermediate-) valence, dense Kondo, and heavy-fermion systems.[1-4] The weak delocalization of the $f$ electrons through the interaction with conduction electrons should play an important role in the instability of the $f$ electrons. Recently, the $C15$ cubic Laves-phase compounds $Yb_{1-x}In_xCu_2$ with $x \simeq 0.6$ have been reported to show a sharp transition attributable to a valence change of Yb.[5,6] The $Yb^{3+}$ state with angular momentum $J = \frac{7}{2}$ is stable above the transition temperature $T_v \simeq 50$ K, while the valence of Yb is reduced suddenly below $T_v$. On the other hand, $Yb_{0.5}Ag_{0.5}Cu_2$ with the $C15b$ structure has been reported to show a broad maximum in the magnetic susceptibility $\chi$ at around 40 K associated with the dense Kondo effect.[7]

To elucidate the behavior of unstable $4f$-electron magnetic moments in these two intermetallic systems, $Yb_{1-x}In_xCu_2$ and $Yb_{1-x}Ag_xCu_2$, we investigated the magnetization and the forced volume magnetostriction by using high pulsed magnetic fields up to 39 T. The Zeeman energy in such high magnetic fields is similar to the crystalline field splitting and also the Kondo coupling energy with the conduction electrons.[8-12] Thus, a magnetic field of 40 T may exceed the transition energy $k_BT_v$ of the $Yb_{1-x}In_xCu_2$ system. In the mixed-valence Yb compounds, Yb ions fluctuate between divalent ($4f^{14}$) and trivalent ($4f^{13}$) states in time. Since the ionic volume of Yb in the divalent nonmagnetic $^1S_0$ state is substantially larger than that in the trivalent $^2F_{7/2}$ state, the measurement of volume change in magnetic fields (volume magnetostriction), $\Delta V/V$, gives us valuable information about the Yb valence. In the present paper, we report a newly found field-induced metamagnetic transition and evidence for the valence change at the metamagnetic transition deduced from the volume magnetostriction in the mixed-valence system $Yb_{1-x}In_xCu_2$ together with the gradual valence change in the magnetization process of the dense Kondo system $Yb_{1-x}Ag_xCu_2$.

The samples were prepared from 99.9%-pure Yb, 99.999%-pure In, Ag, and Cu metals by argon-arc melting and subsequent annealing at 750 °C for one week in evacuated quartz tubes. No foreign phase other than $C15$ was detected by the Debye-Scherrer x-ray analysis for the composition ranges of $0.35 \leqq x \leqq 0.75$ in $Yb_{1-x}In_xCu_2$ and $0.40 \leqq x \leqq 0.60$ in $Yb_{1-x}Ag_xCu_2$. The composition was determined by chemical analysis. For the present high-field study, we aimed at two typical compounds, $Yb_{0.38}In_{0.62}Cu_2$ and $Yb_{0.50}Ag_{0.50}Cu_2$. A vibrating-sample magnetometer was used to measure the temperature dependence of the magnetic susceptibility. Magnetization $M$ in high pulsed magnetic fields was measured at 1.3 K by an induction method with well-balanced pickup coils. For the measurements, we used powdered specimens to exclude the eddy-current effect by pulsed field with duration time of 12 msec. The specimens for the forced-magnetostriction measurements were cut from the polycrystalline ingots and were shaped into a thin rectangle of $5 \times 1 \times 1$ mm$^3$ to diminish the skin effect, of which the longest side (5 mm) was used for the

 

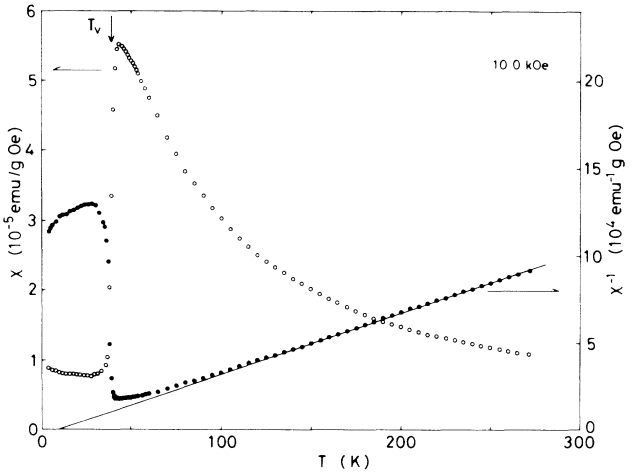


FIG. 1. Temperature variations of $\chi$ and $\chi^{-1}$ of $Yb_{0.38}In_{0.62}Cu_2$.

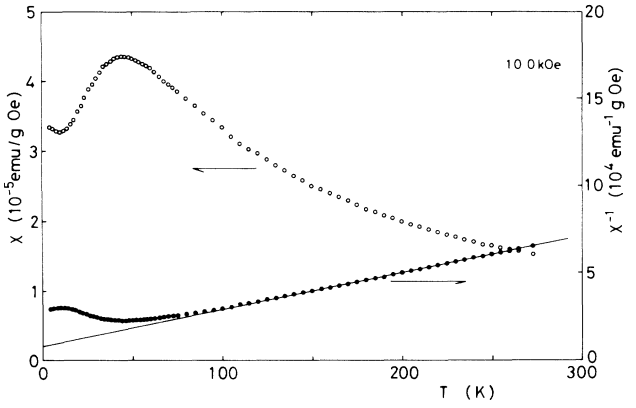


FIG. 2. Temperature variations of $\chi$ and $\chi^{-1}$ of $Yb_{0.50}Ag_{0.50}Cu_2$.

measurements. Forced magnetostriction was measured by the three-terminal capacitance method in high pulsed field. With the capacitance method, the temperature in the sample cell is a little higher than 4.2 K, because we have to exclude liquid He from the cell so that the electrode of the probe condenser is freely movable with the change of sample length. The eddy-current effect may also cause an increase of the temperature. A composite wire consisting of multifilamentary NbTi embedded in the Cu substrate was used for the coil of the pulsed-field magnets.

As shown in Fig. 1, the temperature dependence of $\chi$ of $Yb_{0.38}In_{0.62}Cu_2$ clearly indicates the first-order-like sharp transition at $T_v$ of 38 K in agreement with previous results.[5,6] No thermal hysteresis was observed within an experimental error of 1 K. Using NMR we confirmed that this transition cannot be attributed to antiferromagnetic ordering; no change in the Cu NMR spectrum with a sharp quadrupole splitting was observed at $T_v$, implying paramagnetism below $T_v$. Above $T_v$, $\chi^{-1}$ in Fig. 1 obeys the Curie-Weiss (CW) law with the paramagnetic effective Bohr-magneton number $p_{\text{eff}}$ of about $4.0\mu_B$/Yb, indicating that the Yb valence is close to +3. The thermal expansion measurement with use of x-ray-diffraction and x-ray-absorption measurements revealed that the valence of Yb decreases from +2.9 to +2.8 at the transition with decreasing temperature.[6] Paramagnetism with such high valence suggests the system to be in the coherent Kondo state below $T_v$. Furthermore, the Weiss temperature $\theta$ varies between $-10$ and +10 K depending sensitively on the heat treatment. The small value of $\theta$ implies the weak interaction between Yb moments above $T_v$.

In good agreement with the result of Rossel *et al.*[7] the $\chi$-vs-$T$ curve of $Yb_{0.50}Ag_{0.50}Cu_2$ has a broad maximum around 40 K and obeys the CW law with $p_{\text{eff}}=4.4\mu_B$/Yb and $\theta=-32$ K at high temperatures (see Fig. 2). This implies that the trivalent Yb in $Yb_{0.50}Ag_{0.50}Cu_2$ shows dense Kondo behavior. Furthermore, this $\chi$-vs-$T$ curve can be well described by calculations[13] based on the Coqblin-Schrieffer thermodynamic model for $Yb^{3+}$ impurities.[7] The successful interpretation based on the impurity model indicates that the intersite interaction between Yb moments is very small, which suggests a possible heavy-fermion state in agreement with the considerable mass enhancement in the electronic specific-heat coefficient.[7]

Figure 3 shows the magnetization curves at 1.3 K in fields up to 39 T for $Yb_{0.38}In_{0.62}Cu_2$ and $Yb_{0.50}Ag_{0.50}Cu_2$. A sharp and prominent jump of $M$ is found in $Yb_{0.38}In_{0.62}Cu_2$ at a critical field $H_c$ of 33 T accompanied with a hysteresis of about 1 T. As far as the authors are aware, this is the first observation of such a clear metamagnetic transition of first order in the mixed-valence system with a nonmagnetic ground state. The magnetization amounts to about $2.6\mu_B$/Yb at 39 T and looks like the approach toward the trivalent ionic

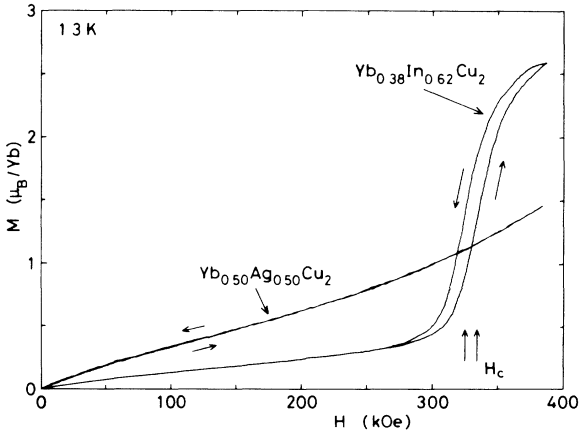


FIG. 3. Magnetization curves of $Yb_{0.38}In_{0.62}Cu_2$ and $Yb_{0.50}Ag_{0.50}Cu_2$ at 1.3 K. The transition fields, $H_c$, with both increasing and decreasing fields are indicated by arrows.

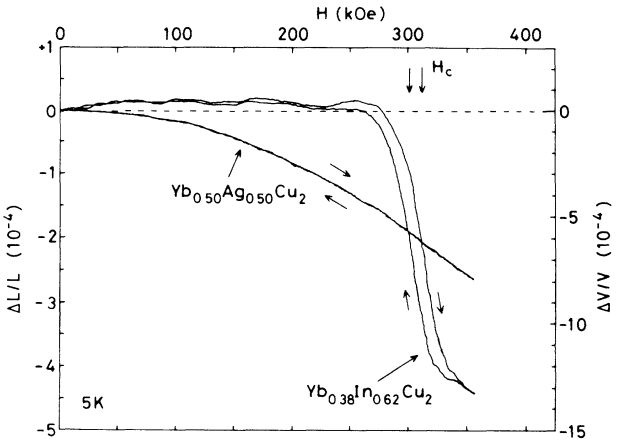


FIG. 4. Magnetic field variations of $\Delta L/L$ and $\Delta V/V$ in $Yb_{0.38}In_{0.62}Cu_2$ and $Yb_{0.50}Ag_{0.50}Cu_2$ at 5 K.

moment of $4.0\mu_B$. The Zeeman energy at $H_c$ of 3.1 $\times 10^{-15}$ erg is comparable to the thermal energy at $T_v$ of $5.3\times 10^{-15}$ erg. Therefore, it is expected that the transitions by both external field and temperature are attributable to the same valence transition. Because 1 T corresponds to about 1 K, thermal hysteresis should be unobservable unless the experimental accuracy exceeds 1 K. Furthermore, we investigated the concentration dependence of this field-induced metamagnetic transition and will exhibit it elsewhere.[14]

To confirm the valence change in the magnetic field, we investigated the forced volume magnetostriction $\Delta V/V$ at 5 K in high pulsed fields. Since the transverse magnetostriction was found to agree quantitatively with the longitudinal magnetostriction within the experimental error, $\Delta V/V$ was evaluated as the treble value of the longitudinal magnetostriction $\Delta L/L$ as shown in Fig. 4. A distinct decrease of volume at $H_c$ of about 31 T is found in $Yb_{0.38}In_{0.62}Cu_2$ in Fig. 4, although the $H_c$ is smaller than that in the magnetization by about 2 T. This discrepancy may be due to the difference between the temperatures of the measurements, i.e., 5 and 1.3 K. The present observation of the prominent negative forced volume magnetostriction is the clear evidence for abrupt increase of the Yb valence. From $\Delta V/V$, the valence change at the metamagnetic transition is estimated to be about 0.03, on the assumption of the volume difference of 4.6% between the divalent and the trivalent Yb states.[15]

The evaluated valence change is rather small compared with the value deduced from thermal expansion at $T_v \simeq 0.1$.[6] The difference may be ascribed to the lack of contributions to $\Delta V/V$ in high fields of the band term due to the conduction electrons and of the interaction term between Yb moments. $\Delta V/V$ due to the itinerant electrons is proportional to the square of the magnetization, i.e., the magnetic state has a large volume compared with the nonmagnetic state,[16-18] in contrast to $\Delta V/V$ due to the Yb valence change. Another magnetic contribution to $\Delta V/V$, i.e., the interaction term between the local moments, originates from the volume dependence of the exchange integral between $i$ and $j$ moments described as $\Delta V/V = \sum_{i,j} C_{i,j}^{\text{int}} \langle \mathbf{m}_i \cdot \mathbf{m}_j \rangle$, where $\langle \mathbf{m}_i \cdot \mathbf{m}_j \rangle$ is the two-spin correlation function and $C_{i,j}^{\text{int}}$ the magnetovolume coupling constant.[17,18] The spin-correlation function has a finite value in the field for the volume magnetostriction measurement, while it is zero in the thermal expansion measurement without magnetic field unless a magnetic ordering takes place. The interaction term can be positive or negative, depending upon $C_{i,j}^{\text{int}}$, but is not very large. Many of the $R\text{Ni}_2$ and $R\text{Al}_2$ compounds ($R$ denotes rare earth) were reported to show a positive $\Delta V/V$ because of the interaction between $R$ moments.[19,20] Therefore, we can expect a positive contribution from the interaction term also in the present systems.

From these facts, the observed volume shrinkage due to the abrupt increase of the Yb valence is diminished in magnitude by the other positive magnetic contributions. Consequently, it is concluded that the metamagnetic transition in (Yb-In)$Cu_2$ system can be attributed to the remarkable change of Yb valence.

A gradual but definite positive deviation from the linear magnetization process is observed at 1.3 K in the possible coherent Kondo state of $Yb_{0.50}Ag_{0.50}Cu_2$, as shown in Fig. 3. Similar magnetic field dependences of the magnetization have been reported in some Ce and Yb compounds.[10-12] The metamagneticlike transition at about 8 T along the $c$ axis was found in the dense Kondo or mixed-valence compound $CeRu_2Si_2$.[10] The slight upturn of the $M$-vs-$H$ curve was also observed in the dense Kondo compounds, $CeCu_6$ above 30 T along the $b$ axis[11] and $Yb_{1-x}Y_xCuAl$ above 20 T.[12] This kind of behavior in the dense Kondo system has been theoretically predicted from the calculations[8,9] based on the Coqblin-Schrieffer model when a level crossing occurs between low-lying states split by the crystalline field. In the case of a cubic Ce compound, the $J=\frac{5}{2}$ multiplet splits into a $\Gamma_7$ doublet and a $\Gamma_8$ quartet, and if the $\Gamma_7$ doublet is the ground state, a high density of states at the Fermi level can be theoretically expected at the crossing field, leading to a steep increase of the magnetization.[9] It should be noted that the steep increase is broadened by the interaction with the conduction electrons which causes the dense Kondo effect. In fact, dense Kondo systems have rather broad increases in $M(H)$. In the cubic Yb compound, the $J=\frac{7}{2}$ multiplet splits into a $\Gamma_6$ doublet, a $\Gamma_7$ doublet, and a $\Gamma_8$ quartet in the cubic crystalline field. The increase of magnetization due to the level crossing may be possible in the (Yb-Ag)$Cu_2$ system.

A gradual volume shrinkage is observed in $Yb_{0.50}Ag_{0.50}Cu_2$ as shown in Fig. 4, implying a gradual increase of the Yb valence. From the volume decrease at

36 T, the increase of the valence was found to be at least +0.02, which may also be underestimated because we did not take into account the interaction and the band terms. The present result indicates that the remarkable upturn in the $M$-vs-$H$ curve is due not only to the level crossing between the low-lying trivalent states split by the crystalline field but also to the change of the Yb valence. This suggests that the valence of Yb in this dense Kondo compound should thermally decrease from +3.0 with decreasing $T$ through the $\chi$ peak. We believe that this valence-changed state close to the trivalent state is characteristic and intrinsic also in dense Kondo systems, as is thus important in the mixed-valence systems.

The remaining problem is the understanding of the mechanism of the abrupt valence transition in the (Yb-In)$Cu_2$ system. It is likely that the single-site excitation of the Yb Kondo lattice, the electron-phonon interaction as in the BCS superconductor, and/or the elastic energy should be taken into account. To elucidate the problem, NMR, electric resistivity, thermal expansion, and Young's-modulus investigations are now in progress.

This study is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

[1]J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).

[2]N. B. Brandt and V. V. Moshchalkov, Adv. Phys. **33**, 373 (1984).

[3]G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[4]T. Kasuya, O. Sakai, K. Takegahara, and M. Takeshige, J. Magn. Magn. Mater. **52**, 1 (1985).

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

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

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

[8]A. Ogawa and A. Yoshimori, Prog. Theor. Phys. **53**, 315 (1975).

[9]A. Okiji and N. Kawakami, J. Magn. Magn. Mater. **54-57**, 327 (1986).

[10]J. Flouquet, P. Haen, F. Lapierre, D. Jaccard, and G. Remenyi, J. Magn. Magn. Mater. **54-57**, 322 (1986).

[11]T. Sakakibara, T. Goto, Y. Onuki, and T. Komatsubara, J. Magn. Magn. Mater. (to be published).

[12]G. van Kalkeren, H. van Nassou, and F. R. de Boer, J. Magn. Magn. Mater. **47&48**, 105 (1985).

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

[14]T. Shimizu, K. Yoshimura, T. Nitta, T. Sakakibara, T. Goto, and M. Mekata, to be published.

[15]A. Iandelli and A. Palenzona, J. Less-Common Met. **29**, 293 (1972).

[16]T. Moriya and K. Usami, Solid State Commun. **34**, 95 (1980).

[17]M. Shiga, J. Phys. Soc. Jpn. **50**, 2573 (1981).

[18]I. A. Campbell and G. Creuzet, in *Metallic Magnetism,* edited by H. Capellmann (Springer-Verlag, Berlin, 1987), pp. 207–227.

[19]F. Pourarian, J. Phys. Chem. Solids **41**, 123 (1980).

[20]M. R. Ibarra, A. del Moral, and J. S. Abell, J. Phys. Chem. Solids **45**, 789 (1984).