First-order valence phase transition in cubic $Yb_xIn_{1-x}Cu_2$

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(Received 13 May 1985)

Magnetic-susceptibility measurements of a new Laves-phase cubic system, $Yb_xIn_{1-x}Cu_2$ ($0.30 \leq x \leq 0.65$), exhibit very sharp $Yb^{2+} \rightarrow Yb^{3+}$ valence phase transitions at temperatures $T_v = 40$–80 K. A simple valence-fluctuation model predicts first-order phase transitions and agrees with the experimental observations. For $Yb_{0.4}In_{0.6}Cu_2$ the theoretical fit shows that below $T_v = 46$ K, the Γ_6 state of Yb^{3+} is 190 K above Yb^{2+}, changing abruptly to -210 K above T_v. The present compounds exhibit the sharpest temperature-dependent valence phase transition in any metallic system.

Intermediate valencies generally change slowly with temperature.[1] The well-known sharp valence phase transitions with temperature are those in the $Sm_xR_{1-x}S$ systems,[2] which are also insulator-metal transitions. Less sharp is the transition in metallic $EuPd_2Si_2$.[3] Here we present magnetic-susceptibility measurements of an extremely sharp valence phase transition, from Yb^{2+} to Yb^{3+}, at $T_v = 46$ K in metallic Laves-phase cubic $Yb_{0.4}In_{0.6}Cu_2$. A model previously used for $EuCu_2Si_2$ (Ref. 4) and for $EuPd_2Si_2$ (Ref. 3) is applied to Yb in $Yb_xIn_{1-x}Cu_2$. Under suitable conditions it predicts, first-order discontinuous valence phase transitions, in agreement with the experimental observations. A fit of the theoretical model to the experimental results yields an interconfiguration excitation energy (E_{exc}, positive when Yb^{3+} Γ_6 state above Yb^{2+}) of 190 K below T_v and changing sign abruptly to -210 K at T_v. The cubic crystal field acting on the Yb^{3+} ion is $A_4\langle r^4\rangle = 40$ K leading to Γ_6 ground state, Γ_8 and Γ_7 at 50, and 135 K above Γ_6.

The compound $YbCu_2$ has the orthorombic $CeCu_2$-type structure, $YbIn_2$ crystallizes in the hexagonal $CaIn_2$-type structure. While trying to form ternary compounds of these three elements x-ray studies revealed a new single Laves-phase cubic compound of the form $Yb_xIn_{1-x}Cu_2$, where x can obtain the values 0.30–0.65. The unit cell sizes of these compounds at room temperature are 7.157 Å for $x = 0.3$ to 7.133 Å for $x = 0.65$. It seems quite certain that in this system the In ions occupy the rare-earth site; Yb^{3+} and In have similar ionic radii. It is not clear whether the In and Yb are distributed randomly in this site. If they are, then the Yb ions will experience a distribution of local environments. The local environments may have an effect on the Yb valence state.[5]

Magnetic-susceptibility measurements were performed with Princeton Applied Research vibrating sample magnetometer, on samples $Yb_xIn_{1-x}Cu_2$, $x = 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6$, and 0.65. The temperature dependence of the magnetic susceptibility, which was magnetic-field independent up to 15 kOe, is displayed in Figs. 1 and 2 for some of the samples investigated. One observes a very sharp rise in susceptibility at about 45 K in the $x = 0.4$ sample and several steps or continuous rise in the other samples. The initial rise for all samples is at about the same temperature ~ 40 K. For comparison, we have measured the magnetic susceptibility of $Gd_{0.4}In_{0.6}Cu_2$ ($a = 7.268$ Å), $Lu_{0.4}In_{0.6}Cu_2$ ($a = 7.154$ Å), and $Yb_{0.5}In_{0.5}Ni_2$ ($a = 7.133$ Å), all of the same cubic structure. In $Yb_{0.5}In_{0.5}Ni_2$ the Yb ion is trivalent down to 2 K and the susceptibility follows a Curie-Weiss law and $Gd_{0.4}In_{0.6}Cu_2$ is paramagnetic down to 4.2 K. In all $C15$ rare-earth RM_2, where M is a nonmagnetic element, the R-R interactions are governed by the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism with the highest magnetic ordering temperature found in the GdM_2 compounds. An absence of magnetic ordering in $Gd_{0.4}In_{0.6}Cu_2$ rules out the possibility that the sharp transition in $Yb_{0.4}In_{0.6}Cu_2$ is a magnetic phase transition. Moreover, neutron diffraction measurements[6] on $Yb_{0.4}In_{0.6}Cu_2$ show that the spectra obtained at 4.2 K and room temperature are quite similar and contain only the peaks belonging to the $C15$ structure without evidence of any magnetic ordering. The observed temperature dependence of the magnetic susceptibility of $Yb_xIn_{1-x}Cu_2$ looks similar to curves of Yb intermediate valence compounds such as $YbAl_3$ (Ref. 7) or Ce intermediate valent compounds.[1] However, the present case is

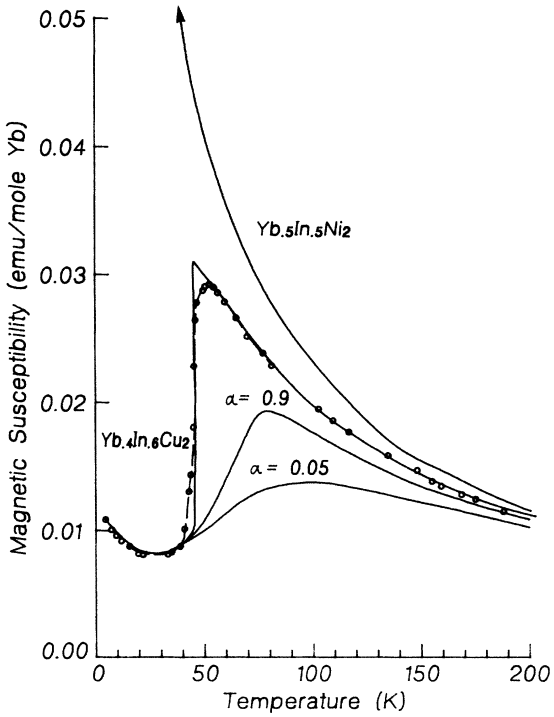

FIG. 1. Temperature dependence of magnetic susceptibility of $Yb_{0.4}In_{0.6}Cu_2$ and $Yb_{0.5}In_{0.5}Ni_2$. The solid line through the experimental points is a least-squares-fit theoretical curve with $\alpha = 2.1$.

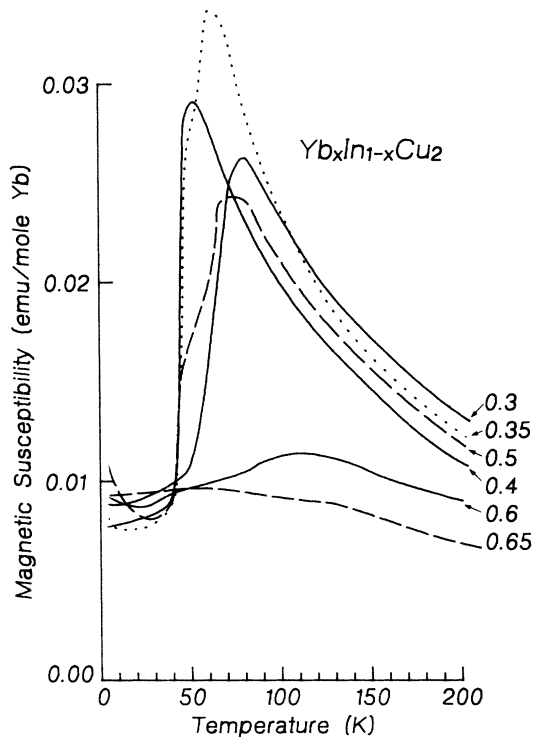

FIG. 2. Temperature dependence of magnetic susceptibility of $Yb_xIn_{1-x}Cu_2$.

unique, since, in contrast to the previous cases, the rise in magnetic susceptibility is extremely sharp. Any effort to fit the experimental observations within a valence-fluctuation model with a temperature-independent or slowly varying interconfigurational excitation energy will fail, since it leads to a gradual valence change, as in $YbAl_3$. It is tempting to assume that the interconfigurational excitation energy depends on the fractional valency (p_3 - the Yb^{3+} probability) of the Yb ion.[3,4] If the excitation energy(Yb^{3+} above Yb^{2+}) decreases when p_3 increases, one obtains a positive feedback which may lead to a cooperative sharp-phase transition. We adopt the conventional fluctuation models[8,9] and express the magnetic susceptibility in the form

$$\chi = \chi_2(1-p_3) + \chi_3 P_3 + \chi_0 , \tag{1}$$

where χ_3 for Yb^{3+} in a cubic crystalline field (E_6, E_7, and E_8 correspond to the Γ_6, Γ_7, and Γ_8 cubic states) is given by

$$\chi_3 = \frac{2C_6 e^{-E_6/kT^*} + 2C_7 e^{-E_7/kT^*} + 4C_8 e^{-E_8/kT^*}}{Z_3(T^*)(T^*+\theta)} , \tag{2}$$

here C_6, C_7, and C_8 are the Curie constants corresponding to the Γ_6, Γ_7, and Γ_8 states. $Z_3(T^*)$ is the Yb^{3+} partition function. T^* is given by $(T^2+T_f^2)^{1/2}$, where T is the temperature and T_f is the valence-fluctuation temperature. χ_0 is the lattice and conduction electron contribution to the susceptibility. θ is the paramagnetic Curie temperature which itself must depend linearly on p_3, $\theta = \theta_0 p_3$. The Yb^{3+} probability p_3 is given by

$$p_3 = \frac{Z_3(T^*)}{Z_3(T^*) + \exp(E_{exc}/T^*)} . \tag{3}$$

If we assume that E_{exc} is itself a function of p_3,[3,4,10,11] of the form $E_{exc} = E_0(1-\alpha p_3)$, then one has to solve Eq. (3) self-consistently. Such a dependence of E_{exc} on p_3 can be thought of as due to the crystal contraction mechanism.[5,12,13] For simplicity, as a model calculation we have chosen the case where Yb^{3+} is represented by only one doublet, the other two states far above in energy. In this case $p = p_3$ is a function of only $x = E_0/T^*$ and the parameter α. The equation to be solved is

$$p = \{1 + \tfrac{1}{2}\exp[x(1-\alpha p)]\}^{-1} = f(p) . \tag{4}$$

Surprisingly enough, the solutions of this equation for $\alpha > 1$ lead to a sharp valence transition from Yb^{2+} at low temperatures to Yb^{3+} at high temperatures. In Fig. 3 the solutions of Eq. (4) for p as a function of x for various values of α are shown. The solutions were obtained for each x value by iterations $[p_{n+1} = f(p_n)]$ starting always with the initial value $p_0 = 0$. This procedure converges in all temperature ranges and follows the solution which is the physical ground state at low temperatues. At low temperatures the equation has three solutions as shown for $\alpha = 2.0$ in Fig. 3. It is obvious from Fig. 3 that above the phase transition Eq. (4) has only one solution. The curve for $\alpha = 2$ with the three solutions for p was obtained by plotting x as a function of p, $x = \ln[2(1/p-1)]/(1-\alpha p)$.

For fitting the experimental data in Fig. 1, the full expression for χ and p_3, Eqs. (2) and (3) have been used. A least-squares-fit procedure of the theory to the experimental observations, solid curve in Fig. 1, yields the following parameters: $\alpha = 2.1 \pm .1$, $E_0 = 190 \pm 10$ K, $\theta_0 = 20 \pm 10$ K, $T_f = 5 \pm 5$ K. χ_0 was found negative, ~ -0.0005 emu/mole, identical to the value found for $Lu_{0.4}In_{0.6}Cu_2$. The value of θ_0 is similar to that obtained for $Yb_{0.5}In_{0.5}Ni_2$, 8 K, and for $Gd_{0.4}In_{0.6}Cu_2$, 40 K. Assuming dominance of the fourth-order cubic crystal field the parameter $A_4\langle r^4\rangle$ obtains the value of 40 ± 20 K (Γ_6 ground state and Γ_8 and Γ_7 at 50 and 135 K above). This value for $A_4\langle r^4\rangle$ is consistent in sign and absolute value with values obtained for other trivalent Yb in Laves-phase compounds.[14]

The rise in susceptibility at very low temperatures is probably due to paramagnetic impurities. One observes in Fig. 2 that this rise is not present in all the samples investigated. The relatively high Yb^{2+} susceptibility below T_v, 0.0075 emu/mole, in spite of the very low T_f value, indicates that the Yb ion below T_v is in an intermediate valency state and thus has an almost temperature-independent susceptibility

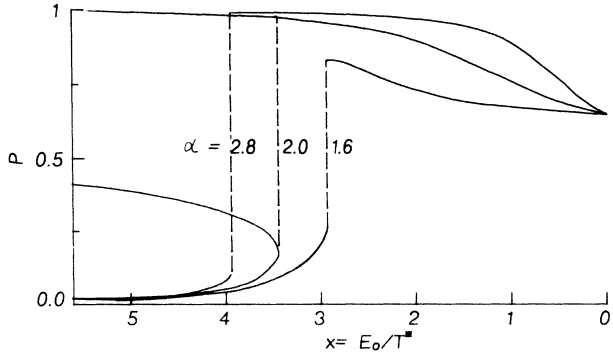

FIG. 3. The probability of the Yb ion being trivalent as a function of inverse temperature solutions of Eq. (4).

as observed for SmB_6.[15] It also indicates that at low temperatures the fluctuation-valency model with its phenomenological T_f parameter is not valid.[9]

Figure 2 shows that the magnetic-susceptibility curves of $Yb_xIn_{1-x}Cu_2$ change drastically as a function of x. Considering that both E_0[5] and α may depend on Yb local environment, this result is not surprising. It seems that the increase or decrease of x from the critical value $x_c = 0.37 \pm 0.04$ in which the first-order valence-phase transition is most prominent, leads to an increase in E_0 and decrease in α, and to a smear out of these values. In Fig. 1, theoretical susceptibility curves are reproduced for various α values, keeping the other parameters as those for $Yb_{0.4}In_{0.6}Cu_2$. The resemblance to the experimental curves shown in Fig. 2 are evident.

The results reported here seem to indicate that the new sharp valence-phase transition in $Yb_{0.4}In_{0.6}Cu_2$ is of first order, not as most other valence-phase transitions observed to date. Though the present paper reports only susceptibility studies of this transition, the temperature at which this transition occurs is very convenient for studies by many other experimental techniques. The theoretical model presented here, in spite of being simple, does predict sharp transitions and is capable to fit the experimental data with a very limited number of free physical parameters. Other similar phase transitions may be explained within a similar model.

[1]For a recent review, see *Valence Instabilities: Proceedings of the International Conference on Valence Instabilities, Zurich, Switzerland, April, 1982,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), and J. Magn. Magn. Mater. **47–48** (1985).

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