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Pressure, substitution, and magnetic-field dependence of the valence phase transition in $Yb_{0.4}In_{0.6}Cu_2$

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Magnetization, resistivity, thermal expansion coefficient, and x-ray unit-cell measurements of $Yb_{0.4}In_{0.6}Cu_2$ under pressure (P up to 25 kbar) and in magnetic fields (H_{ext} up to 180 kOe) at temperatures 4.2–80 K have been performed. The valence-phase-transition temperature, T_v, is pressure dependent and surprisingly enough also field dependent. One obtains $dT_v/dP=-2.1$ K/kbar for $P<6$ kbar. Negative chemical pressure obtained by substituting Yb by La or Cu by Ag increases T_v. A theoretical analysis within a previously published model shows that the interconfigurational excitation energy below T_v changes with pressure at a rate $dE_0/dP=-11$ K/kbar. The external magnetic field does not affect E_0, but it increases the Yb^{3+} excited-state population and thus drives the phase transition to a lower temperature at a rate $dT_v/dH_{ext}=-0.022$ K/kOe.

I. INTRODUCTION

The recent publications[1-4] on the Yb valence-phase transition in $Yb_{0.4}In_{0.6}Cu_2$ have shown the many features of this transition. The sharp phase transition is between a nonmagnetic Yb state, of formal intermediate valence 2.8, to an Yb^{3+} magnetic state.[2] The valence-phase transition-temperature T_v is strongly volume dependent, and changes drastically under substitution of the Yb by other elements.[3] These results indicate that T_v should be strongly pressure dependent. The model suggested[1,2] to explain the many experimental observations assumes that the phase transition in $Yb_{0.4}In_{0.6}Cu_2$ is driven by a positive feedback mechanism of the increase in the Yb^{3+} excited-state population. This implies that a strong enough external magnetic field should also drive the transition. To test these ideas we present here studies of magnetic susceptibility and resistivity of $Yb_{0.4}In_{0.6}Cu_2$ under external pressures up to 25 kbar. $Yb_{0.4}In_{0.6}Cu_2$ under negative chemical pressures was studied by x-ray diffraction and magnetic susceptibility. The magnetization of $Yb_{0.4}In_{0.6}Cu_2$ at 4.2, 20, and 40 K and the magnetization of $Yb_{0.35}In_{0.65}Cu_2$ at several temperatures in magnetic fields of up to 180 kOe have been recorded. Thermal expansion measurements show very clearly that the valence phase transition occurs in two steps.

The studies under external pressure show strong changes in T_v, $dT_v/dP=-2.1$ K/kbar. The negative pressure obtained by substituting Yb by a larger ion like La, or Cu by Ag, increases T_v significantly. The magnetization curves of $Yb_{0.4}In_{0.6}Cu_2$ at 4.2 and 20 K are similar, almost linear with the external magnetic field H_{ext}. At 40 K the magnetization curve starts with the slope similar to that at 4.2 K but at 70 kOe starts to rise sharply. A theoretical analysis of the experimental observations within the model of Ref. 1 reproduces the experimental magnetization curve at 40 K assuming $E_0=240$ K with Lorentzian width of 10 K, the analysis shows that $dT_v/dH_{ext}=-0.022$ K/kOe. It also shows that E_0 must change with pressure at a rate -11 K/kbar.

II. MAGNETIC SUSCEPTIBILITY AND RESISTIVITY OF $Yb_{0.4}In_{0.6}Cu_2$ UNDER PRESSURE

The high-pressure magnetization experiments have been performed using a beryllium copper cell. The low pressure is applied by means of compressed helium which produces hydrostatic pressures up to 7 kbar.

Magnetic fields up to $H=70$ kOe were produced by a superconducting coil and the magnetization (M) was measured by the extraction method. The magnetization measurements on $Yb_{0.4}In_{0.6}Cu_2$ have been performed in a field of 60 kOe: so the susceptibility recorded was the ratio M/H. The experimental results of the magnetic-susceptibility measurements of $Yb_{0.4}In_{0.6}Cu_2$ under pressure are shown in Fig. 1. The shape of these curves is the same as those shown in the previous studies.[1-3] The change of the phase transition temperature as a function of pressure is evident. In Fig. 2 the temperature at which the magnetic susceptibility reaches its maximum (a well-defined temperature) is displayed as a function of pressure. In this pressure range the curve in Fig. 2 is quite linear, with slope of $dT_v/dP=-1.9$ K/kbar. In Fig. 3, the resistivity measurements are shown in a much larger pressure range. All the figures are similar to those previously reported.[2] Here the pressure dependence of the

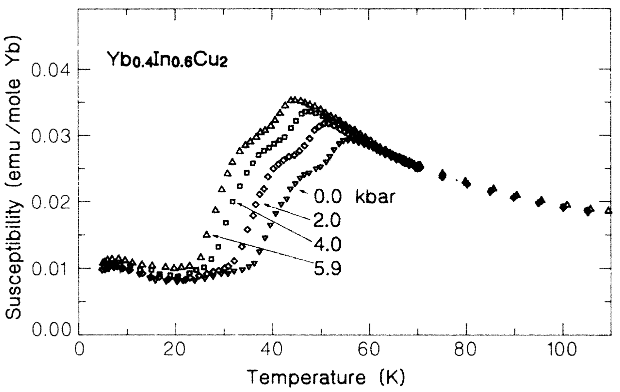

FIG. 1. Temperature dependence of the magnetic susceptibility of $Yb_{0.4}In_{0.6}Cu_2$ in 60 kOe under various pressures.

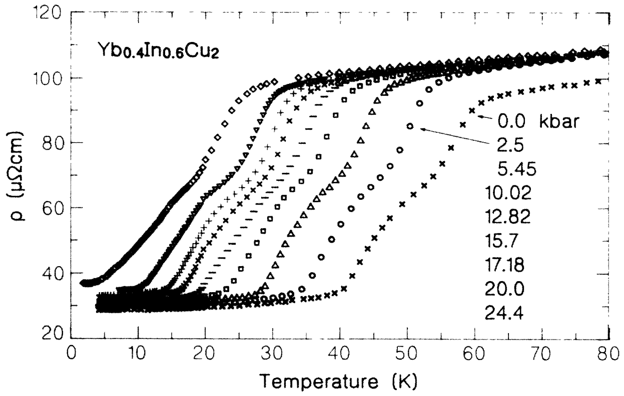

FIG. 3. Temperature dependence of the resistivity of $Yb_{0.4}In_{0.6}Cu_2$ under various pressures.

valence-phase transition is even more obvious than in the magnetic-susceptibility measurements, Fig. 1.

In the susceptibility, Fig. 1, and resistivity, Fig. 3, the valence phase transition is composed of two stages. By plotting the temperature derivative of the resistivity one can determine two points of maximal slope.

The pressure dependence of the upper transition temperature (considered as the point of maximum slope) is shown in Fig. 4. Here one observes that T_v is not a linear function of pressure. At the low pressure (up to 6 kbar) $dT_v/dP = -2.3$ K/kbar (which agrees well with that obtained by the susceptibility measurements) and decreases to -1.1 K/kbar at higher pressures. It should be mentioned that both pressure dependence measurements have been performed on the same sample.

III. SUBSTITUTION DEPENDENCE

Studies of the valence phase transition in systems where the Yb was substituted by other rare earths have been reported in Ref. 3. It was shown that the phase transition temperature may increase, decrease or even be smeared out. Here we report more evidence for this phenomenon. X-ray unit-cell studies of $Yb_{0.3}La_{0.1}In_{0.6}Cu_2$ and $Yb_{0.3}Lu_{0.1}In_{0.6}Cu_2$ have been performed. No distortion has been detected in any of the substituted systems. The temperature dependence of the unit-cell parameter, Fig. 5, has been obtained by averaging the line positions of the [422], [333], and [444] reflexes. The curves in Fig. 5 show clearly that the phase transition temperature moves up or down depending on the size of the ion substituting the room-temperature Yb^{3+} ion. Since both La^{3+} and Lu^{3+} are chemically similar to Yb^{3+}, their effect on T_v resembles the effect of pressure. Lu is smaller than Yb^{3+} and thus substitution by Lu is just positive chemical pressure. On the other hand, substitution by La has the effect of negative chemical pressure and T_v increases.

The situation is completely different when the substitution is performed in the Cu site, Fig. 6. Substitution of

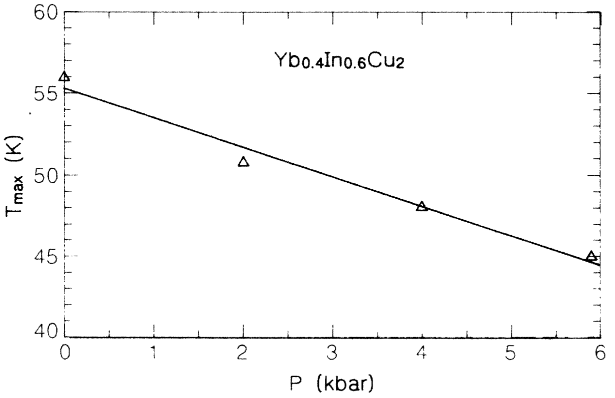

FIG. 2. Pressure dependence of the temperature at which the susceptibility obtains its maximum value, derived from Fig. 1.

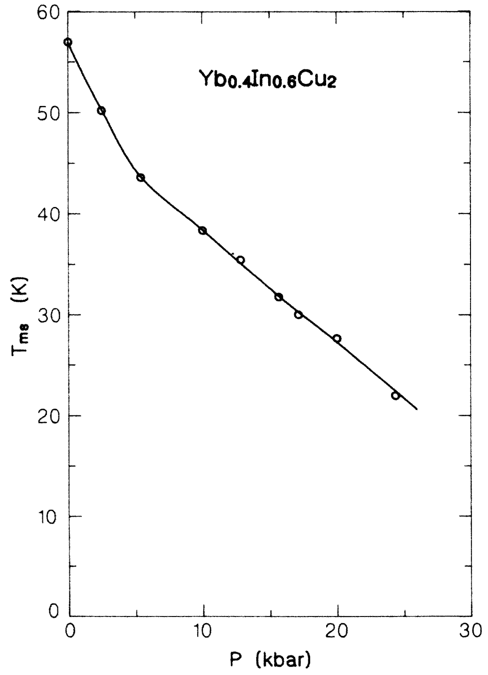

FIG. 4. Pressure dependence of the temperature at which the resistivity has the largest slope in Fig. 3.

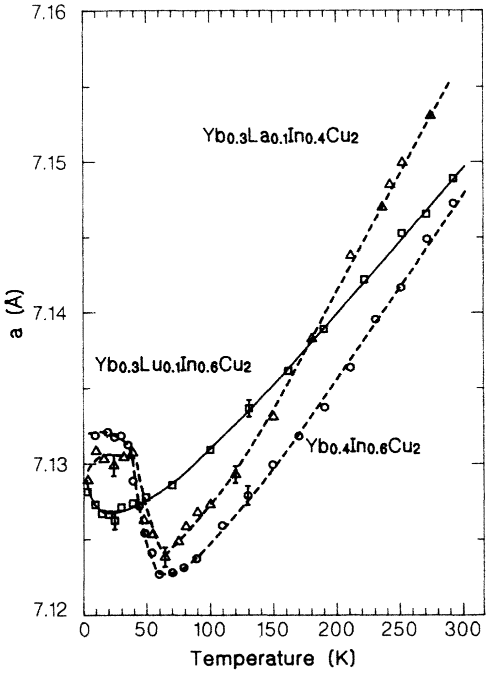

FIG. 5. Temperature dependence of the unit-cell size of $Yb_{0.3}La_{0.1}In_{0.6}Cu_2$ and $Yb_{0.3}Lu_{0.1}In_{0.6}Cu_2$.

Cu by Ag, in $Yb_{0.4}In_{0.6}Cu_{1.75}Ag_{0.25}$, ($a=7.189$ Å) increases T_v up to 80 K but also reduces the susceptibility. On the other hand, when Cu is replaced by Ni in $Yb_{0.4}In_{0.6}Cu_{1.75}Ni_{0.25}$ the lattice parameter does not change ($a=7.152$ Å) but the valence transition disappears and Yb is trivalent down to 4.1 K. It is clear that pressure or volume change are not enough to explain these phenomena. In Fig. 7 we display the temperature dependence of the magnetic susceptibility of $Yb_{0.35}In_{0.65}Cu_2$ exhibiting the same behavior as $Yb_{0.6}In_{0.4}Cu_2$. Both samples were studied in high magnetic fields at the Service National des Champs Intenses, Grenoble.

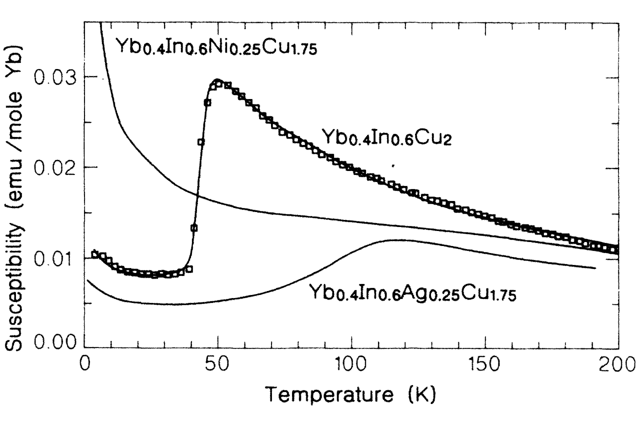

FIG. 6. Magnetic susceptibility of $Yb_{0.4}In_{0.6}Cu_{1.75}Ag_{0.25}$ and $Yb_{0.4}In_{0.6}Cu_{1.75}Ni_{0.25}$ as a function of temperature. The solid line through the $Yb_{0.4}In_{0.6}Cu_2$ experimental points is the least-squares-fit theoretical susceptibility calculated using Eq. (2).

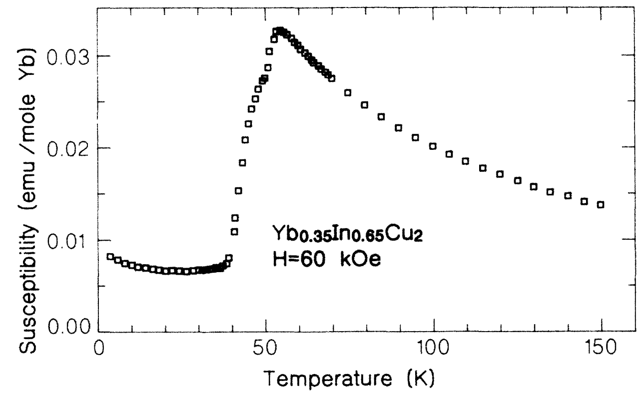

FIG. 7. The magnetic susceptibility of $Yb_{0.35}In_{0.65}Cu_2$ as a function of temperature.

IV. MAGNETIC FIELD DEPENDENCE

The question whether a valence phase transition is magnetic field dependent has never been answered by experimental facts. Here we present such evidence, proving that the present valence transition is affected by external magnetic fields. In Fig. 8 we display the magnetization versus magnetic field curves of $Yb_{0.4}In_{0.6}Cu_2$ at 4.2, 20, and 40 K. While the 4.2- and 20-K curves are very similar, of constant susceptibility $\chi=1.3\times10^{-3}\mu_B$/kOe ($7.5\times10^{-3}$ emu/mol) the 40-K curve above 70 kOe rises sharply. This may indicate that at 40 K, close to T_v, the external magnetic field enhances the valence transition. In Fig. 9 we display detailed studies of the magnetic mo-

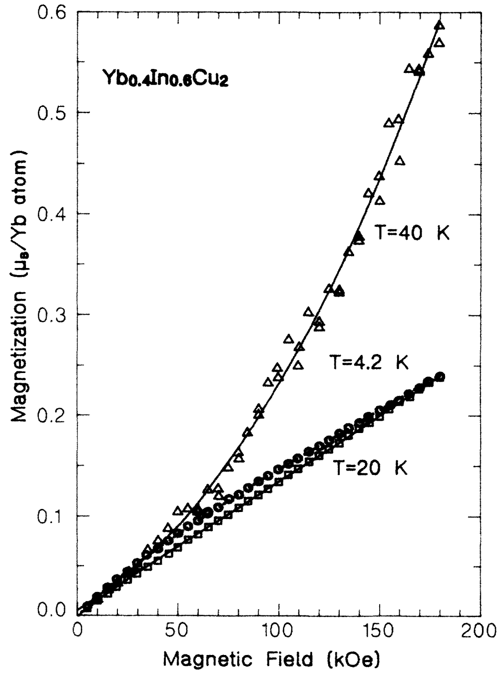

FIG. 8. The magnetization of $Yb_{0.4}In_{0.6}Cu_2$ at 4.2, 20, and 40 K, as a function of external magnetic field. The solid curves for 20 and 40 K were theoretically calculated.

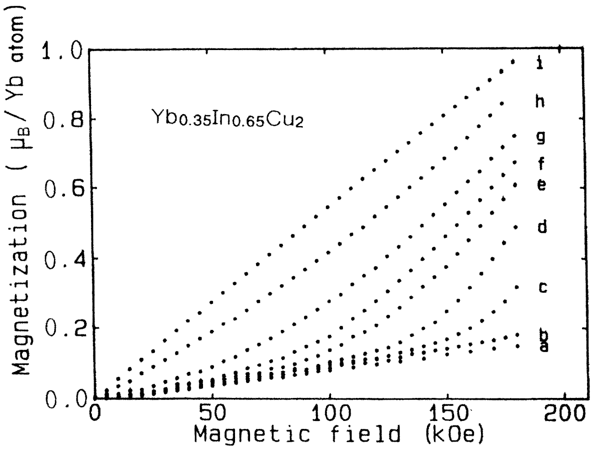

FIG. 9. The magnetic moment of Yb in $Yb_{0.35}In_{0.65}Cu_2$ as a function of external magnetic field at various temperatures *a*, 4.2 K; *b*, 32 K; *c*, 35 K; *d*, 37 K; *e*, 38.5 K; *f*, 39.7 K; *g*, 41.4 K; *h*, 45.7 K; and *i*, 55.5 K.

ment of the sample $Yb_{0.35}In_{0.65}Cu_2$ as a function of magnetic field at various temperatures. The curves are linear at temperatures below and above the transition region, Fig. 7. In the transition region the curves display a field-induced valence transition, like in Fig. 8; the critical field decreases when the temperature is raised. In the discussion to follow we show that the model[1] we adopted for this valence transition predicts external field dependence consistent quantitatively with the experimental observations.

V. THERMAL EXPANSION

Linear thermal expansion measurements of $Yb_{0.4}In_{0.6}Cu_2$ and $Lu_{0.4}In_{0.6}Cu_2$ from 9 K up to room temperature, using an automatic tube type capacitance dilatometer, have been performed. The heating rate was 0.5 K/min. Figure 10 shows the thermal variation of the linear thermal expansion coefficient, $\delta L/L\delta T$ for both samples and the integral curves are shown in the inset.

The $Lu_{0.4}In_{0.6}Cu_2$ thermal expansion curve exhibits a Debye behavior with a Debye temperature of 240(10) K.

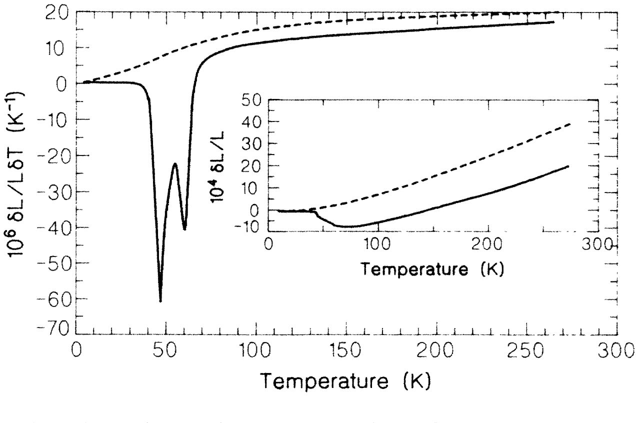

FIG. 10. Linear thermal expansion of $Yb_{0.4}In_{0.6}Cu_2$ and $Lu_{0.4}In_{0.6}Cu_2$ (dashed lines).

For $Yb_{0.4}In_{0.6}Cu_2$ the thermal expansion coefficient remains zero up to 40 K and then two minima are observed in the region of the Yb valence phase transition. The behavior is similar to that observed in the specific-heat measurements (Fig. 8 in Ref. 2) and in the susceptibility and resistivity measurements shown in Figs. 1 and 3. The thermal expansion integral curves, Fig. 10, are similar to those of the unit-cell size shown in Fig. 5. All these measurements indicate that the valence phase transition occurs in two steps. Since the thermal expansion measurements were most indicative of the double transition, the measurements were repeated with another sample prepared by a very different method and yet the behavior was the same.

VI. THEORETICAL ANALYSIS

The model suggested in Ref. 1 was capable of explaining many of the experimental observations reported.[1,2] In terms of the same model we shall try to understand the changes of the valence phase transition as a function of pressure, substitution, and external magnetic field.

The model assumes that the Yb^{3+} state at low temperatures is E_{exc} above the nonmagnetic intermediate valent state. If p_3 is the Yb^{3+} population, E_{exc} will change as $E_{exc}=E_0(1-\alpha p_3)$ where α is a constant. p_3 itself is a function of E_{exc}, crystalline and magnetic field splittings of the Yb^{3+} eightfold-degenerate state, and of course, the temperature. This interconnection between E_{exc} and p_3 leads to a first-order valence phase transition at T_v. Below T_v the only solution for p_3 is $p_3\approx 0$ whereas above $T_v, p_3\approx 1$.

Within this model it is quite clear that T_v is a very sensitive function of the parameters E_0 and α, where E_0 is in fact E_{exc} below T_v. The sensitivity to the parameter α is shown in Fig. 1 and Fig. 3 of Ref. 1.

As long as we are dealing with a single system and only changing the volume by pressure or p_3 by an external magnetic field we assume that α, which depends on Yb neighbor distribution, stays constant, and only E_0 changes. In Fig. 11 we display the dependence of T_v on E_0 for fixed $\alpha=2.1$ and crystalline field $A_4\langle r^4\rangle=40$ K. We obtain $dT_v/dE_0=0.2$. From the measurements of the susceptibility and resistivity at low pressures we obtain $dT_v/dP=-2.1(2)$. We thus obtain $dE_0/dP=-11$ K/kbar. At higher pressures $dE_0/dP=-5.5$ K/kbar. Such a rate of change of the interconfigurational excitation energy as a function of pressure is also evident for Eu compounds, $EuCu_2Si_2$ (Ref. 5), $EuPd_2Si_2$ (Ref. 6), and $EuNi_2P_2$.[7]

Now we turn to the question whether T_v may depend on the external magnetic field. Within our model any increase in p_3 decreases E_{exc} which then increases p_3 and by this positive feedback mechanism may drive the first-order phase transition. In zero external magnetic field the only physical parameter which increases p_3 is the temperature T. When T reaches T_v the valence phase transition occurs. However, if we are at a fixed temperature, slightly below T_v, at 40 K in Fig. 8, and apply a strong magnetic field it will split the Yb^{3+} eightfold-

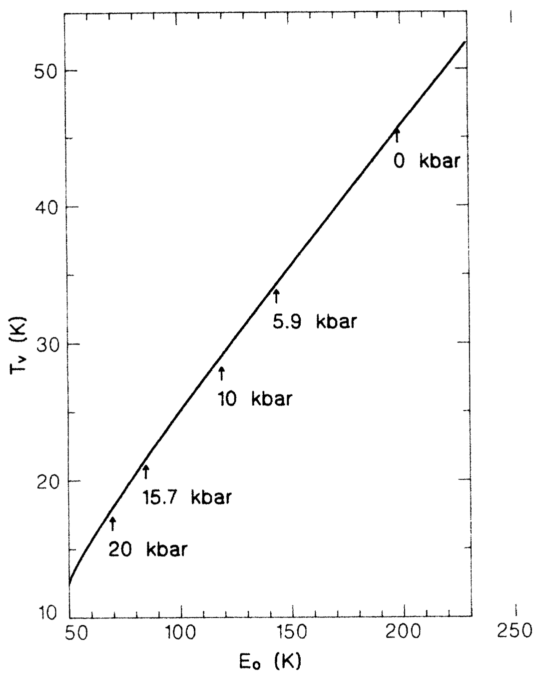

FIG. 11. Theoretical dependence of T_v vs E_0, for fixed values of $A_4\langle r^4\rangle$.

degenerate state and lead, because of the nature of Boltzmann statistics to an increase in p_3. Again E_{exc} will decrease and a phase transition will occur. We tested this idea within our model assuming $\alpha=2.1$ and $A_4\langle r^4\rangle=0$, which simplifies the calculation. In Fig. 12 (lower panel) and Fig. 12 (upper panel), respectively, we show the change of p_3 and magnetization as a function of external magnetic field H_{ext} for various values of the parameter E_0. We observe that within the range of experimental magnetic fields (0–180 kOe), at 40 K when $E_0=210$ K, the Yb ion is trivalent, when $E_0=240$ K the Yb ion is nonmagnetic. However, for E_0 in the range 220–230 K, the experimental external magnetic field may drive the first-order valence phase transition.

We have calculated p_3 as a function of temperature for various values of E_0 and H_{ext}. From these curves we obtained T_v as a function of H_{ext} and E_0. In Fig. 13 we display the dependence of T_v on H_{ext} for various values of E_0. We notice that $dT_v/dH_{\text{ext}}=-0.022$ K/kOe is little dependent on the value of E_0.

The experimental observation shown in Fig. 8 indicates a change in valency as the field increases, but it is not sharp as the theory predicts. Also the change in susceptibility Fig. 1 and resistivity Fig. 3 as a function of temperature do not exhibit a very sharp transition predicted by theory.[1] We may understand all these results in terms of an inhomogeneity in the value of E_0 across the samples investigated. It is well known that E_0 depends on local environment.[8] Since in $\text{Yb}_{0.4}\text{In}_{0.6}\text{Cu}_2$ the Yb and In are randomly distributed in the same locations one may expect a distribution in E_0 excitation energy values. If we assume a Lorentzian distribution of E_0 of half width at half height $\Gamma=10$ K, the thermal magnetic-susceptibility curves resemble much more the experimental curves. A least-squares fit to the magnetic-susceptibility curve of Ref. 1 is shown in Fig. 6. The same Lorentzian distribution, namely $\Gamma=10$ K, reproduces also the magnetization curve shown in Fig. 8.

Let us summarize the calculation procedure of the susceptibility and magnetization. For the susceptibility we use Eq. (1) of Ref. 1 except that p_3 as a function of temperature is no longer a step function. p_3 is a function of E (the excitation energy for $\alpha=0$) and E has a Lorentzian distribution of width Γ, around the value of E_0. Thus the average p_3 is given by

$$\bar{p}_3(E_0,\Gamma,T)=\frac{\Gamma}{\pi}\int_{-\infty}^{\infty}\frac{dE}{\Gamma^2+(E-E_0)^2}p_3(E,T)\ , \tag{1}$$

where $p_3(E,T)$ is solved self-consistently using Eq. (3) of Ref. 1. $\bar{p}_3$ is now a smooth function of temperature, and so is the susceptibility

$$\chi=\chi_2(1-\bar{p}_3)+\chi_3\bar{p}_3 \tag{2}$$

in Fig. 6.

The magnetization was calculated in the zero-crystalline-field approximation. If E and H are the exci-

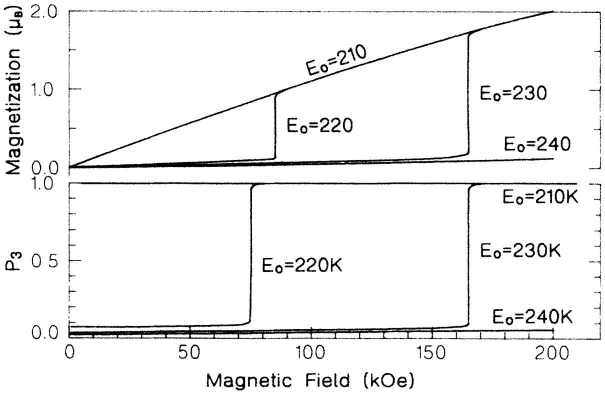

FIG. 12. A theoretical calculation of the value of p_3 and the magnetization of $\text{Yb}_{0.4}\text{In}_{0.6}\text{Cu}_2$ at 40 K as a function of the external magnetic field for various values of E_0.

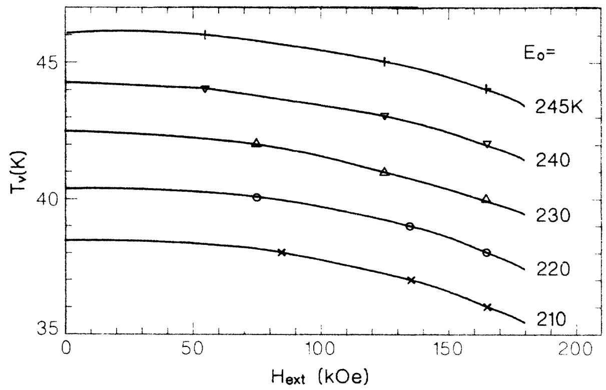

FIG. 13. Theoretical dependence of T_v on H_{ext} for various values of E_0.

tation energy (for $\alpha=0$) and external magnetic field, then the partition function of the system is given by

$$Z(E,H,T)=1+e^{-E_{\mathrm{exc}}/kT}Z_3(H,T) , \qquad (3)$$

where

$$E_{\mathrm{exc}}=E(1-\alpha p_3)$$

and Z_3 is the Yb^{3+} free-ion partition function. $p_3(E,T,H)$ is solved again self-consistently by the equation

$$p_3(E,T,H)=\frac{Z-1}{Z} . \qquad (4)$$

The magnetization is now given by

$$M(E_0,H,T)=\chi_2 H(1-\bar{p}_3)+\bar{p}_3 M_3(H,T) , \qquad (5)$$

where $\bar{p}_3$ is again an average of $p_3(E,T,H)$ like in Eq. (1).

$\chi_2=0.0075$ emu/mol is the magnetic susceptibility of the intermediate valent state of Yb below T_v and $M_3(H,T)$ is the free-ion Yb^{3+} magnetic moment. It is worth mentioning again that for each value of E one has to solve for p_3 and then calculate $\bar{p}_3$ for inserting in the equation for $M(E_0,H,T)$.

We turn now to the sensitivity of the valence transition to substitution in the Cu site. We observe that when Cu is substituted by Ni ($\mathrm{Yb_{0.4}In_{0.6}Cu_{1.75}Ni_{0.25}}$) T_v is pushed downwards very drastically, in fact the Yb is trivalent in the whole range of observation, $T>4.2$ K. Substitution by the same amount, Cu by Ag, leads to a large increase in T_v and strong reduction in χ. Both these observations show that the substitution in the Cu site cannot be explained only by the pressure effect. Ni is very similar in size to Cu and yet so strongly affects the Yb valency. Ag replacing Cu increases the crystal volume but not more than the La did and yet increases T_v much more than La. We conclude that substitution in the Cu site, first nearest neighbor to the Yb ion, strongly affects the parameter α of our model. In fact, a small value of α (~ 0.1) leads to a susceptibility curve, Fig. 1 in Ref. 1, very similar to that of $\mathrm{Yb_{0.4}In_{0.6}Cu_{1.75}Ag_{0.25}}$. A large value of α ($\gg 2$) leads to the situation in which T_v is much below 4.2 K. At all temperatures the Yb is trivalent, this agrees with the case of Ni substitution.

VII. CONCLUSIONS

The observations reported in the present paper lead to the following conclusions.

(a) The sharp valence phase transition in the cubic Laves-phase system is very sensitive to external parameters such as temperature, pressure, and magnetic field. Application of pressure decreases T_v at a rate of -2.1 K/kbar and application of magnetic field also decreases T_v, at a rate -0.022 K/kOe.

(b) Substitution of Yb in $\mathrm{Yb_{0.4}In_{0.6}Cu_2}$ simulates the effect of pressure, in this case simulating even negative pressure.

(c) Substitution of Cu in $\mathrm{Yb_{0.4}In_{0.6}Cu_2}$ by Ni or Ag influences the valence phase transition far beyond the effect of equivalent pressure. This indicates that this substitution has strong electronic band effects, in particular changing strongly the density of states at the Fermi level. Ni substitution drives the Yb to become trivalent, Ag substitution makes the intermediate valent Yb state stable to higher temperatures.

(d) All measurements indicate that the valence phase transition in $\mathrm{Yb_{0.4}In_{0.6}Cu_2}$ occurs in two steps. The origin of this bimodal compositional variation is not clear. It does not occur for example in $\mathrm{Yb_{0.4}Ga_{0.1}In_{0.6}Cu_2}$.[2]

ACKNOWLEDGMENT

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