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Ytterbium valence phase transition in $\mathrm{Yb}_x\mathrm{In}_{1-x}\mathrm{Cu}_2$

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The recently reported sharp valence phase transition in cubic $\mathrm{Yb}_{0.4}\mathrm{In}_{0.6}\mathrm{Cu}_2$ at $T_v \simeq 50$ K has been studied by a variety of experimental techniques. X-ray diffraction studies from 4.2 to 300 K reveal the cubic Laves phase structure at all temperatures with a jump in the unit-cell size at the transition temperature T_v. Neutron diffraction proves the absence of magnetic order down to 10 K. Magnetic susceptibility data show that the transition temperature T_v increases when Yb or In are substituted by La, Eu, and Sn and decreases when they are substituted by Y, Lu, and Ga. Mössbauer studies of ^{170}Yb show that at 4.2 K the Yb ion is nonmagnetic in a cubic environment, whereas at 60 K it is magnetic. Mössbauer studies of ^{119}Sn exhibit changes in both the spectral area and isomer shift at T_v. Electrical resistivity measurements exhibit a large increase in resistivity at T_v. Specific-heat measurements reveal a characteristic increase of c_p around T_v. Comparison with $\mathrm{Lu}_{0.4}\mathrm{In}_{0.6}\mathrm{Cu}_2$ behavior yields the increase in entropy due to the valence transition, 13.3(3) J/mole K, in very good agreement with a model calculation of a cubic-split Yb^{3+} and an interconfigurational excitation energy of 220 K. Finally, x-ray-absorption measurements at the Yb L_{III} edge reveal a sudden change in the $4f$-electron occupancy at T_v and temperature-independent valences, $v(L_{\mathrm{III}})=2.9$ and 2.8, above and below T_v, respectively.

I. INTRODUCTION

In a recent publication[1] a first-order valence phase transition of $\mathrm{Yb}^{2+}\rightarrow\mathrm{Yb}^{3+}$ in $\mathrm{Yb}_{0.4}\mathrm{In}_{0.6}\mathrm{Cu}_2$ was reported. Such phenomena in rare-earth metallic systems are extremely rare. The only known transition of this kind is that of α-Ce to γ-Ce. The increasing interest in the related phenomena of magnetic-nonmagnetic transitions, Kondo states, intermediate valences, and heavy fermions in f-electron systems, all of which are displayed in the above system, initiated the present extensive research conducted at six institutions.

We present here studies of this transition in $\mathrm{Yb}_x\mathrm{In}_{1-x}\mathrm{Cu}_2$, and in systems in which Yb and In are substituted by Sn, La, Eu, Y, Lu, and Ga. The systems were studied by a wide variety of experimental techniques: x-ray diffraction, electrical resistivity and specific-heat measurements (Wien); neutron diffraction (Beer-Sheva); L_{III}-edge x-ray absorption (Berlin); magnetic susceptibility measurements (Jerusalem); and Mössbauer spectroscopy of four isotopes, ^{170}Yb (München), ^{119}Sn (Groningen), ^{57}Fe and ^{151}Eu (Jerusalem). Since $\mathrm{Yb}^{2+}(4f^{14}, S_0)$ and $\mathrm{Yb}^{3+}(4f^{13}, {}^2F_{7/2})$ differ strongly in ionic size and in magnetic properties, all the applied experimental techniques are sensitive in detecting the transition between these two ionic states.

X-ray diffraction studies at 4.2 to 300 K exhibit the same cubic Laves phase diffraction patterns at all temperatures. The change in Yb valence at $T_v = 50$ K is observed through a jump in the unit-cell size, which can be interpreted as a change in valency by $\simeq 0.1$ f electrons. The neutron diffraction studies prove that below and above the valence phase transition, $\mathrm{Yb}_{0.4}\mathrm{In}_{0.6}\mathrm{Cu}_2$ has the cubic Laves phase structure and there is no magnetic order at any temperature down to 10 K.

The magnetic susceptibility data show a sharp valence phase transition even when the Yb or In ions in $\mathrm{Yb}_{0.4}\mathrm{In}_{0.6}\mathrm{Cu}_2$ are substituted up to 25% by Sn, La, Eu, Y, Lu, and Ga. The effect of Sn, La, and Eu substitution, since those ions have an ionic radius larger than that of In or Yb^{3+}, is to move the valence transition to higher temperatures. Y, Lu, and Ga, having smaller ionic radii than that of Yb^{2+} or In, lower the transition temperature.

^{170}Yb Mössbauer studies prove that at 4.2 K the Yb ion is nonmagnetic and located in a cubic environment. At 60 K the Yb ion is paramagnetic, producing spin-relaxation broadening in the Mössbauer spectra. Doping of $Yb_{0.4}In_{0.6}Cu_2$ with ^{119}Sn (1 at. % of In) moves the phase transition from 50 K to 60 K. The ^{119}Sn Mössbauer spectra display a change in isomer shift and recoil-free fraction at the phase transition. ^{151}Eu Mössbauer studies of the isomer shift in $Eu_xYb_{0.5-x}In_{0.5}Cu_2$ also sense the valence change of the Yb ions. The Eu ion is divalent and exhibits spin-glass ordering in $Eu_{0.14}Yb_{0.36}In_{0.5}Cu_2$ at low temperatures.

The electrical resistivity measurements exhibit an increase by a factor of $\simeq 6$ within a temperature range of about 20 K. Specific-heat measurements display two peaks in the phase-transition region (43–63 K). The increase in entropy in comparison to that of $Lu_{0.4}In_{0.6}Cu_2$ is 13.3 J/mol K and agrees very well with the expected value from a calculation based on the model from Ref. 1. X-ray-absorption spectroscopy reveals a nearly trivalent state of the Yb ions in $Yb_{0.4}In_{0.6}Cu_2$ at temperatures above T_v. The valence transition is manifested by a sudden change of $\simeq 0.1$ in the $4f$-electron occupancy. Below T_v, the Yb ions are pinned in a strong intermediate-valence state with $v(L_{\rm III})=2.8$.

It is a unique property of $Yb_{0.4}In_{0.6}Cu_2$ that a relatively small change in the $4f$ configuration leads to a complete loss of the magnetic moment of the Yb ions. This behavior is attributed to a strong $4f$-$5d$ hybridization, typical for the cubic rare-earth Laves phases. Below T_v, the Yb ions, though in an intermediate-valence state as evidenced by the lattice constant and $L_{\rm III}$ edge, resemble, in a magnetic sense, the properties of Yb^{2+} ions, in that they are in a nonmagnetic singlet state. Only in this way can one explain the magnetic susceptibility, Mössbauer, and specific-heat observations. The susceptibility and specific-heat measurements indicate that below T_v $Yb_{0.4}In_{0.6}Cu_2$ also exhibits characteristic properties associated with a heavy-fermion system.

II. EXPERIMENTS AND RESULTS

All compounds were prepared by melting the appropriate amounts of elements in an induction furnace in argon atmosphere.[1,2] The studies reported in the following were performed on identical samples.

A. X-ray diffraction measurements

The x-ray diffraction patterns of $Yb_{0.4}In_{0.6}Cu_2$ were taken in the temperature range 4.2 to 300 K. The data presented in Fig. 1 are consistent with the cubic Laves phase structure over the whole temperature range. The temperature dependence of the unit-cell parameter a was obtained by averaging the temperature dependence of the line positions of various reflections. In particular, the lines corresponding to the (422), (333), and (440) Miller indices were used. The precise line positions were obtained by least-squares fitting the experimental data with Lorentzians. The full width at half maximum, Δ, for the (422) reflection is also shown in Fig. 1.

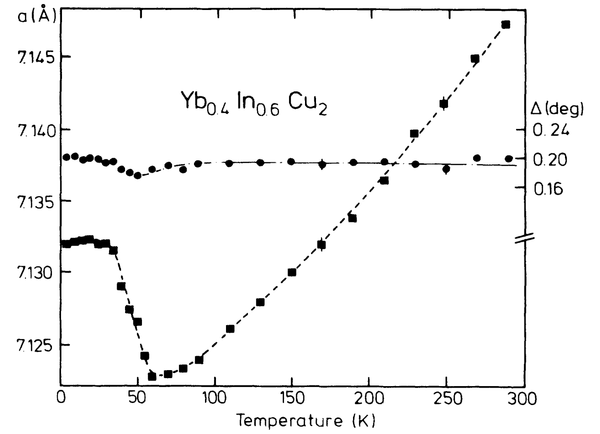

FIG. 1. Temperature dependence of the $Yb_{0.4}In_{0.6}Cu_2$ cubic cell parameter a and the x-ray diffraction linewidth Δ of the (422) reflection.

The unit-cell parameter a decreases in a normal way from 300 K down to 60 K, as seen in Fig. 1. Between 60 and 40 K the cell dimension increases, consistent with the expected valence change from Yb^{3+} towards the larger Yb^{2+} ion. Below 60 K no splitting or at least broadening of the x-ray line profile could be detected within the experimental error. This proves that the observed transition is pure electronic in nature and that there is no lattice distortion through the whole investigated temperature range.

From the absolute change in the cell dimension below 60 K one can estimate the magnitude of the valence change. The lattice parameter $a(T)$ increases by $\simeq 0.15\%$ at T_v. This change is produced by a valence transition of the 40% Yb on the rare-earth site. Among the cubic Laves phases of Yb only $YbAl_2$ exhibits intermediate-valence behavior with a fractional valency of $\simeq 2.5$. Its lattice parameter differs from that expected for pure $Yb^{3+}Al_2$, as estimated by an interpolation between $TmAl_2$ and $LuAl_2$, by about 1.5%. Considering the partial occu-

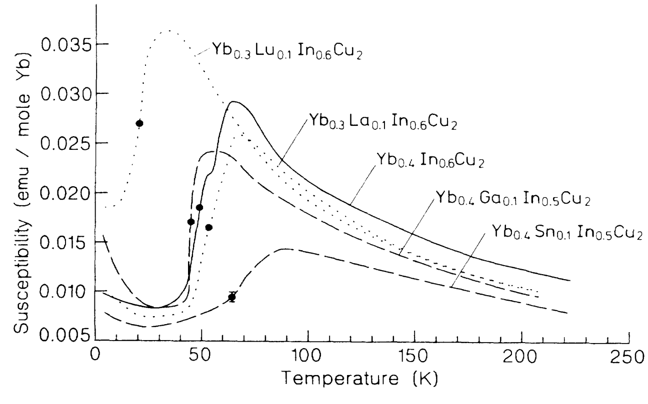

FIG. 2. Magnetic susceptibility curves of $Yb_xIn_{1-x}Cu_2$ in which Yb or In is replaced by La, Lu, Sn, and Ga.

pation of Yb in $Yb_{0.4}In_{0.6}Cu_2$ and the fractional valency of Yb in $YbAl_2$, the valence change at the T_v in $Yb_{0.4}In_{0.6}Cu_2$ is only about 0.1, in good agreement with the x-ray-absorption measurement described later.

B. Neutron diffraction measurements

Neutron diffraction patterns of $Yb_{0.4}In_{0.6}Cu_2$ at 10 and 300 K have been obtained using the IRR-2 nuclear reactor (Nuclear Research Center, Negev) with neutrons of wavelength 2.45 Å. The patterns obtained at the two temperatures were essentially identical. At both temperatures the observed reflections could be indexed according to a fcc lattice, with $a=7.150(5)$ Å and 7.134(5) Å for 300 and 10 K, respectively, in agreement with the x-ray diffraction measurements. These results prove that the observed phase transition is not of magnetic character.

C. Substitution dependence of the valence phase transition

Magnetic susceptibility studies of the Yb valence phase transition[2] have been performed on the $Yb_xIn_{1-x}Cu_2$ system with substitution of the Yb ion by La, Eu, Y, and Lu ions, and of the In ion by Sn and Ga ions. It was found that substitution of Yb or In by ions with larger ionic radii than that of Yb^{3+}, like La, Eu^{2+}, and Sn, leads to a shift of the phase transition to higher temperatures, while substitution with ions of smaller radii, like Lu, Y, and Ga, shifts the valence transition to lower temperatures. This observation is consistent with the expectation that a larger volume available to the Yb ions enhances the stability of the Yb^{2+} state. Some of the data obtained, including the transition temperatures of the various compounds, are shown in Fig. 2.

In Fig. 3, the magnetic susceptibility curves of $Eu_xYb_{0.5-x}In_{0.5}Cu_2$ are shown. On the right-hand side of Fig. 3 the inverse susceptibilities of the systems with $x=0.10$, 0.14, and 0.25 are shown. The effective moment of the high-temperature part of the curves agrees well with that expected from the relative amounts of the Eu^{2+} and Yb^{3+} ions. One observes in Fig. 3 that for all three systems at a given temperature there is a break in the linear behavior of the inverse susceptibility. This break must be associated with the change in Yb valency. Below the break the inverse susceptibility is linear again and corresponds to what is expected from divalent Eu and nonmagnetic Yb. The Eu ions stay divalent and even order magnetically at lower temperatures. The ordering temperature is 25, 13, and 8 K for the systems with $x=0.25$, 0.14, and 0.10, respectively. The magnetic susceptibility of the $x=0.14$ system below 13 K depended on whether or not the sample was cooled in an external magnetic field. This phenomenon is typical for spin glasses. Considering that the Eu is quite dilute (only 5 at. %) it is not surprising that the Eu ions behave like a spin glass. Additional evidence to the fact that the system is a spin glass is obtained from Mössbauer spectroscopy.

D. Mössbauer spectroscopy

The valence transition of Yb in $Yb_{0.4}In_{0.6}Cu_2$ can be studied by Mössbauer spectroscopy by the use of the ^{170}Yb Mössbauer nucleus or other probe nuclei which can be introduced into $Yb_{0.4}In_{0.6}Cu_2$. Such probes are ^{119}Sn which replaces In, ^{151}Eu which replaces Yb or In, and ^{57}Fe which replaces Cu. While the study of ^{170}Yb yields direct information on the valence of the Yb ion, the stud-

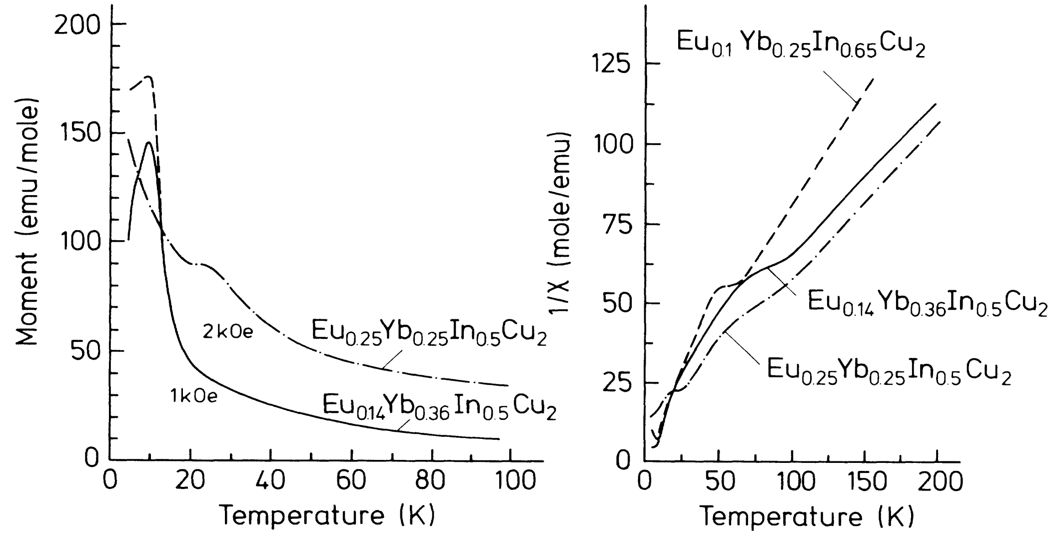

FIG. 3. Left panel, magnetic susceptibility curves of $Eu_xYb_{0.5-x}In_{0.5}Cu_2$. Notice the difference between the field cooled (dashed curve) and zero-field cooled (solid curve) for $x=0.14$. Right panel, inverse magnetic susceptibilities of the system with various concentrations.

ies of the other isotopes yield indirect information; they sense the changes that occur in the crystal due to the Yb valence change. These changes may concern conduction-electron densities (isomer shift), electric field gradients (quadrupole interaction), and lattice vibrations (change in recoil-free fraction). It turns out that all four isotopes reveal the valence transition with relatively high sensitivity.

1. ^{170}Yb (84.3-keV transition)

The magnetic properties of Yb compounds can be studied in detail by ^{170}Yb Mössbauer spectroscopy.[3] The properties of Yb ions in external magnetic fields have been studied by Mössbauer spectroscopy in the past, in particular the case of Yb in $YbPd_3$.[4] We used a conventional Mössbauer spectrometer in which the source, $^{170}TmAl_2$, was kept at 4.2 K and the absorber ($\simeq 150$ mg/cm^2 $Yb_{0.4}In_{0.6}Cu_2$) was contained in a plastic oven.[5] Both source and absorber were inside a superconducting coil producing a magnetic field of up to 6 T. The temperature of the absorber was measured by a calibrated carbon resistor. A constant-current heating coil could produce absorber temperatures from 4.2 to 75 K with a stability of 1 K. Measurements were performed with the absorber at 4.2 and 60 K in 0- and 6-T external magnetic fields. The experimental spectra are shown in Fig. 4.

The spectrum at 4.2 K in zero magnetic field [Fig. 4(a)] displays a narrow single absorption line. This by itself proves that $Yb_{0.4}In_{0.6}Cu_2$ is not magnetically ordered at 4.2 K. However, this measurement does not differentiate between two possibilities: (i) the Yb ion is divalent or at least nonmagnetic; or (ii) the Yb ion is trivalent but in the fast-spin-relaxation limit. A measurement in an external magnetic field of 6 T shows that the response is that of nonmagnetic Yb. The spectrum in Fig. 4(b) is almost identical to that in Fig. 4(a). This can only be so if the hyperfine splitting in $Yb_{0.4}In_{0.6}Cu_2$ is identical to that in the $TmAl_2$ source[4] (both in 6 T). This proves that $Yb_{0.4}In_{0.6}Cu_2$ behaves as Yb in cubic $TmAl_2$, namely that it is nonmagnetic in a cubic environment.

The measurements above T_v, at 60 K, exhibit a broad line in zero external field [Fig. 4(c)] and an even broader line or a split line in 6 T [Fig. 4(d)]. In the latter spectrum, where the magnetic field was parallel to the γ rays, one expects to observe only two absorption lines,[4] split by $2g_n\mu_n(H_a - H_s)$ where H_a and H_s are the fields acting on the Yb nuclei in the absorber and source, respectively.[4]

The best fit to the spectra in Fig. 4(d) yields a value of 19(7) T for the Yb^{3+} hyperfine (hf) field at 60 K. By comparing the magnetic susceptibility value at 60 K to that of an Yb^{3+} free ion, one can obtain the expected experimental hf field from the free-ion hf field at 60 K. The value obtained is 14 T, in agreement with the experimental observation. It is thus concluded that the magnetic behavior of the Yb ions above 60 K is as that expected for a $J=\frac{7}{2}$ state of Yb^{3+}, in agreement with the susceptibility measurements.

In contrast to ^{151}Eu Mössbauer spectroscopy, the ^{170}Yb isomer shift is not a good measure of the valence state of the Yb ion. However, a full conversion of Yb^{2+} to Yb^{3+} corresponds to a change in isomer shift of $\simeq 0.4$ mm/s.[3] In the $Yb_{0.4}In_{0.6}Cu_2$ system the change in isomer shift between 4.2 to 60 K is less than 0.08 mm/s, tending to support the small valence change revealed by the x-ray diffraction and x-ray absorption measurements.

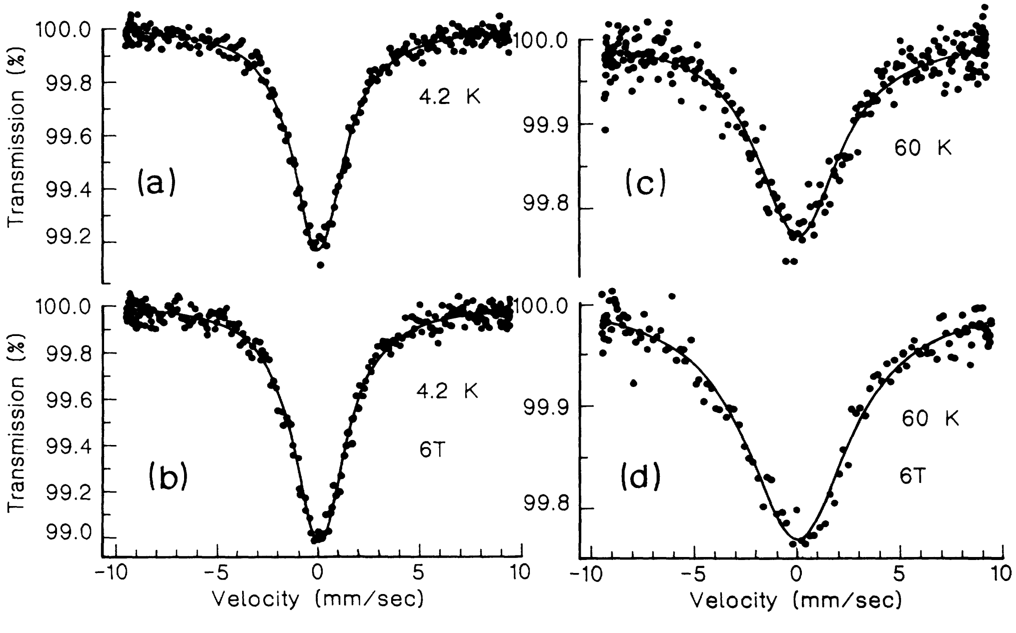

FIG. 4. Mössbauer spectra of the 84-keV transition of ^{170}Yb in $Yb_{0.4}In_{0.6}Cu_2$.

2. ^{119}Sn (23.8-keV transition)

The ^{119}Sn spectra were measured with an absorber of ^{119}Sn (1 at. % of In) in $Yb_{0.4}In_{0.6}Cu_2$ and $Lu_{0.4}In_{0.6}Cu_2$ at temperatures from 4.2 to 180 K using a $Ca^{119}SnO_3$ source. A typical spectrum is shown in Fig. 5. The average isomer shift and the total spectral area are displayed in Fig. 6.

If the Yb ion changes its valency at 50 K, the ^{119}Sn probe substituted in the cubic In site should sense this transition by the change in conduction-electron density and change in lattice dynamics. ^{119}Sn substituted in the Cu site should also experience a change in electric field gradient as observed by Cu NMR in $EuCu_2Si_2$.[6] In view of the insensitivity of the ^{119}Sn probe for moderate electric field gradients, due to the small quadrupole moment of the 23.8-keV state, it is not surprising that we do not observe the latter effect. Further, ^{119}Sn spectra (Fig. 5) do not display enough structure to be able to resolve uniquely the subspectra belonging to Sn in the In and Cu sites. However, it is clear from the spectral shape that Sn occupies both sites. In Fig. 6 the average isomer shift (center of mass of the spectrum) and total spectral area (proportional to the Mössbauer recoil-free fraction) are displayed. These two parameters are independent of any model analysis of the spectra, and exhibit the average behavior on the ^{119}Sn ions in $Yb_{0.4}In_{0.6}Cu_2$. One observes in Fig. 6 characteristic changes in both parameters in the temperature range of 50–70 K at slightly higher temperatures than where the transition is observed in the susceptibility, specific-heat, and resistivity measurements. The difference can be due to the different sample used in the ^{119}Sn Mössbauer studies. In Fig. 6, the behavior of ^{119}Sn in $Lu_{0.4}In_{0.6}Cu_2$ is also shown. In this case the temperature dependence of both parameters is smooth and normal in the whole temperature range. It is thus clear that the ^{119}Sn probe reveals the Yb valence transition in $Yb_{0.4}In_{0.6}Cu_2$ by both the change in conduction-electron density and in lattice dynamics. The fact is of *major importance,* since apparently ^{119}Sn may serve as an easy probe to reveal valence changes in rare-earth compounds which are not easily accessible to direct Mössbauer studies in a wide range of temperatures. This includes all Yb compounds and, *even more important, all Ce compounds.*

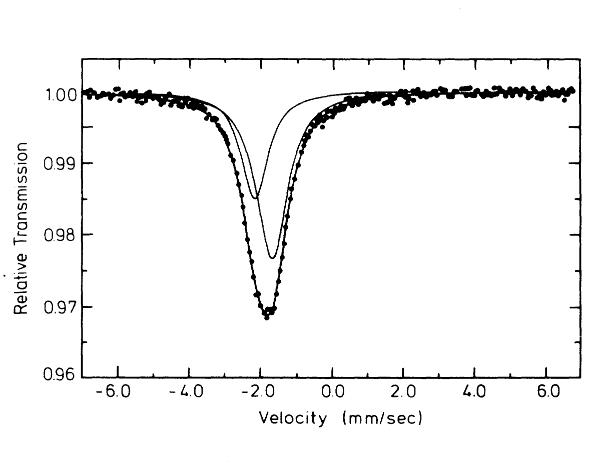

FIG. 5. A typical Mössbauer spectrum of the 24-keV transition of dilute ^{119}Sn in $Yb_{0.4}In_{0.6}Cu_2$.

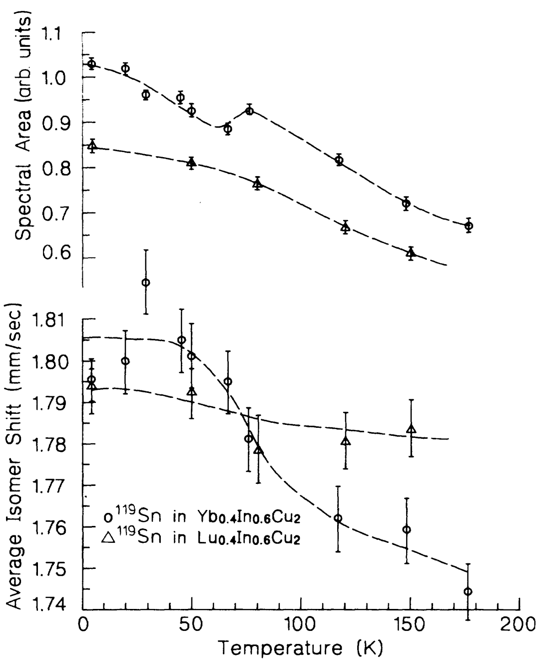

FIG. 6. Temperature dependence of the spectral area and average isomer shift of the Mössbauer spectra of ^{119}Sn in $Yb_{0.4}In_{0.6}Cu_2$.

3. ^{151}Eu (21.5-keV transition)

Mössbauer spectroscopy studies of ^{151}Eu in $Eu_xYb_{0.5-x}In_{0.5}Cu_2$, $x=0.10$, 0.14, and 0.25 at temperatures of 4.1, 90, and 300 K have been performed. The $x=0.10$ sample, according to the magnetic susceptibility studies, is nonmagnetic down to 8 K. The Mössbauer studies show a single resonance at 90 K and a magnetically split, very smeared out spectrum at 4.1 K. One may conclude that this sample orders magnetically, probably to a spin-glass state. The samples with $x=0.14$ and 0.25 show also magnetically split spectra at 4.1 K and isomer shifts of $-9.3(5)$ and $-10.4(2)$ mm/s, respectively. The $x=0.25$ spectrum is typical for a well-defined hyperfine field, as expected for a magnetically ordered system. The $x=0.14$ spectrum was fitted with broad absorption lines and a distribution of hyperfine fields, consistent with the spin-glass state of this system. The observed hyperfine field at 4.1 K in both $x=0.14$ and 0.25 samples is 290(15) kOe. At 90 K both $x=0.14$ and 0.25 samples exhibit a single absorption line at isomer shifts of $-8.8(1)$ and $-9.3(1)$ mm/s, respectively. Comparing these with those observed at 4.1 K shows that the charge density at the Eu site is quite sensitive to the valence change of the Yb ion.

4. ^{57}Fe (14.4-keV transition)

Mössbauer spectra of dilute ^{57}Fe (0.25 at. % of Cu) in $Yb_{0.4}In_{0.6}Cu_2$ at 90 and 4.1 K display a superposition of inequivalent Fe sites. One subspectrum can be identified as belonging to pure Fe metal, indicating that iron is not welcome in this system, even when very dilute. Another iron site displays a quadrupole split spectrum. This spectrum corresponds probably to iron in the Cu site. The spectra at 4.1 and 90 K look different; the ^{57}Fe quadrupole splitting below T_v ($e^2qQ/2=5(2)$ Mc/s) is almost twice as large as that above T_v.

E. Resistivity

The electrical resistivity of $Yb_{0.4}In_{0.6}Cu_2$ and $Lu_{0.4}In_{0.6}Cu_2$ has been studied both in Jerusalem and Wien by standard four-contact-point methods. The temperature dependence of the resistivities is shown in Fig. 7. While in the Lu system the resistivity has an ordinary smoothly increasing behavior; in the Yb system a strong increase in resistivity (by a factor of 6) is observable at the expected valence transition temperature. The inset in Fig. 7 shows details of the transition on an expanded scale together with, for the sake of comparison, specific-heat data. In both experiments we clearly see that the transition takes place within about 20 K, starting around 60 K. Within experimental uncertainty no hysteresis effects at the transition could be detected.

Above T_v, the resistivity of $Yb_{0.4}In_{0.6}Cu_2$ is similar to that of $Lu_{0.4}In_{0.6}Cu_2$, where both Yb and Lu are trivalent. The low resistivity below T_v, where the Yb is of intermediate valence, is probably associated with the formation of a high density of electronic states at the Fermi level.

F. Specific heat

The specific heat of $Yb_{0.4}In_{0.6}Cu_2$ and $Lu_{0.4}In_{0.6}Cu_2$ in the temperature range 4.2 to 80 K is shown in Fig. 8. If one calculates the difference between the two curves one obtains the contribution of the Yb 4f electrons to the specific heat, as shown in Fig. 8. One observes that this contribution has two peaks in the region of the Yb valence transition. This is similar to the behavior of the unit-cell size (Fig. 1), the susceptibility (Fig. 2), resistivity and specific-heat data (Fig. 7 and Fig. 8), which all display that the valence phase transition occurs in two stages. This is, however, attributed to inhomogeneities in the sample, since other samples did not exhibit this phenomenon (see Fig. 2 and also Fig. 2 in Ref. 1).

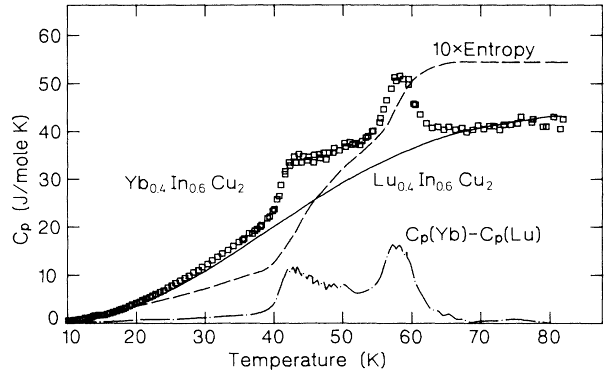

FIG. 8. Temperature dependence of the specific heat of $Yb_{0.4}In_{0.6}Cu_2$, $Lu_{0.4}In_{0.6}Cu_2$, the difference between the two, as well as the entropy corresponding to this difference. For a system with 100% Yb, the Yb specific heat and entropy will be 2.5 times larger.

If one calculates from the Yb specific heat the change in entropy per mole Yb in the 10- to 80-K temperature interval one obtains a value of 13.3(3) J/Yb-mole K, which corresponds to the flattening of the entropy curve at 5.3 J/mole K for the formula unit in Fig. 8. One can compare this value of change in entropy with that expected from the model proposed in Ref. 1. We calculate the entropy of the system for two cases. At first, the ground state is a singlet and the Γ_6 state of $Yb^{3+}(F_{7/2})$, split by a cubic crystalline electric field (CEF), which is represented by the CEF parameter $A_4\langle r^4\rangle=40$ K, is at E_0 above the ground state. In the second case, the Γ_6 state of Yb^{3+} is the ground state and the singlet state lies by $(\alpha-1)E_0$ above it.[1] Plotting the difference in entropy between the

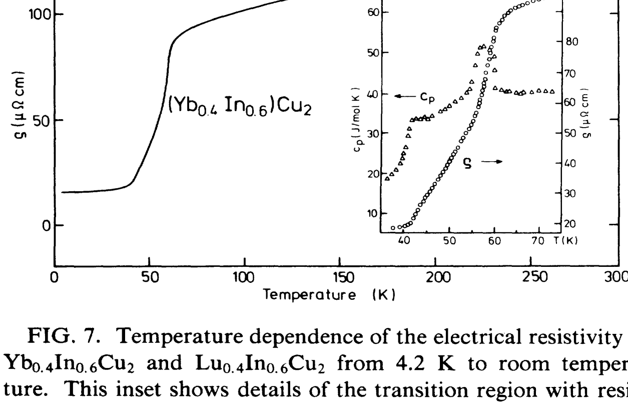

FIG. 7. Temperature dependence of the electrical resistivity of $Yb_{0.4}In_{0.6}Cu_2$ and $Lu_{0.4}In_{0.6}Cu_2$ from 4.2 K to room temperature. This inset shows details of the transition region with resistivity and specific-heat data on an expanded scale.

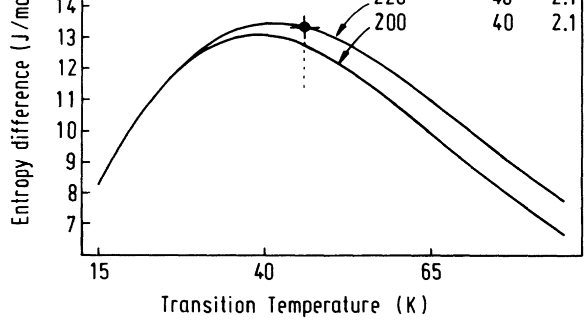

FIG. 9. The theoretically calculated entropy difference between Yb^{3+} and Yb^{2+} according to the model suggested in Ref. 1, as a function of the phase-transition temperature.

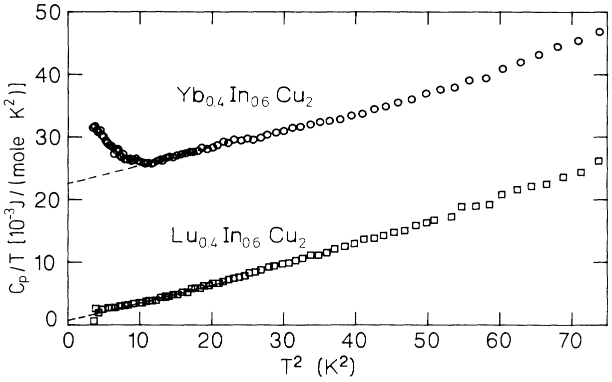

FIG. 10. The specific heat divided by temperature as a function of the temperature squared for $Yb_{0.4}In_{0.6}Cu_2$ and $Lu_{0.4}In_{0.6}Cu_2$ at low temperatures. For a system with 100% Yb, the Yb specific heat will be 2.5 times larger.

two cases for various values of $A_4\langle r^4\rangle$, E_0, and α within the error bars given in Ref. 1, one obtains the curves shown in Fig. 9. One observes that the experimental value of 13.3 J/mole K is in good agreement with the theoretical value for the entropy difference at $T_v = 46$ K. Of major interest is the fact that the phase transition occurs at the point of maximum entropy difference.

In Fig. 10 the specific heat divided by temperature of $Yb_{0.4}In_{0.6}Cu_2$ and $Lu_{0.4}In_{0.6}Cu_2$ are displayed as a function of the temperature squared, for temperatures below 9 K. From the intersections of the linear parts of these curves with the vertical axis one finds the conduction-electron specific-heat factors γ to be 55.7 mJ/Yb mole K^2 (corresponding to 22.3 mJ/mole K^2) and 0.8 mJ/Lu mole K^2 (0.32 mJ/mole K^2) for the Yb and Lu systems, respectively. The extremely high γ value of the Yb system relative to the Lu systems indicates with little doubt that the Yb at low temperatures is not in a pure divalent state but in a highly intermediate valence state.

G. L_{III} x-ray absorption spectroscopy

The x-ray absorption (XA) measurements were performed in the temperature range from 6 to 300 K at the EXAFS-II beamline of the Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY (Hamburg, Germany) using a Si(111) double-crystal monochromator with an energy resolution of $\simeq 2.0$ eV at 9 keV. The investigated samples were the same as those used in the ^{119}Sn Mössbauer measurements, namely $Yb_{0.4}In_{0.6}Cu_2$ and $Lu_{0.4}In_{0.6}Cu_2$, both doped with ^{119}Sn (1 at. % of In). Typical spectra of the Yb L_{III} edge are shown in Fig. 11. They are governed by strong white-line peaks at energy positions typical for Yb^{3+} ions. Additional structures typical for Yb^{2+} are observable on the low-energy side of the dominant Yb^{3+} resonance. It is remarkable that the white lines of Yb^{3+} ($2p^5 4f^{13} 5d^*$ final states) reveal an almost-resolved doublet structure, a quite unusual behavior in L_{III}-edge spectroscopy of rare-earth systems. It can be attributed to a strong interaction of the Yb $5d^*$ electrons with the CEF. Similar white-line features are observed in the Lu L_{III}-edge spectra of $Lu_{0.4}In_{0.6}Cu_2$ as well as in similar studies of other cubic Laves phases of Eu and Yb.[7]

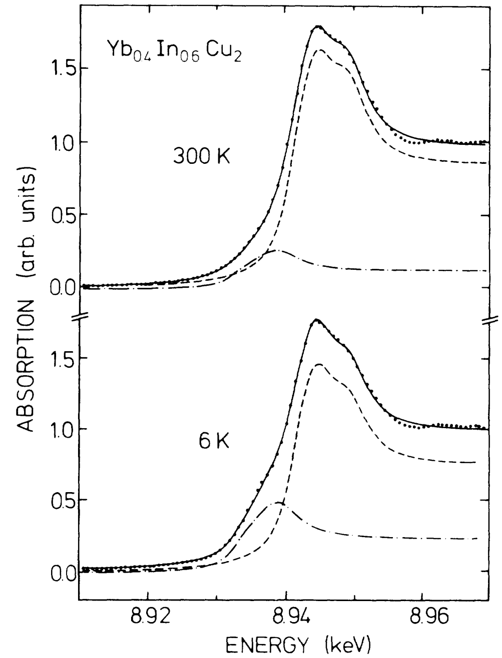

FIG. 11. Yb L_{III} x-ray absorption spectra of $Yb_{0.4}In_{0.6}Cu_2$ at various temperatures.

The Yb L_{III} XA spectra were fitted by a superposition of two edge profiles typical for Yb^{2+} and Yb^{3+} final states. Each profile contains the sum of an arctan function (representing the edge) plus two Lorentzians (representing the CEF-split white line).

From the fitted intensities $I(2^+)$ and $I(3^+)$ of the respective Yb^{2+} and Yb^{3+} subspectra, the term $v(L_{\mathrm{III}}) = 2 + I(3^+)/[I(2^+) + I(3^+)]$ was derived. $v(L_{\mathrm{III}})$ is commonly defined as the valence measured by L_{III} XA spectroscopy. Its temperature dependence is plotted in Fig. 12. The sharp valence transition around 60 K agrees well with the observation of all the other experimental techniques. The temperature-independent behavior of $v(L_{\mathrm{III}})$ above and below T_v is in contrast to that observed for other Yb systems with valence instabilities, for instance $YbPd_2Si_2$,[8] where a continuous variation of $v(L_{\mathrm{III}})$ is observed. This points again to the first-order character of the valence transition in $Yb_{0.4}In_{0.6}Cu_2$.

One should comment on the reliability of L_{III} edge spectroscopy in determining valencies in heavier rare-earth systems. It has been demonstrated recently that final-state effects may influence the 4*f*-electron occupancy measured by this method,[9] similar to the observations in other deep-core or high-energy spectroscopies.[10] Final-state effects are connected with 4*f*-ligand hybridization and are likely to occur also in the present system. Therefore, the $v(L_{\mathrm{III}})$ values shown in Fig. 12 may be shifted in their *absolute* magnitude by final-state effects. However, the *relative* variation of $v(L_{\mathrm{III}})$ still provides a good mea-

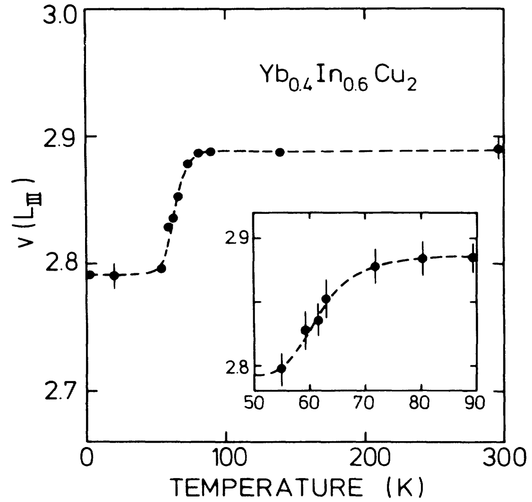

FIG. 12. Temperature dependence of the Yb valence as obtained from the Yb L_{III} XA measurements.

sure of changes in the 4f occupancy.[11] The relatively small change of $v(L_{III})$ by 0.1 at T_v agrees well with the x-ray diffraction measurements.

III. CONCLUSIONS

The system $Yb_{0.4}In_{0.6}Cu_2$ has been studied by seven different experimental techniques, all of which show that the system undergoes a valence phase transition at about 50 K. The methods which sense the magnetic properties of the Yb ions, namely the magnetic susceptibility, ^{170}Yb Mössbauer spectroscopy, and specific heat, indicate that above T_v the Yb ion can be described well in terms of the $(4f^{13}, {}^2F_{7/2})$ configuration of Yb^{3+} and below T_v in terms of a magnetic singlet, resembling the $4f^{14}$ configuration of Yb^{2+}. The methods which measure directly the change in valency, x-ray diffraction and x-ray absorption, indicate that at T_v the change in valency is only $\simeq 0.1$. It is concluded that while above T_v the Yb ion behaves like Yb^{3+}, below T_v the Yb ion is in an intermediate valence state of unique character. Although the formal fractional valency below T_v is $\simeq 2.8$ it behaves like a nonmagnetic singlet state. Apparently the total angular momentum of the Yb 4f electrons is completely compensated by the hybridization with conduction electrons and electrons from neighboring ligands. This nonmagnetic state of Yb in $Yb_{0.4}In_{0.6}Cu_2$ leads to a relatively high zero-temperature magnetic susceptibility, $\chi(0) \simeq 0.0075$ emu/mole (Ref. 1) and a high conduction-electron specific-heat factor $\gamma \simeq 56$ mJ/mole K^2. High $\chi(0)$ and γ values and the low-temperature rise in c_p (see Fig. 10) are characteristic for heavy-fermion systems.[12] Keeping in mind that the 4f electrons of Yb are much more localized than those of Ce and the actinides, which form up to now all known heavy-fermion systems, one may speak of $Yb_{0.4}In_{0.6}Cu_2$ as a "*light heavy-fermion system.*" Considering that $\chi(0)$ of $Yb_{0.4}In_{0.6}Cu_2$ may contain magnetic impurity contributions,[1] then the relation between γ and $\chi(0)$ of $Yb_{0.4}In_{0.6}Cu_2$ is quite similar to that found for heavy-fermion systems.[12,13] It should also be mentioned that many properties of $Yb_{0.4}In_{0.6}Cu_2$ resemble those of YbCuAl (Ref. 12) and YbPd (Ref. 14). In this respect measurements of the properties of $Yb_{0.4}In_{0.6}Cu_2$ in the millidegrees Kelvin region would be highly desirable.

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