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Characterization of the valence transition in $Yb_xIn_{1-x}Cu_2$ and anomalous ^{115}In Knight-shift behavior

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^{115}In nuclear-magnetic-resonance Knight-shift studies in $Yb_xIn_{1-x}Cu_2$ microscopically confirm the existence of an anomalous valence transition of Yb ions for some values of x. The rate of variation as well as the overall variation of the Knight shift is the largest ever observed in any Yb system. The Knight shift does not track the susceptibility at low temperatures, the possible implications of which are discussed. Specific-heat results prove the intermediate-valence character of Yb ions in the ground state of these compounds.

While trying to form ternary compounds of the three elements Yb, In, and Cu, the existence of Laves-phase cubic compounds of the form $Yb_xIn_{1-x}Cu_2$ ($0.3 \le x \le 0.7$) was noticed.[1] The most interesting aspect of the properties of this series is that, for certain values of x, there is a sharp fall in the magnetic susceptibility (χ) below 50 K and this finding was interpreted in terms of an anomalous valence transition.[1] In view of the unusual nature of the proposed valence transition among Yb systems, it is necessary to characterize this transition with as many microscopic techniques as possible, since similar χ behavior could, in principle, arise due to an antiferromagnetic transition. It would also be interesting to explore whether Yb is mixed valent in its ground state.

In this paper, we report the results of magnetic susceptibility (χ), ^{115}In nuclear-magnetic-resonance (NMR) Knight-shift (KS) (both 4.2–300 K), and specific-heat (1.5–18 K) measurements in $Yb_xIn_{1-x}Cu_2$ ($x=0.3$, 0.4, and 0.6) samples. We find that there is an anomalous decrease in the KS below about 50 K, thereby directly proving the interpretation of χ data by Felner and Nowik[1] in terms of valence transition. The observed magnitude as well as the rate of change of variation of the KS with temperature (T) is the largest ever observed in any Yb system. Another observation, interesting in its own right, is that the linear relationship between the KS and χ breaks down at low temperatures and the possible significance of this result is discussed. The measured value of the linear coefficient of specific heat [$\gamma = \sim 55$ mJ/(mole Yb) K^2] proves that Yb ions are in a mixed-valence state in the low-temperature phase.

Samples of $Yb_xIn_{1-x}Cu_2$ ($x=0.3$, 0.4, and 0.6) were prepared by arc melting the stoichiometric amounts of the constituent elements but with a slight excess of Yb to compensate for the loss while melting. X-ray diffraction patterns showed that, while the major phase crystallizes in Laves-phase cubic structure, there were some weak unidentified lines. Magnetic susceptibility (χ) studies were carried out in a field of 6 kOe using a Faraday balance on the temperature interval 4.2–300 K. ^{115}In NMR KS (4.2–300 K) as well as spin-lattice relaxation time, T_1 (at 4.2, 30, and 125 K) values were obtained employing a Bruker pulsed spectrometer. Specific-heat measurements (1.5–18 K) were performed by a semiadiabatic heat-pulse method.

Figure 1 shows the results of χ measurements. χ for all the samples increases with decreasing temperature and there is a fall at low temperatures. The temperature as well as the rate at which this occurs depends on x. The fall is the sharpest for $x=0.3$ and sluggish for $x=0.6$. We notice a small discrepancy between our data and that of Ref. 1. We see systematics in the x dependence of the rate of change of χ with T around 50 K as well as of the peak position of χ; as the indium concentration is increased, the variation is getting sharper, but in Ref. 1, these systematics are absent. We attribute this discrepancy to different preparative conditions of the samples. Nevertheless, such problems do not interfere with the main conclusions of this paper. There is a sharp rise in χ of $Yb_{0.4}In_{0.6}Cu_2$ and $Yb_{0.6}In_{0.4}Cu_2$ at low temperatures presumably due to impurities (see below).

In Fig. 2, the results of ^{115}In KS measurements are reported for $Yb_{0.3}In_{0.7}Cu_2$. The width of the signal keeps increasing as the temperature is lowered till 55 K and suddenly, for $T < 45$ K, the line becomes narrow with significant improvement in the signal strength. Interestingly enough, for $T < 45$ K, the satellites due to the first-order quadrupolar interaction ($I = \frac{9}{2}$) are clearly observable. The quadrupolar coupling constant e^2qQ derived from the separation of the satellite positions is found to be 3.6 MHz and almost temperature independent below 45 K. These satellites could not be observed above 45 K presumably due to an enormous increase in the electrical field gradient due to the change in the charge state[2] of the Yb ion (see below). We were able to track the signal for $Yb_{0.4}In_{0.6}Cu_2$ in the temperature range 45 K $> T$ and $T >$ 125 K, but not for 45 K $< T <$ 125 K, and the values of the KS for this sample follow closely that of $Yb_{0.3}In_{0.7}Cu_2$. Contrary to the rise seen in χ at low temperatures, the KS remains constant below 40 K for $Yb_{0.4}In_{0.6}Cu_2$. This proves that this rise in χ is not intrinsic. The ^{115}In signal in $Yb_{0.6}In_{0.4}Cu_2$ was too weak to do any detailed NMR

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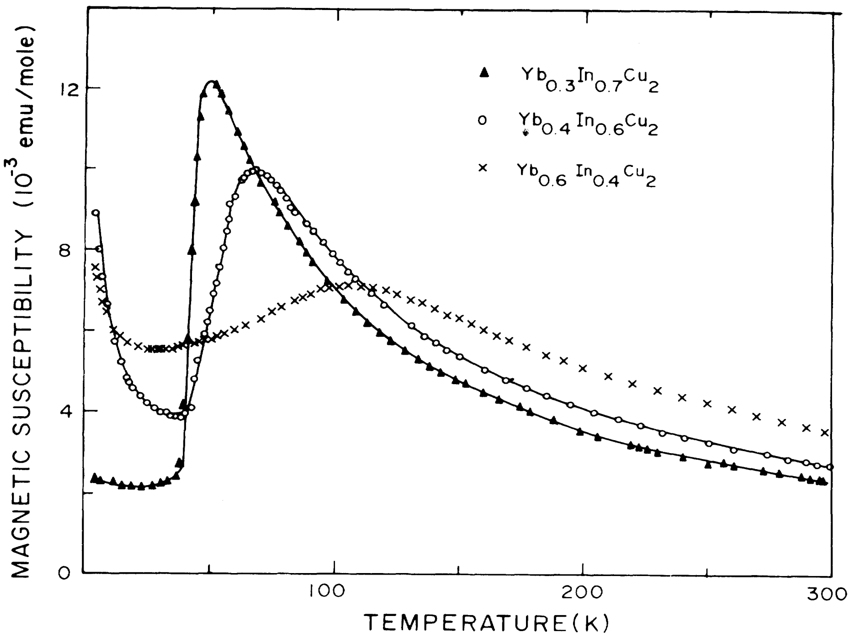

FIG. 1. Magnetic susceptibility (χ) as a function of temperature for $Yb_xIn_{1-x}Cu_2$ ($x=0.3$, 0.4, and 0.6).

study. Our conclusion, drawn below, therefore, is mainly from the results for $Yb_{0.3}In_{0.7}Cu_2$.

It is evident from Fig. 2 that the KS at 300 K is small, decreases to $\sim -1.8\%$ at 55 K, and increases to $+0.12\%$ at 45 K and below. We would like to remark that such a large value of the KS (to an extent of $\sim -1.8\%$) as well as the large temperature dependence of the KS (at a nonmagnetic site), with a steep fall at 50 K is reported for the first time in any Yb system. For comparison, the absolute value as well as the overall variation of the KS (at the nonmagnetic site) in other intermediate-valence Yb materials is less than 0.5%.[3] As is well known,[4] the KS is a microscopic measure of local susceptibility, and hence we conclude that there is a sudden transition from a strongly paramagnetic state to a weakly paramagnetic state at about 50 K as $Yb_{0.3}In_{0.7}Cu_2$ is cooled. This means that there is a discontinuous variation in the mean valence of Yb from near trivalency above 50 K to (near) divalency below 50 K, thus ruling out conclusively the possibility of an antiferromagnetic transition, consistent with neutron scattering data.[1] This conclusion is also consistent with the increase in the values of e^2qQ for $T > 50$ K (see above).

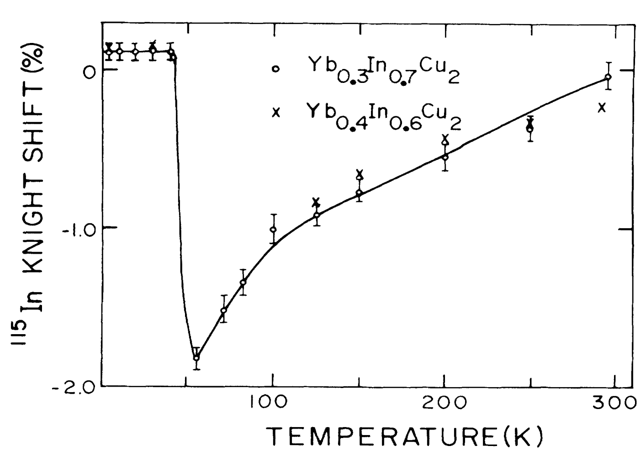

FIG. 2. ^{115}In NMR Knight shift [with respect to $In_2(SO_4)_3$] as a function of temperature of $Yb_xIn_{1-x}Cu_2$.

We could measure the spin-lattice relaxation time of ^{115}In only at a few selected temperatures (125, 30, and 4.2 K). The values of T_1 thus obtained were ~ 1.35, 12, and 50 ms, respectively. The observed values of T_1T indicate that the $4f$ contribution to T_1 below 40 K has decreased, again supporting the idea of a valence transition. All our results render conclusive microscopic evidence to the interpretation of Felner and Nowik.[1]

In Fig. 3, χ vs the KS is plotted with T as an implicit parameter, for $Yb_{0.3}In_{0.7}Cu_2$. As in many other intermediate valence systems,[3] KS tracks χ above T_{max} (the temperature at which the KS exhibits a maximum), and fails to do so at lower temperatures. There is an additional positive contribution to the KS below T_{max}. Earlier it was shown[5] conclusively on the basis of NMR data in $EuNi_2P_2$ that this breakdown of the linear relationship between the KS and χ is the result of the modification of the hyperfine coupling mechanism, arising not due to crystal fields or thermal expansion or contraction, but due to the formation of the $4f$-conduction-band hybridized ground state. An interesting question remaining unanswered is whether the formation of this state requires the coherency or the periodicity of the rare-earth ions. It appears that the data shown in Fig. 3 may shed some light on this aspect. It is obvious that there cannot be any regular periodicity of Yb ions in a disordered lattice such as $Yb_{0.3}In_{0.7}Cu_2$ as Yb and

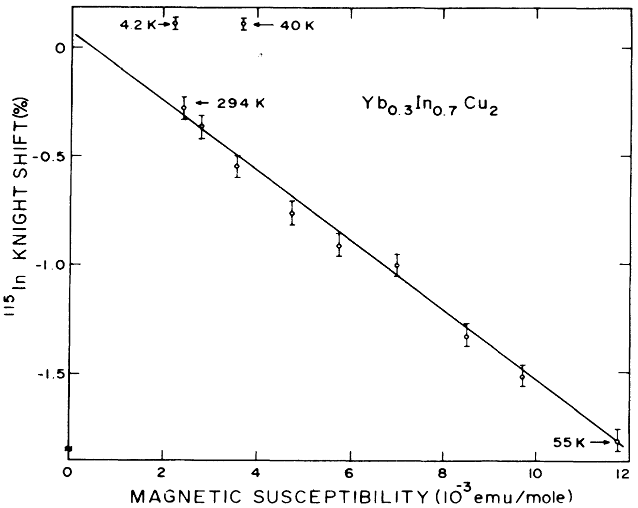

FIG. 3. The plot of ^{115}In NMR Knight shift vs susceptibility (with temperature as an implicit parameter) for $Yb_{0.3}In_{0.7}Cu_2$.

In ions must be randomly distributed at this (Yb) site. In spite of the absence of periodicity, KS vs χ linear relationship breaks down. Therefore, we are tempted to conclude that the formation of the $4f$ hybridized ground state and the consequent modification of the hyperfine coupling mechanism at low temperatures is essentially a local phenomenon. However, we are reluctant to put this interesting conclusion on a firm basis, as at present there is no information on possible changes in the electronic band structure across the sharp valence transition, which may also cause modification of the hyperfine coupling mechanism. It will be interesting to pursue this question further.

In all our discussions above, it was assumed that in the phase below 45 K, Yb ions are in an intermediate-valence state and it would be interesting to verify this. Direct evidence comes from the measurement of specific heat (C) at low temperatures (see the plot of C/T vs T^2 in Fig. 4). There is a peak at 2.2 K in all the samples and this is attributed to the Yb_2O_3 impurity phase. The data above this peak (4.4–18 K) were fitted using the relation $C/T = \gamma + \beta T^2 + \delta T^4$. Such a fit gives a value of $\gamma \simeq 55$ mJ/(mole Yb) K^2 and Debye temperature, $\Theta_D \simeq 276$ K (inferred from β) in all the samples. This value of γ is much larger than that observed in pure Yb^{2+} materials and typical of intermediate valent materials[6] (possibly classified as moderate heavy fermions). Nearly identical values of γ for all the three values of χ suggest that the ground state is the same for all of them. Another observation we have made is that the ratio of γ to χ (4.2 K) in $Yb_{0.3}In_{0.7}Cu_2$ is of the order of 1, consistent with the theoretical predictions of the local Fermi-liquid theory of Newns, Hewson, Rasul, and Read.[7] Such a comparison cannot be made for the other two compositions due to the interference from the impurity phase dominating the low-temperature susceptibility.

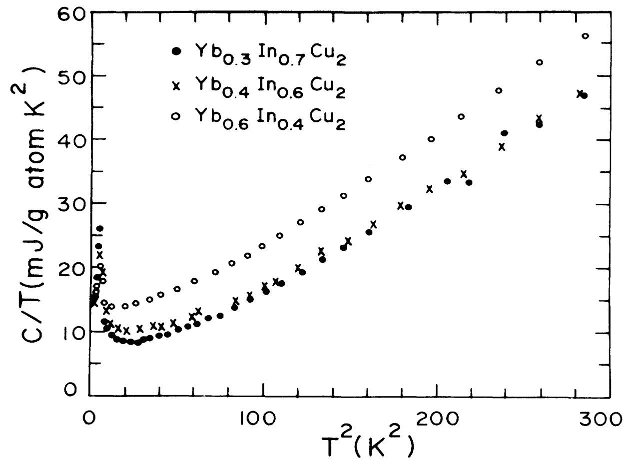

FIG. 4. Specific heat (C) divided by temperature (T) vs T^2 for $Yb_xIn_{1-x}Cu_2$ (x =0.3, 0.4, and 0.6).

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