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## Structure and disorder in $\text{YbInCu}_4$

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We present neutron diffraction results for  $\text{YbInCu}_4$ , and Rietveld refinements of the structure. The ground state has the same structure (C15B) as the high temperature state, so that the first-order phase transition at  $T_s=40$  K is indeed isomorphic, i.e., the lattice constant changes without a change of crystal symmetry. The site disorder and the diffraction linewidths decrease systematically on going from polycrystal samples with two transitions (at 40 and 70 K) to polycrystals with a single (40 K) transition to flux-grown single crystals with a sharp transition at 40 K. We argue that in site-disordered samples, the effect of doping Yb onto the In site is to increase  $T_s$  and cause the transition to become continuous. [S0163-1829(96)05734-7]

$\text{YbInCu}_4$  has the cubic C15B structure at room temperature<sup>1,2</sup> rather than the disordered C15 structure  $\text{Yb}_{1-y}\text{In}_y\text{Cu}_2$  as originally supposed.<sup>3,4</sup> This was first demonstrated<sup>2</sup> by the observation of x-ray-diffraction lines that are forbidden in the C15 structure, and later<sup>1</sup> by Rietveld refinement of the structure using neutron diffraction data. A first order transition at  $T_s=40$  K occurs for polycrystalline samples<sup>1-4</sup> to a low temperature state which is believed to also have the C15B structure. If so, then the transition is analogous to the  $\alpha-\gamma$  transition in Ce metal, i.e., it is an isomorphic valence transition where the lattice parameter changes [by 0.15% in  $\text{YbInCu}_4$ ; see Fig. 1(b)] with no change in crystal symmetry. While the valence change has been confirmed by  $L_{\text{III}}$  x-ray absorption,<sup>3</sup> the proposed low temperature structure has not been confirmed by structural refinement utilizing high resolution diffraction data. In addition, there is a disagreement in the literature as to the temperature and order of the transition: one group found<sup>5</sup> a continuous transition at  $T_s=70$  K in a single crystal grown by the Bridgman technique. In the older work<sup>3,4</sup> in  $\text{Yb}_{1-y}\text{In}_y\text{Cu}_2$  polycrystals, both transitions were sometimes observed. In this paper we attempt to clarify the intrinsic behavior.

We have grown a large series of  $\text{YbInCu}_4$  samples under three different growth conditions. Samples of type A and B are polycrystals grown in sealed Ta tubes; type A samples are homogenized at 1420 K for 24 h, cooled slowly (over an 8–10 day period) to 1120 K and then annealed for 10 days at 1120 K; type B samples are homogenized at 1420 K for 24 h, quenched rapidly to room temperature, and then annealed at 1120 K for ten days. Samples of type C are single crystals grown in an InCu flux: the starting elements are mixed in a one-to-one ratio of  $\text{YbInCu}_4$  to InCu, placed in an  $\text{Al}_2\text{O}_3$  crucible sealed under vacuum in a quartz tube, homogenized

at 1370 K for 2 h then cooled at 20 K/h to 1070 K; the molten flux is then removed in a centrifuge.

The temperature dependence of the susceptibility  $\chi(T)$ , as measured in a SQUID magnetometer, and of the change in sample length  $\Delta L=L(T)-L(0\text{ K})$ , as measured in a capacitive dilatometer, for the three types of samples is shown in Fig. 1. We find that whether one or two transitions occurs in stoichiometric polycrystals depends on the rate of quenching from the melt. For rapid quenching (type B), a single first-order (discontinuous) transition consistently occurs at 40 K. For slow cooling from the melt (type A), a significant fraction of the sample has a continuous transition near 70 K, as can be seen from the s-shaped temperature dependence of  $\chi$  and  $\Delta L$ . Furthermore, in our flux-grown crystals (type C) a first order transition consistently occurs at 40 K, and is consistently sharper than in polycrystalline samples.

Neutron powder diffraction data were collected for samples of all three types in the  $\pm 150^\circ$ ,  $\pm 90^\circ$ , and  $\pm 60^\circ$  detector banks of the General Purpose Powder Diffractometer (GPPD) at the Intense Pulse Neutron Source (IPNS) at Argonne National Laboratory. Samples were approximately 5 g of annealed powders ground from the polycrystalline boules or from a collection of small flux-grown single crystals. The samples, placed in vanadium tubes, were mounted on a cold finger of the GPPD cryostat, which was cooled by a closed-cycle He refrigerator. We collected data at 20 and 100 K, where the samples are in the low and high temperature phases, respectively, and also at 55 K, which lies between the two transition temperatures for samples of type A.

Data for the single crystal sample at 20 and 55 K are shown in Fig. 2; on the scale of this plot the diffraction pattern is essentially identical at the two temperatures, and indeed is similar for all three types of sample at all tempera-

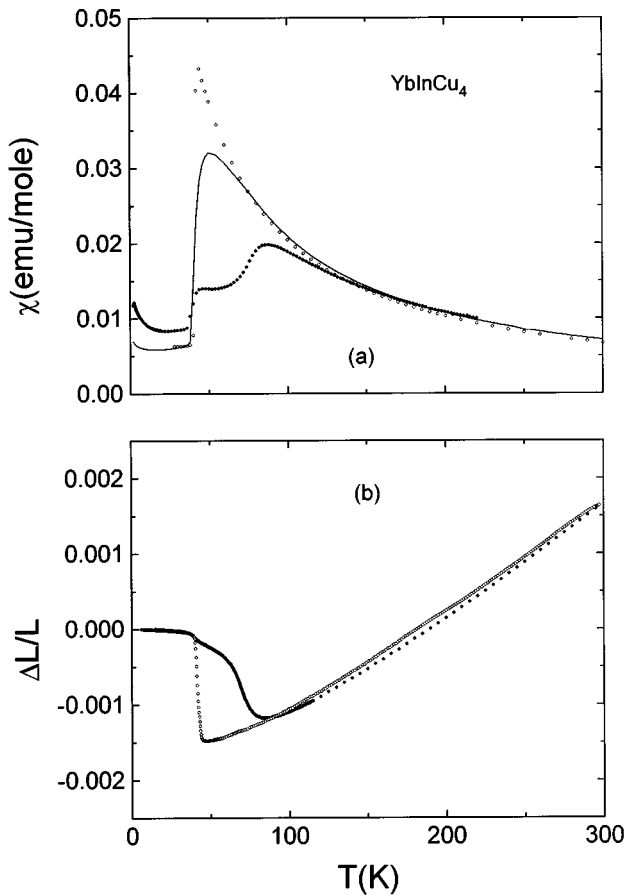


FIG. 1. (a) The susceptibility  $\chi(T)$  versus temperature for the three types of sample of  $\text{YbInCu}_4$  ( $\bullet$ , type A polycrystal; —, type B polycrystal;  $\circ$ , flux grown crystals). (b) The sample length  $\Delta L = L(T) - L(0 \text{ K})$  of a flux grown crystal and a type A polycrystal of  $\text{YbInCu}_4$ . The transition at 40 K is a first-order isomorphous valence transition; the flux-grown crystals have the sharpest transition.

tures studied. Peaks with odd values of  $(h+k+1)/2$  are observed [e.g., the (6,0,0) peak at  $d=1.188 \text{ \AA}$  (Fig. 2)]; these are forbidden in the C15 structure, but are allowed in the C15B structure. This suggests that the C15B phase is the correct phase in all sample types at all temperatures below 300 K. We thus refined the structure in the  $F43m$  space group using the GSAS software package<sup>6</sup> for Rietveld refinement. The results of the refinement are shown in Table I. In addition to the lattice parameters, Cu positions, site occupancies [with  $f(\text{Cu})$  fixed at unity] and isotropic thermal parameters shown in Table I, we also refined terms for the sample absorption, extinction and background as well as strain terms in the profile coefficients. Our results for 100 K ( $T > T_s$ ) are in good agreement with those reported earlier<sup>1</sup> for the high temperature phase.

The first point to be made is that the C15B structure fits the data just as well at low temperature as at high temperature. The  $R$  factors and reduced  $\chi^2$  are quite respectable, especially for the flux-grown single crystals. The Cu position is essentially  $x=5/8$ ; the lattice constants vary as expected with temperature [see Fig. 1(b)]; and the isotropic thermal parameters  $U_{\text{iso}}$  increase as expected with increasing tem-

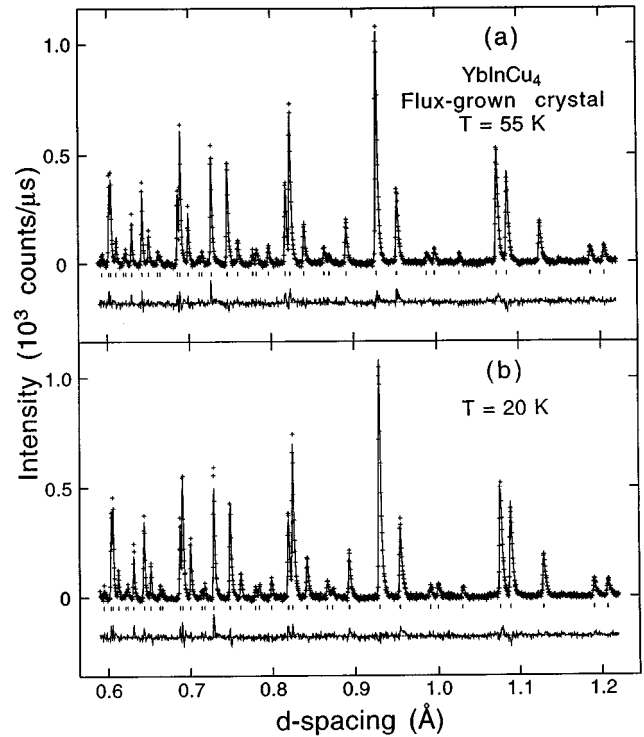


FIG. 2. Neutron diffraction data for a powder prepared from flux-grown crystals of  $\text{YbInCu}_4$  at (a) 55 K and (b) 20 K. The + marks are the observed profile (data). The line through the data is the calculated profile from Rietveld refinement for the C15B structure ( $F43m$  space group; for parameters, see Table I). The tick marks below the data correspond to allowed reflections. The lower curve represents the difference between the observed and calculated profiles.

perature. This supports the contention that the C15B is the correct phase for all three types of sample and that the transition is indeed isomorphous.

The second point is that the relative Yb/In site disorder increases on going from type C flux-grown crystals to type B (single transition) polycrystals to type A (two transition) polycrystals. The absolute values of the site occupancies  $f(\text{Yb})$  and  $f(\text{In})$  are uncertain to the extent that they are correlated with other parameters in the refinement, and in particular to the isotropic thermal parameters  $U_{\text{iso}}$ . At any fixed temperature the  $U_{\text{iso}}$  for a given site should have the same value for all three samples; the variation between samples observed in Table I is, we believe, due to correlation with the site occupancies. However, the site-occupancy difference  $\Delta f = f(\text{In}) - f(\text{Yb})$  is roughly independent of this correlation. For example, at 20 K  $\Delta f = 0.159, 0.092,$  and  $0.062$  for type A, B, and C samples, respectively; but if we fix the  $U_{\text{iso}}$  for each site at the same value for all three samples (see the “frozen  $U_{\text{iso}}$ ” section of Table I) the site occupancies change, but  $\Delta f$  remains approximately the same for each type of sample (0.142, 0.091, and 0.078). Furthermore, these values of  $\Delta f$  are nearly independent of temperature. Hence we argue that  $\Delta f$  is a good measure of the relative site disorder and that  $\Delta f$  increases on going from type C, to type B, to type A samples. If we assume that the parameter  $x$  in the

TABLE I. Structural parameters for  $\text{YbInCu}_4$  (space group  $\overline{F}43m$ ) from Rietveld refinement using neutron powder diffraction data.  $R$  values are given in %. Typical uncertainties are 0.0003 Å for  $a_0$ ; 0.0001 for  $x(\text{Cu})$ ; 0.011 and 0.007 for  $f(\text{In})$ ,  $f(\text{Yb})$  [ $f(\text{Cu})=1$ ]; 0.04, 0.02, and 0.01 for  $100U_{\text{iso}}$  for In, Yb, and Cu; 1 for  $\sigma_1$ .

	$a_0(\text{Å})$	$x(\text{Cu})$	$f(\text{In})$	$f(\text{Yb})$	$100U_{\text{iso}}(\text{Å}^2)$		
					In	Yb	Cu
$T=100\text{ K}$							
Flux-grown crystal (C):	7.1319	0.6250	0.995	0.914	0.120	0.239	0.424
		$\sigma_1=36$	$\chi_{\text{red}}^2=1.83$		$R_{\text{wp}}/R_{\text{exp}}=6.18/4.40$		
Two-transition polycrystal (A):	7.1246	0.6254	1.094	0.929	0.310	0.423	0.443
		$\sigma_1=137$	$\chi_{\text{red}}^2=2.29$		$R_{\text{wp}}/R_{\text{exp}}=7.74/5.53$		
$T=55\text{ K}$							
Flux-grown crystal (C):	7.1290	0.6251	0.993	0.925	0.090	0.198	0.356
		$\sigma_1=38$	$\chi_{\text{red}}^2=1.89$		$R_{\text{wp}}/R_{\text{exp}}=6.32/4.50$		
One-transition polycrystal (B):	7.1264	0.6252	1.043	0.955	0.130	0.277	0.327
		$\sigma_1=46$	$\chi_{\text{red}}^2=2.07$		$R_{\text{wp}}/R_{\text{exp}}=7.67/5.64$		
Two-transition polycrystal (A):	7.1259	0.6253	1.096	0.920	0.230	0.306	0.368
		$\sigma_1=71$	$\chi_{\text{red}}^2=2.27$		$R_{\text{wp}}/R_{\text{exp}}=7.78/5.56$		
$T=20\text{ K}$							
Flux-grown crystal (C):	7.1399	0.6253	0.997	0.935	0.040	0.174	0.326
		$\sigma_1=39$	$\chi_{\text{red}}^2=1.87$		$R_{\text{wp}}/R_{\text{exp}}=6.31/4.49$		
One-transition polycrystal (B):	7.1359	0.6251	1.061	0.969	0.130	0.228	0.279
		$\sigma_1=90$	$\chi_{\text{red}}^2=2.19$		$R_{\text{wp}}/R_{\text{exp}}=7.88/5.73$		
Two-transition polycrystal (A):	7.1293	0.6254	1.083	0.924	0.180	0.254	0.339
		$\sigma_1=165$	$\chi_{\text{red}}^2=2.53$		$R_{\text{wp}}/R_{\text{exp}}=8.23/5.86$		
$T=20\text{ K (frozen } U_{\text{iso}})$							
Flux-grown crystal (C):	7.1399	0.6253	1.025	0.947	0.120	0.250	0.320
		$\sigma_1=39$	$\chi_{\text{red}}^2=1.87$		$R_{\text{wp}}/R_{\text{exp}}=6.31/4.49$		
One-transition polycrystal (B):	7.1360	0.6251	1.052	0.961	0.120	0.250	0.320
		$\sigma_1=90$	$\chi_{\text{red}}^2=2.19$		$R_{\text{wp}}/R_{\text{exp}}=7.88/5.71$		
Two-transition polycrystal (A):	7.1293	0.6254	1.071	0.929	0.120	0.250	0.320
		$\sigma_1=165$	$\chi_{\text{red}}^2=2.54$		$R_{\text{wp}}/R_{\text{exp}}=8.24/5.89$		

alloy formula  $(\text{Yb}_{1-x}\text{In}_x)(\text{In}_{1-x}\text{Yb}_x)\text{Cu}_4$  measures the site disorder, then given the scattering lengths (1.243 and  $0.407 \times 10^{-12}$  cm for Yb and In, respectively) it follows that  $\Delta f = 2.73x$ . Hence  $x \approx 0.02$  for the flux-grown crystals,  $x \approx 0.03$  for the type B polycrystals, and  $x \approx 0.06$  for the type A polycrystals. Given the uncertainties in the refinement and the simplifying assumption, these numbers should not be taken as absolute. They do, however, give a clear indication that flux-grown single crystals are more highly ordered than Ta-tube-grown polycrystals, and that the sample exhibiting two transitions has the strongest site disorder.

A feature of the data which confirms this is that the diffraction linewidths consistently decrease in the sequence type A, type B, type C. This is shown for the (3,1,1) reflection in Fig. 3; it is also true for other well-resolved reflections. In addition it is indicated by the decrease in the profile coefficient  $\sigma_1$ , which measures both instrumental and sample-intrinsic (e.g., strain-induced) contributions to the line shape. It is especially clear at 20 K [Fig. 3(c)] that the flux-grown crystal sample has a smaller linewidth than the polycrystalline samples; and that the sample with two transitions has a particularly large linewidth. This supports our contention that the flux-grown crystals are the most highly ordered.

In recent studies<sup>7</sup> of the effect of alloying on the phase transition, we find for alloys of the form  $\text{YbIn}_{1-y}\text{M}_y\text{Cu}_4$  ( $M = \text{Ag, Sn, etc.}$ ) that  $T_s$  increases with  $y$  at rates 1–4 K/atomic % and that the transition is driven to a critical point at a concentration  $y_c(M) \sim 0.07$  to 0.15; for  $y > y_c$  the transitions are continuous. This suggests a natural explanation for the existence of continuous transitions at 70 K for some samples of  $\text{YbInCu}_4$ : in site-disordered samples the effect of alloying the Yb onto the In site is to increase  $T_s$ , and if the degree of disorder (as measured by  $\Delta f$ , or by the parameter  $x$  defined above) is sufficiently large the transition will be continuous rather than first order. The value  $x = 0.06$  found for the type A polycrystals is of the correct order to give a continuous transition at 70 K.

A common feature to both our type A (two-transition) polycrystals and the Bridgman single crystals<sup>5</sup> is that they are cooled slowly from the melt. That polycrystals that are rapidly quenched from the melt (type B) have better site order suggests that the compound forms peritectically. Under these conditions, growth in molten flux can give better ordered single crystals than growth by the Bridgman technique, because the latter requires solid state diffusion to ameliorate incorrect stoichiometry, while the former can form the crys-

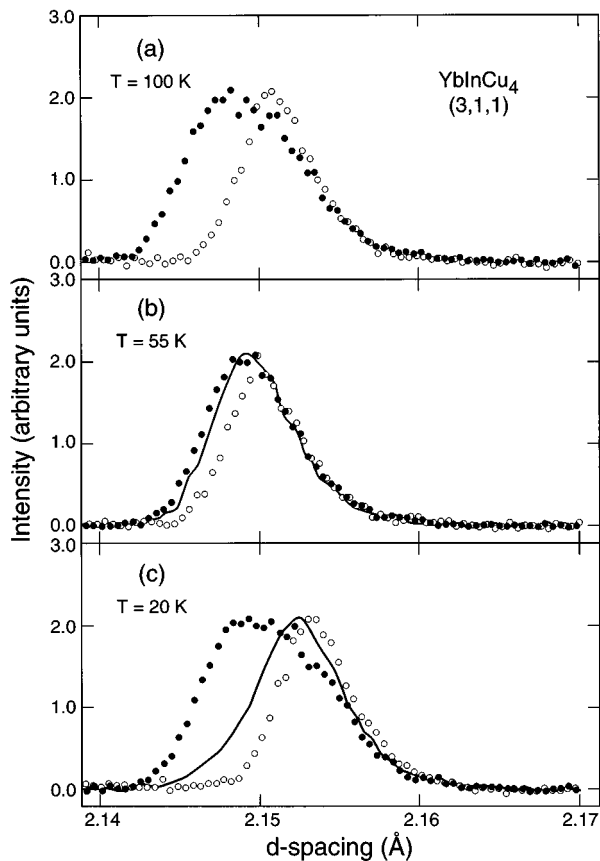


FIG. 3. The (3,1,1) reflection for the three types of sample (same symbols as in Fig. 1) at (a) 100 K, (b) 55 K, and (c) 20 K. All data has been normalized to give equal peak heights. The flux-grown crystals have the smallest linewidths.

tals at the correct stoichiometry by direct inclusion of material at the liquid-solid interface.

Given site disorder, whether one or two (or more) transitions occur depends on whether the site occupancies, coarse-

grained over a suitable length scale, are homogeneous. The existence of two transitions suggests the existence in the polycrystal of two sets of crystallites, one with good site order ( $x \approx 0$ ) and the other with larger (though homogeneous) disorder ( $x \approx 0.1$ ). The large linewidth of the type A sample at 100 K seen in Fig. 3(a) indicates that there are two such subsets of crystallites, the highly disordered subset having a slightly smaller lattice parameter. (The smaller lattice constant suggests that Yb on In sites is trivalent, and hence smaller than in the bulk where it is weakly mixed valent). At 55 K this subset has transformed to the low temperature phase, so that its lattice parameter equals that of the high temperature phase of the well-ordered crystallites; this narrows the linewidth, making it comparable to that of the type B sample [Fig. 3(b)]. At 20 K the well-ordered crystallites have entered the low temperature phase and their lattice parameter increases, while the disordered crystallites retain the value they have at 55 K, so the linewidth increases back to the same value as at 100 K.

In conclusion, we have argued that the intrinsic behavior of well-ordered  $\text{YbInCu}_4$  is to have a first order isomorphous phase transition near 40 K, where the structure remains C15B but the lattice constant increases by 0.15%. Higher temperature and continuous transitions can occur due to YbIn site disorder. The compound probably forms peritectically, so that growth techniques which require solid state diffusion can lead to enhanced site disorder. Growth of single crystals in InCu flux gives the best ordered samples to date.

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