

## Three states of $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ : Amorphous, crystalline, and quasicrystalline

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$\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ , prepared by magnetron sputtering and subsequently annealed, has been observed in three distinct states: amorphous, metastable crystalline, and quasicrystalline. The structural and physical properties of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  have been studied in these three different atomic arrangements. Distinct values of magnetic moment, resistivity, and hyperfine interactions at the Fe sites have been measured for the three states.

Quasicrystalline order with icosahedral symmetry in metastable form was discovered by Shechtman *et al.*,<sup>1</sup> prompting an intense interest worldwide. More recently, stable icosahedral quasicrystals, most notably Al-Li-Cu and Al-Cu-Fe, have been discovered,<sup>2,3</sup> dispelling the notion that the quasicrystals are inherently metastable. Despite extensive theoretical and experimental investigations, many outstanding issues about the structural and physical properties of quasicrystals remain.<sup>4,5</sup> Of those, the actual atomic arrangement in quasicrystals continues to be a fundamental question. There are now several theoretical models of quasicrystals, with suitable relaxation and decorations, all capable of predicting diffraction patterns that are remarkably close to those observed experimentally.<sup>4</sup> Quasicrystals are anticipated to exhibit a variety of unique physical properties, as a result of their unique quasiperiodic structure, but few have been identified to be directly associated with the quasicrystalline order.<sup>5</sup> In order to identify physical properties that are structure specific, it would be advantageous to study the same alloy in more than one structural phases. In this work, we report the observation of *three* different phases of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ . The  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  quasicrystal is of particular interest because it is a stable quasicrystal and its Bravais lattice in six-dimensional space has been indicated to have the least distortions from perfect icosahedral symmetry.<sup>6</sup> In addition to the amorphous and quasicrystalline phases, a metastable crystalline state, intermediate between the amorphous and the quasicrystalline states, has also been observed. Structural and physical properties of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  can be examined and compared in three distinct atomic arrangements. Both long-range atomic ordering and local ordering surrounding the probe atom have been analyzed using x-ray diffraction and Mössbauer spectroscopy. We have also measured the magnetic properties, which depend sensitively on the structures.

We have used sputter deposition, taking advantage of its high effective-quenching rate, to capture first the amorphous state of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ , which is not attainable by rapid solidification from the melt. Upon annealing to suitably high temperatures, a metastable crystalline phase with a cubic structure is formed. At still higher temperatures, the formation of the quasicrystalline phase follows. Thin films of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  have been made using a high-

rate dc magnetron sputtering system with a base pressure of about  $2 \times 10^{-7}$  torr and 4 mtorr of Ar as the sputtering gas. Films about 10  $\mu\text{m}$  in thickness, have been deposited onto liquid-nitrogen-cooled substrates, from which they have been removed for analyses and measurements. Structural characterizations have been made using a Philips APD3720 diffractometer in the  $\theta-2\theta$  geometry using Cu  $K\alpha$  x rays. Differential scanning calorimetry (DSC) measurements have been made using a Mettler DSC unit to detect the phase transformations. A conventional Mössbauer spectrometer with a  $^{57}\text{Co}$  in a Rh source has been used to obtain  $^{57}\text{Fe}$  Mössbauer spectra. Finally the magnetic properties have been measured using a SHE superconducting-quantum-interference-device magnetometer.

The diffraction patterns of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ , without background correction, after annealing at different temperatures are shown in Fig. 1. The as-sputtered samples of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  are amorphous, with a diffraction pattern, shown in Fig. 1(a), typical of those of amorphous metallic solids. To detect phase transformations at elevated temperatures, small quantities ( $\sim 5$  mg) of samples have been measured by DSC from room temperature to 600 °C at a heating rate of 10 °C/min. A DSC scan between 150 and 600 °C is shown in Fig. 2, where two exothermic peaks have been observed at  $T_1 = 310$  °C and  $T_2 = 515$  °C, indicating two phase transformations. Based on this result, we have annealed larger quantities of samples to an annealing temperature ( $T_a$ ) for 5–10 min in a tube furnace in an Ar atmosphere, before cooling back to room temperature for subsequent measurements.

In Fig. 2(b) we show the diffraction pattern of a sample annealed to  $T_a = 450$  °C, where  $T_1 < T_a < T_2$ . All the diffraction peaks can be indexed to a cubic CsCl crystal structure with a lattice constant of  $a = 2.94$  Å, a structure consisting of two interpenetrating simple cubic sublattices. It is noted that at the base of the most intense (110) peak near  $2\theta = 45^\circ$  there is a small broadening. This may be caused by the small grain sizes of some of the crystalline phase with the CsCl structure, or the remnant of the amorphous phase, although the peak width is about a factor of 2 smaller than that of the broad peak of the amorphous phase shown in Fig. 1(a). Judging from the areas of the diffraction peaks shown in Fig. 1(b), one can conclude that more than 90% of the sample have the

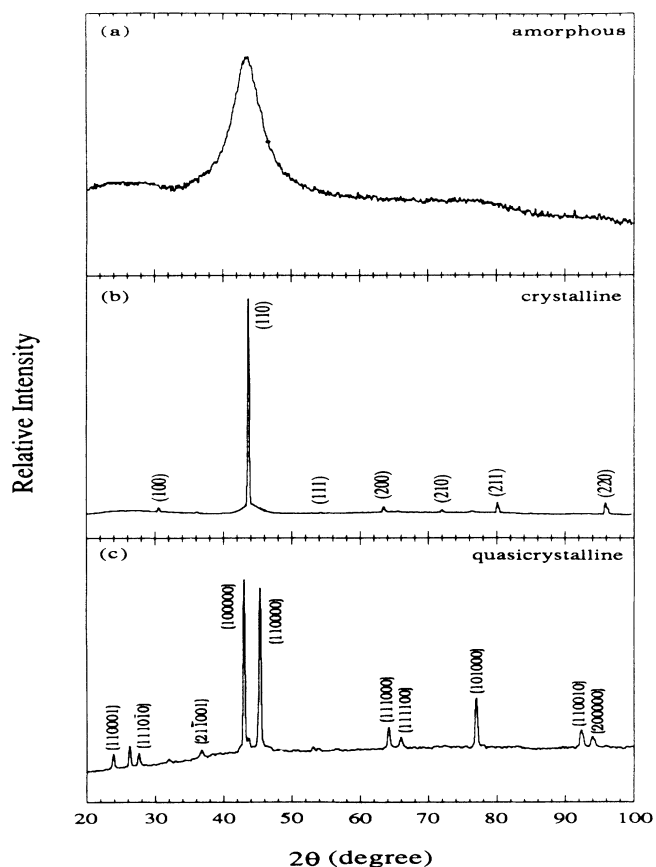


FIG. 1. X-ray diffraction patterns at room temperature of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ : (a) as sputtered, (b) annealed at  $450^\circ\text{C}$ , indexed as a cubic CsCl structure with a lattice constant  $a = 2.94 \text{ \AA}$ , and (c) annealed at  $600^\circ\text{C}$ , indexed using the Bancel's scheme of six Miller indices with a lattice parameter of  $4.46 \text{ \AA}$ .

CsCl structure. When the sample is annealed at  $T_a = 600^\circ\text{C}$ , where  $T_a > T_2 > T_1$ , the diffraction pattern changes completely into that of the quasicrystalline phase as shown in Fig. 1(c). All the diffraction peaks can be indexed using Bancel's scheme<sup>7</sup> with six Miller indices as

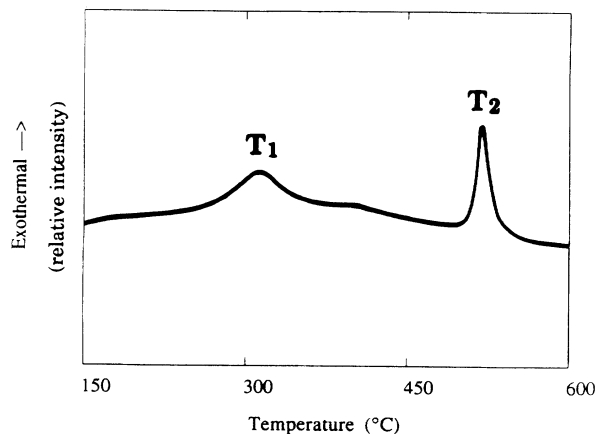


FIG. 2. Differential scanning calorimetry scan of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  from  $150$  to  $600^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ , where two exothermic peaks at  $T_1 = 310^\circ\text{C}$  and  $T_2 = 515^\circ\text{C}$  are observed.

shown in Fig. 1(c). A quasilattice parameter of  $4.46 \text{ \AA}$  has been determined for the quasicrystalline phase, in agreement with previous results.<sup>3</sup>

All metastable phases transform into their ground-state configurations at suitably high temperatures. However, in almost all cases, whether from amorphous to crystalline, or from metastable crystalline to stable crystalline, they are accomplished in one transformation. Most often the final crystalline state consists of several crystalline phases, making a meaningful comparison between the metastable and the stable states difficult. The amorphous  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  alloy is highly unusual in that the transformation proceeds first to yet another metastable but crystalline phase before finally descending into the quasicrystalline state. Furthermore, in all three states, the materials are essentially single phase. Precisely due to this rare occurrence, one can study and compare the physical properties of three distinct phases of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ .

Mössbauer spectroscopy has long been established as a valuable tool in measuring the local environment of the probe atom, most often the Fe atom.<sup>8</sup> Indeed, many quasicrystals have been investigated by Mössbauer spectroscopy where Fe is either a dopant (e.g., Al-Mn),<sup>9,10</sup> or a constituent (e.g., Al-Cu-Fe).<sup>11,12</sup> The structural implications of these results have been presented and argued in the literature. For these reasons, we have measured these samples using  $^{57}\text{Fe}$  Mössbauer spectroscopy. Mössbauer spectra of the three structures of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  at room temperature are shown in Fig. 3. It is immediately clear that the Fe site symmetry in all three cases are noncubic,

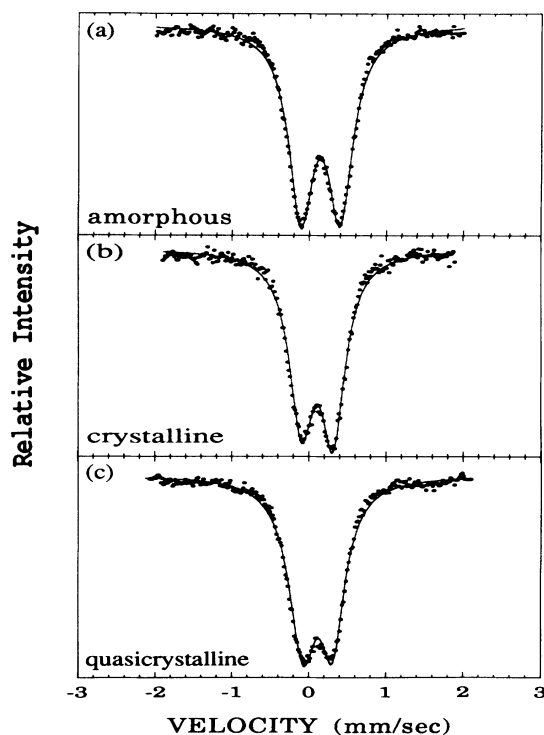


FIG. 3.  $^{57}\text{Fe}$  Mössbauer spectra at room temperature of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ : (a) as sputtered amorphous, (b) annealed at  $420^\circ\text{C}$ , crystalline, and (c) annealed at  $600^\circ\text{C}$ , quasicrystalline.

resulting in quadrupole-split doublet spectra. Noncubic environment are not surprising for the amorphous and the quasicrystalline states. For the intermediate crystalline state with a cubic CsCl structure, the noncubic symmetry comes from the disordered atomic occupation on the two interpenetrating simple cubic sublattices. A similar situation occurs in crystalline  $\text{Fe}_{50}\text{Al}_{50}$ , whose structure is also CsCl. In the ordered configuration of  $\text{Fe}_{50}\text{Al}_{50}$ , the Fe site symmetry is cubic, and hence without a quadrupole splitting, whereas in the disordered configuration, there is a sizable quadrupole splitting of about 0.35 mm/sec and a room-temperature isomer shift (relative to  $\alpha$ -Fe) of 0.17 mm/sec.<sup>13,14</sup>

The quadrupole splitting (QS) of a doublet spectrum is proportional to the electric-field gradient (EFG) at the Fe site. The centroid of the quadrupole spectrum gives the isomer shift (IS). The existence of a distribution of EFG's and IS's causes a slight broadening of the line widths and a small asymmetry in the two peaks. A fit using distributions would be aesthetically more desirable, but in the present case it would not provide much more useful information. We can take the separation of the doublet as the effective QS, and the centroid as the effective IS. From the spectra shown in Fig. 3, we have determined the effective QS values of the amorphous ( $0.50 \pm 0.008$  mm/sec), crystalline ( $0.41 \pm 0.008$  mm/sec), and quasicrystalline ( $0.38 \pm 0.008$  mm/sec) states, and the corresponding effective IS values of 0.26, 0.23, and  $0.24 \pm 0.008$  mm/sec (relative to  $\alpha$ -Fe at room temperatures) for the three states. The values for the quasicrystal are in good agreement with the reported values.<sup>11</sup> It should also be emphasized that these isomer shift values are totally different from those of the Fe-Al alloys.<sup>13,14</sup> In fact, these values are higher than those of all compositions of Fe-Al alloys. The values of the effective QS (hence, the effective EFG) and the IS of the three states of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  are distinctly different but do not vary greatly, particularly between those of crystalline and quasicrystalline states, despite diametrically different x-ray diffraction patterns. One certainly cannot argue that the atomic environments are similar in the three states. This is merely a reflection of the unfortunate situation in which the quadrupole splitting and the isomer shift are not sufficiently sensitive to changes in the local surroundings of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ . Many previous studies had attempted to relate the Mössbauer results to those of various structure models of quasicrystals, from a simple two-site model to more elaborate schemes.<sup>9-12</sup> The present results demonstrate that the utility of hyperfine interactions measured at the Fe site for such purposes is quite limited. We have also examined other samples of  $\text{Al}_{65}\text{Cu}_{20+x}\text{Fe}_{15-x}$  ( $-10 \leq x \leq 10$ ), where the relative contents of Fe and Cu have been varied.<sup>15</sup> Both the quadrupole splitting and isomer shift vary systematically with composition, but changes among the structurally distinct states remain quite small. The values of QS, and particularly those of IS, are apparently dictated more strongly by the composition than the different atomic arrangement of the three states.

The magnetic properties of many quasicrystals, in general, and  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ , in particular, have been unset-

tling. The magnetic susceptibility of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  had been reported to be diamagnetic by some,<sup>16</sup> and paramagnetic by others with an appreciable Fe moment.<sup>17</sup> Very recently, from the Hall coefficient of an amorphous sample of  $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ , a magnetically ordered state had been suggested by Biggs *et al.*<sup>18</sup> In our case, we have found all three states of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  are paramagnetic with no sign of magnetic ordering. The susceptibility ( $\chi$ ) data of the amorphous, metastable crystalline, and quasicrystal states of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  have been measured from 5 to 300 K, and are shown in Fig. 4. In all cases, the data can be well described by

$$\chi = \chi_0 + \frac{np_{\text{eff}}^2\mu_B^2}{3k_B(T - \theta_C)},$$

where the first term is the temperature-independent part, the second the Curie-Weiss term, with  $n$  the number of magnetic moments per volume,  $p_{\text{eff}}$  the effective moment,  $\mu_B$  the Bohr magneton, and  $\theta_C$  the Curie-Weiss temperature. From the susceptibility data, we have determined the effective moment of Fe, assumed to be the only species carrying the local moments ( $p_{\text{eff}}$ ), to be 0.45, 0.24, and  $0.28 \pm 0.02\mu_B$  for the amorphous, crystalline, and quasicrystalline states, respectively. This variation of moments results solely from the differences in the structures of the three states. The small and negative values of  $\theta_C = -4.5, -6,$  and  $-7$  K for the amorphous, crystalline, and quasicrystalline states, respectively, indicate weak interactions among the moments, which are unlikely to result in a magnetic ordering with a substantial magnetic ordering temperature, and none has been detected down to 5 K. Mössbauer spectra at 4.2 K remain as doublets with no sign of magnetic ordering. Therefore, both magnetometry and Mössbauer results show conclusively that *no* magnetic ordering is detectable from any of the three states of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  down to 4.2 K.

The room temperature resistivity  $\rho(300 \text{ K})$  has a value

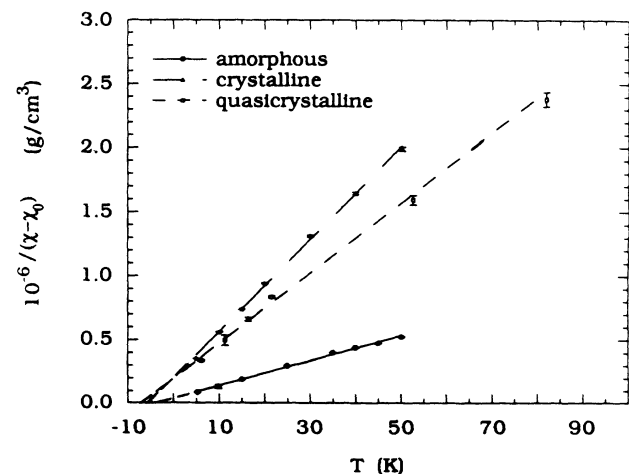


FIG. 4. Inverse magnetic susceptibility [ $1/(\chi - \chi_0)$ ] as a function of temperatures of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  as sputtered amorphous, annealed at 420°C crystalline, and annealed at 600°C quasicrystalline.

of 250, 3200, and 2000  $\mu\Omega$  cm for the amorphous, crystalline, and quasicrystalline states, respectively. The value for the amorphous state is similar to those observed in other amorphous and disordered metals.<sup>19</sup> However, both the intermediate crystalline and the quasicrystalline states have values about an order of magnitude higher. While many quasicrystals of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  show resistivities in the few tens to few hundreds  $\mu\Omega$  cm range,<sup>20</sup> very large resistivities of 4500  $\mu\Omega$  cm (Refs. 21 and 22) have been observed for highly perfect quasicrystalline specimens of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ . The resistivities of both our quasicrystalline and intermediate crystalline samples have comparable values to that.

In summary, we have achieved and investigated three different states of  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ : amorphous, crystalline,

and quasicrystalline. We have observed distinct differences in the magnetic moment, resistivity, and hyperfine interactions at the Fe sites, due to their unique atomic arrangements. The Fe moment varies from 0.24 to 0.45 $\mu_B$ , but none of the three states exhibits magnetic ordering. Both the intermediate crystalline and quasicrystalline states have very high resistivities in the 10<sup>3</sup>- $\mu\Omega$  cm range. The hyperfine interactions at the Fe sites for the three states are clearly distinct but similar in value.

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