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Local environment of iron sites in icosahedral $Al_{65}Cu_{20}Fe_{15}$

Z. M. Stadnik and G. Stroink
Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5

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A novel icosahedral alloy, $Al_{65}Cu_{20}Fe_{15}$, produced in both a thermodynamically metastable and stable phase, has been studied with ^{57}Fe Mössbauer spectroscopy, x-ray diffraction, and differential thermal analysis. It was found that the Mössbauer spectrum of either phase can be successfully analyzed in terms of a distribution of quadrupole-splitting magnitudes. This is interpreted as evidence for a continuous distribution of iron sites. The similarities of Mössbauer parameters of both phases indicate that a high degree of atomic disorder is an intrinsic property of icosahedral materials. Critical examination of previous Mössbauer studies of icosahedral materials together with other published experimental data show that the assertion of two distinct transition-metal sites in these materials is unfounded. Our results can be interpreted in terms of the distorted-icosahedral quasicrystal model.

I. INTRODUCTION

Since the remarkable discovery of the icosahedral phase in a rapidly solidified Al-Mn alloy,[1] many other icosahedral phases have been found.[2] Most icosahedral phases are prepared by nonequilibrium methods and are therefore metastable phases which transform into crystalline phases upon annealing. The only thermodynamically stable quasicrystalline materials known until recently were found in the Al-Li-Cu system.[3-9] Very recently new thermodynamically stable icosahedral phases have been reported in Ga-Mg-Zn,[10] Al-Cu-Fe,[11] and Al-Cu-Cr (Ref. 12) systems. This is a significant development since it indicates that metastability is not an inherent property of quasicrystals.

There are three principal models of the structure of icosahedral materials. The icosahedral quasicrystal (IQ) model is based upon Penrose aperiodic lattices which can be obtained via projections from a regular lattice in a six-dimensional space.[13,14] The icosahedral glass (IG) model[15,16] assumes a dense but random arrangement of icosahedra. The IQ model predicts the existence of both long-range orientational and long-range quasiperiodic translational order, whereas the IG model predicts only long-range orientational order. Both models and their variations are in close agreement with experimental diffraction patterns, although recent experiments seem to favor the IQ model.[17] The third model proposed multitwinning of crystallites as a possible explanation of the icosahedral diffraction pattern.[18,19] However, recent studies demonstrate that this model is at variance with the experimental results.[17,20]

Although the symmetry of the diffraction patterns in icosahedral materials can be, in principle, explained by various structural models, the exact microscopic structure and the atomic positions remain unresolved. The question "where are the atoms in icosahedral materials?" posed by Bak[21] constitutes the next step in structural studies of these materials. The diffraction techniques are of limited value for determining the site environment of constituent elements in icosahedral materials. For example, the attempts to account for x-ray diffraction intensities for various atomic decorations of the prolate and oblate rhombohedra within a model of three-dimensional Penrose tiling fail to give even rough qualitative agreement with the experimental data.[22,23] Therefore, local probes such as nuclear magnetic resonance (NMR), Mössbauer spectroscopy (MS), or extended x-ray-absorption fine structure (EXAFS), when used with discretion, can provide useful complementary information on the local environment of individual atoms. We are concerned in this paper with the use of ^{57}Fe MS to study the local structural environment around Fe atoms in both thermodynamically stable and metastable phases of icosahedral $Al_{65}Cu_{20}Fe_{15}$ alloy.

The first ^{57}Fe MS experiment on an icosahedral alloy of the composition $Al_6(Mn_{0.85}Fe_{0.15})_{1.03}$ was performed by Swartzendruber *et al.*[24] Those authors fitted their spectra with two quadrupole doublets whose intensity ratio was *constrained* to the golden-mean value 1.618. A successful fit was interpreted in terms of two types of transition-metal sites. The justification of a two-doublet fit was based on the speculation that both the oblate and prolate rhombohedra in the model of three-dimensional Penrose tiling should have a unique decoration, with one Mn site in each rhombohedron. The conclusion of Swartzendruber *et al.*[24] of the duality of transition-metal sites is often cited in literature as an established fact,[25] and has been used as a justification of a two-site analysis with the EXAFS technique[26] (criticism of the EXAFS data analysis in terms of two Mn sites is presented in Ref. 27). Furthermore, a two-doublet analysis has been used in ^{57}Fe MS studies of other icosahedral[28-30] and decagonal[29,31] alloys, in spite of clear evidence based on the detailed analysis of the ^{57}Fe Mössbauer spectrum of icosahedral $Al_{86}(Mn_{0.98}Fe_{0.02})_{14}$ by Eibschutz *et al.*,[32] which demonstrated the superiority of a fit based on a distribution of sites. The incorrect assumption[24] of a unique decoration of oblate and prolate rhombohedra with one Mn site has been discussed by Henley.[2] Below we show that the two-doublet analysis of Mössbauer spectra of icosahedral[28–30] and decagonal[29,31] materials is methodologically incorrect, and consequently the conclusion of there being two distinct transition-metal sites[24,30] is false. The central point of this paper is that the ^{57}Fe MS studies of $Al_{65}Cu_{20}Fe_{15}$ and of other icosahedral systems[28–30] are consistent with a continuous distribution of transition-metal sites. It will be shown that this agrees with conclusions based on other experimental and theoretical studies.

II. EXPERIMENT

The $Al_{65}Cu_{20}Fe_{15}$ ingot was prepared by arc melting in an argon atmosphere of high-purity Al, Cu, and Fe. Rapidly quenched ribbons with cross section of about 0.02×1 mm^2 were obtained by induction melting of the ingot in a quartz tube and ejection of the melt through a 0.6-mm-diam orifice with about 50-kPa overpressure of argon. Melts impinged upon a circumferential surface of the copper wheel rotating with a tangential velocity of 30 m/s in a helium atmosphere. A portion of the same ingot was also used to produce a thermodynamically stable phase by vacuum annealing it at 1000 K for 48 h.

Sections of ribbons and of the pulverized annealed ingot were examined by x-ray diffraction using a Siemens D500 diffractometer with Cu $K\alpha$ radiation. The contribution to the spectra from the Cu $K\alpha_2$ radiation was subtracted. The thermal stability of the samples was studied by means of differential-thermal-analysis (DTA) measurements using a Fisher model 260F thermal analyzer. Measurements were performed under an argon atmosphere with a heating rate of 25 K/min. Room-temperature ^{57}Fe MS measurements were carried out using a Wissel MSII Mössbauer spectrometer. The spectrometer was calibrated with a 12.7-μm-thick Fe foil,[33] and the spectra were folded. The surface densities of the Mössbauer absorbers of the rapidly quenched ribbons and of the annealed ingot were, respectively, 1.5 and 1.9 mg Fe/cm^2.

III. RESULTS AND DISCUSSION

A. Analysis of DTA and x-ray diffraction data

DTA scans of both conventionally solidified and rapidly quenched $Al_{65}Cu_{20}Fe_{15}$ alloys between 300 and 1260 K exhibited only a single endothermic peak at 1143 K with a full width at half maximum of 8 K. The value 1143 K is in good agreement with the value 1135 K reported by Tsai *et al.*[11] Since no other peaks were observed, the 1143 K endothermic peak corresponds to the melting point of the alloy.

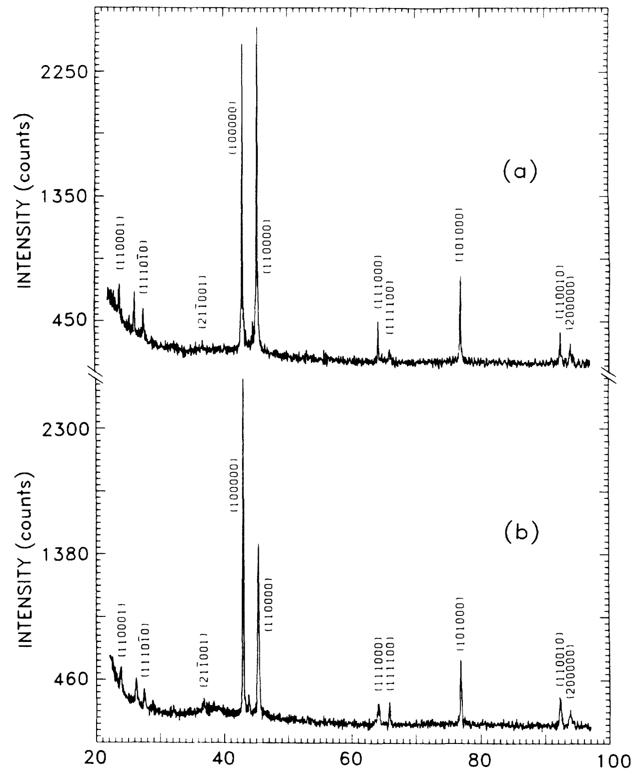

FIG. 1. X-ray diffraction patterns obtained with Cu $K\alpha_1$ radiation of $Al_{65}Cu_{20}Fe_{15}$ alloy annealed at 1000 K for (a) 48 h and (b) rapidly quenched.

The x-ray diffraction patterns of thermodynamically stable and rapidly quenched phases of $Al_{65}Cu_{20}Fe_{15}$ (Fig. 1) could be indexed to the icosahedral structure using the scheme of Bancel *et al.*[34] The patterns show a predominantly single icosahedral phase in both samples. Unidentified peaks at $q=1.850$ Å^{-1} [Fig. 1(a)] and $q=1.855$ Å^{-1} [Fig. 1(b)], we well as at $q=3.044$ Å^{-1} [Fig. 1(b)] suggest a small fraction of a second phase. The icosahedral peaks of the fully annealed alloy are slightly shifted towards larger q values as compared to the peaks of the rapidly quenched alloy. Consequently, the "lattice constant" a_R (the edge length of the rhombic dodecahedron cells that make up the three-dimensional Penrose tiling[14,35]) of the thermodynamically stable phase (4.452 Å) is smaller than a_R of the metastable phase (4.457 Å), which is what can be expected. The widths of icosahedral peaks of the thermodynamically stable phase are appreciably smaller than the widths of the metastable phase, as can be seen by inspection (Fig. 1). The same effect has been observed by Tsai *et al.*,[11] and is indicative of strain release in the thermodynamically stable phase of $Al_{65}Cu_{20}Fe_{15}$.

B. One- and two-site analysis

The ^{57}Fe Mössbauer spectrum of the thermodynamically stable phase of $Al_{65}Cu_{20}Fe_{15}$ is presented in Fig. 2. This spectrum has the largest line asymmetry [area ratio of two peaks $A_1/A_2=1.28(5)$] of all icosahedral materials measured so far. It has been claimed[28] that the ratio $A_1/A_2<1$ is characteristic for icosahedral materials. The spectrum in Fig. 2 shows that this claim is incorrect.

The Mössbauer technique is a powerful tool for studying crystallographically inequivalent sites in various materials.[36] This is based on the fact that the Mössbauer hyperfine parameters (isomer shift δ, quadrupole splitting Δ, and hyperfine magnetic field H_{hf}) have generally different values at different sites, giving rise to spectra

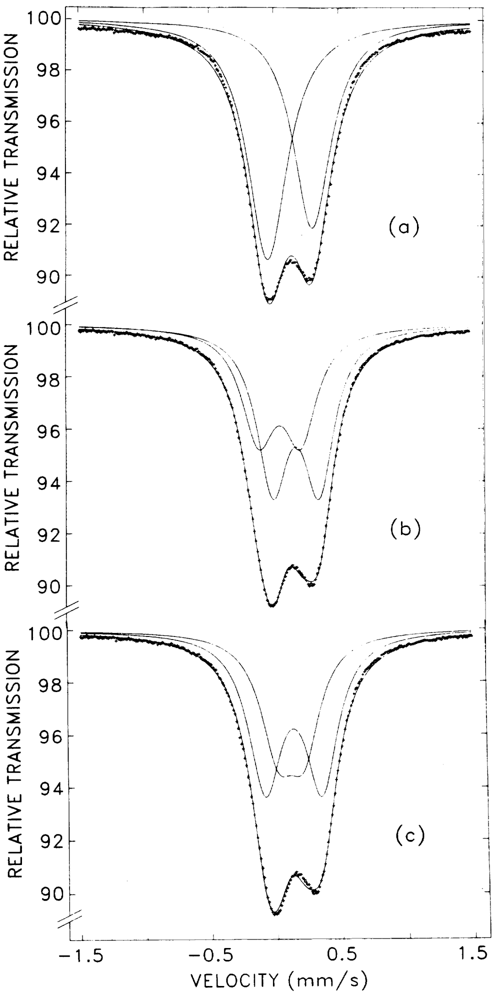

FIG. 2. ^{57}Fe Mössbauer spectrum of the thermodynamically stable $Al_{65}Cu_{20}Fe_{15}$ icosahedral phase. The solid line is a least-squares computer fit to an asymmetric doublet (a) and to two symmetric doublets [(b) and (c)], as described in the text. The component lines are also shown.

with clearly separated or slightly overlapping component patterns. For icosahedral materials, no dipole hyperfine magnetic interaction down to 4.2 K was observed[37,38] ($H_{hf}=0$). Therefore, the search for inequivalent sites is based upon analysis of the hyperfine parameters δ and Δ. Such an analysis is straightforward if the parameters δ and/or Δ differ significantly in inequivalent sites, which is the case, for example, in garnets[39] and in other inorganic materials.[36] The situation is much subtler when the doublets due to inequivalent sites overlap strongly,[40] as is the case for icosahedral materials. For both weak and strong doublet overlaps, one should consider not only the δ and Δ parameters corresponding to a given component doublet, but also the full linewidth at half maximum, Γ, of the two component lines. A failure to do so may result, as is demonstrated below, in good fits which have unphysically broad lines. Conclusions based on such fits, and parameters derived from them, may be meaningless.

The measured linewidth, Γ, can be expressed as $\Gamma=\Gamma_{\mathrm{nat}}+\Delta\Gamma$, where $\Gamma_{\mathrm{nat}}=0.194$ mm/s is the natural linewidth,[41] and $\Delta\Gamma$ is the Γ broadening, which can be caused by several effects. First, there can be a small source line broadening, which usually is smaller than 0.02 mm/s. Secondly, finite absorber thickness[36,41] contributes to the broadening. For example, for a 12.7-μm Fe foil the broadening of the inner lines of a Zeeman pattern is expected to be about 0.01 mm/s. It should be stressed that the Mössbauer absorbers used in this study were very thin (surface densities 1.5–1.9 mg Fe/cm^2), and therefore Γ broadening caused by absorber thickness effects is negligible. Thirdly, instrumental effects (nonideal drive system, vibrations, etc.) can cause a slight increase in Γ. For our experimental setup, the linewidth of the inner Zeeman lines of a 12.7-μm Fe foil absorber, corresponding to an absorber surface density of 10 mg Fe/cm^2, was 0.238(2) mm/s. Thus, for a typical Mössbauer spectrometer with absorbers of surface density smaller than 10 mg Fe/cm^2,[36] one can expect a value of Γ of around 0.24(2) mm/s. Other possible sources of broadening (diffusion effects, relaxation effects, interference effects, etc.[42]) do not occur in icosahedral materials.

A fit of the spectrum of the thermodynamically stable phase with an asymmetric doublet is shown in Fig. 2(a), and the parameters obtained from such a fit for both thermodynamically stable and metastable icosahedral phases are given in Table I. Such a one-site fit clearly fails, as is evidenced by the misfit in the wings of the spectrum [Fig. 2(a)], which gives rise to the high value of χ^2 (Table I), and by unphysically broad lines (Table I). The failure of the fit in Fig. 2(a) shows that Fe atoms occupy more than one crystallographic site. Sometimes a one-site fit is used to obtain isomer shift and quadrupole-splitting average values $\bar{\delta}$ and $\bar{\Delta}$.[28,43] As will be shown

TABLE I. Parameters determined from the fits of the thermodynamically stable (sample α) and metastable (sample β) $Al_{65}Cu_{20}Fe_{15}$ with the models *a*, *b*, and *c* which correspond, respectively, to Figs. 2(a), 2(b), and 2(c). δ_i [relative to the ^{57}Co(Rh) source] and Δ_i ($i=1,2$), $\bar{\delta}$, and $\bar{\Delta}$ are all given in mm/s. A_i ($i=1,2$) is the relative area of the *i*th line for the one-site model *a*, and the relative area of the *i*th doublet for two-site models *b* and *c* ($A_1+A_2=1$). χ^2 is defined as $[\sum_{i=1}^{k}(y_i^{\mathrm{expt}}-y_i^{\mathrm{theor}})^2/y_i^{\mathrm{expt}}]/(k-m)$, where k and m are, respectively, the number of experimental points and the number of fitted parameters.

Sample	Model	δ_1	δ_2	Δ_1	Δ_2	Γ_1	Γ_2	A_1	$\bar{\delta}$	$\bar{\Delta}$	m	χ^2
α	*a*	0.127(2)		0.344(2)		0.374(8)	0.353(8)	0.550(13)			7	15.39
β	*a*	0.140(2)		0.346(2)		0.375(8)	0.329(8)	0.562(10)			7	8.24
α	*b*	0.039(8)	0.164(5)	0.327(4)	0.359(2)	0.316(9)	0.293(8)	0.425(52)	0.111(17)	0.346(39)	9	3.91
β	*b*	0.058(10)	0.182(6)	0.347(3)	0.353(2)	0.307(11)	0.269(10)	0.482(70)	0.122(24)	0.350(51)	9	2.57
α	*c*	0.102(2)	0.124(1)	0.203(6)	0.440(6)	0.314(16)	0.308(5)	0.412(5)	0.115(3)	0.342(10)	9	7.15
β	*c*	0.124(2)	0.131(2)	0.202(33)	0.447(25)	0.263(45)	0.301(14)	0.367(154)	0.128(41)	0.357(128)	9	5.41

below, $\bar{\delta}$ and $\bar{\Delta}$ values so obtained have large relative errors (about 15% for the samples studied here), and are therefore not reliable.

Two-site analyses of Mössbauer spectra have been performed in the literature in two ways. Either two symmetric doublets with significantly different δ values and very similar Δ values have been used[30] [Fig. 2(b)], or two symmetric doublets with similar δ values and appreciably different Δ values were employed[28,29,31] [Fig. 2(c)]. The parameters obtained from such fits are given in Table I. The average values $\bar{\delta}$ and $\bar{\Delta}$ are calculated using δ_i and Δ_i $(i=1,2)$ values for the component doublets, with the relative areas of the doublets as their weighting factors. The fits with two symmetric doublets [Fig. 2(b) and 2(c)] are much better than the fit with one asymmetric doublet [Fig. 2(a)], as shown by a significant decrease of χ^2 (Table I). However, the linewidth of one of the doublets is significantly larger (Table I) than the expected value of 0.24(2) mm/s. The same observation can be made by analyzing the literature Γ values of two-site fits.[24,28-32] It has been argued[24] that the observed line broadening of component doublets can be caused by variations in the second- and third-near neighbor environments of a given Fe atom and by the presence of vacancies and other defects expected in rapidly quenched solids. These arguments are so general that, in principle, they may be even true. We believe they are not likely valid for the following reasons. Variations in second- and third-near neighbor environments, i.e., chemical disorder in a sample, occur also in many crystalline materials in which Fe atoms are replaced by other atoms. For example, in the garnet compound $Eu_3Sc_2Fe_3O_{12}$, whose cation distribution is[44] $\{Eu_3\}[Sc_{1.764}Fe_{0.236}](Sc_{0.236}Fe_{2.764})O_{12}$, where the curly braces, square brackets, and parentheses represent, respectively, dodecahedral, octahedral, and tetrahedral sites, a significant chemical disorder exists in both octahedral and tetrahedral sites. Nevertheless, the linewidths of *well separated* octahedral and tetrahedral doublets for a sample with surface density 5.8 mg Fe/cm^2 are narrow: 0.215(6) and 0.264(1) mm/s, respectively.[39] While vacancies and defects exist in rapidly quenched icosahedral materials, their number is expected to decrease in a thermodynamically stable icosahedral alloy. One would, therefore, expect larger Γ values for the rapidly quenched icosahedral phase as compared to the values for the thermodynamically stable phase. However, these values are the same, within an experimental error (Table I).

In principle, one could attempt to fit the Mössbauer spectra of iscosahedral materials with three or more component doublets. This, however, would be a futile exercise. The number of fitted parameters significantly increases with the number of component doublets, rendering such fits unreliable. More importantly, however, Mössbauer spectra of icosahedral materials are in the form of two smooth and broad quadrupole lines with no apparent structure, and a fit with a discrete number of doublets requires fixing many parameters to *a priori* chosen, but unknown, values, since otherwise a perfect fit with a few doublets would give unphysical values of these parameters.

In conclusion, Mössbauer spectra with strongly overlapping doublets, as observed in all icosahedral materials studied so far, cannot be resolved within the sensitivity of ^{57}Fe MS into discrete component doublets with physically acceptable linewidths. The unphysical line broadening obtained from two-doublet fits reflects the presence of a multiplicity of Fe sites in icosahedral materials. Consequently, the claim[24,30] of two distinct transition-metal sites in icosahedral materials is unfounded.

C. Analysis based upon a multiplicity of sites

The spectra of icosahedral materials[24,28-30,32,37] are very similar to the paramagnetic spectra of amorphous materials.[32,45-48] Therefore, one can expect that the Δ distribution in icosahedral materials can be approximated by a shell model originally introduced by Czjzek *et al.*[49] for amorphous materials. Indeed, Eibschutz *et al.*[32] demonstrated that this model very well describes the Mössbauer spectrum of $Al_{86}(Fe_{0.02}Mn_{0.98})_{14}$ icosahedral alloy. The important point is that the distribution function in this model $P(\Delta)=(\Delta^{n-1}/\sigma^n)\exp(-\Delta^2/2\sigma^2)$ is determined by only two parameters: n and σ. To account for a strong correlation between δ and Δ, as manifested by a strong asymmetry of the spectrum of $Al_{65}Cu_{20}Fe_{15}$, a quadratic relation $\delta=\delta_0+a\Delta+b\Delta^2$ has been assumed, where δ_0, a, and b are fitted parameters. Of course, it does not mean that the "true" δ-Δ correlation has a quadratic form. A quadratic correlation was chosen since it can better approximate the complex "true" correlation than the usually used linear correlation ($b=0$), as was shown for Fe-Ni-B amorphous alloys in Ref. 50. One linewidth parameter Γ was used in the fits. It should be emphasized that the total number of fitted parameter ($m=8$) of this model is smaller than the number for the two-site ($m=9$) model.

The spectrum of the thermodynamically stable icosahedral phase of $Al_{65}Cu_{20}Fe_{15}$ fitted with the shell model together with the $P(\Delta)$ distribution and the δ-Δ correlation are shown in Fig. 3. The parameters obtained from such fits for the thermodynamically stable and metastable phases are given in Table II. In spite of the smaller number of fitted parameters, the fits with the shell model are superior to the fits with the two-site model, as shown by the values of χ^2 (Tables I and II). Furthermore, the values of Γ obtained from the shell-model fits are in the physically acceptable range, as discussed in Sec. III B. We thus conclude that the distribution of Δ values in the studied icosahedral alloys indicates the existence of a continuous distribution of Fe sites, which is indicative of a high degree of atomic disorder. A striking feature of our results is the similarity between the Δ distributions in both thermodynamically stable and metastable phases of icosahedral $Al_{65}Cu_{20}Fe_{15}$ alloy (Table II). Thus, it seems that the observed disorder is an intrinsic property of icosahedral materials.

The $\bar{\delta}$ and $\bar{\Delta}$ values obtained from the shell-model fit (Table II) are in good agreement with the corresponding values obtained from the two-site model fit (model *b*, Table I). This is not surprising in view of the fact that the two-site model, although leading to unphysically

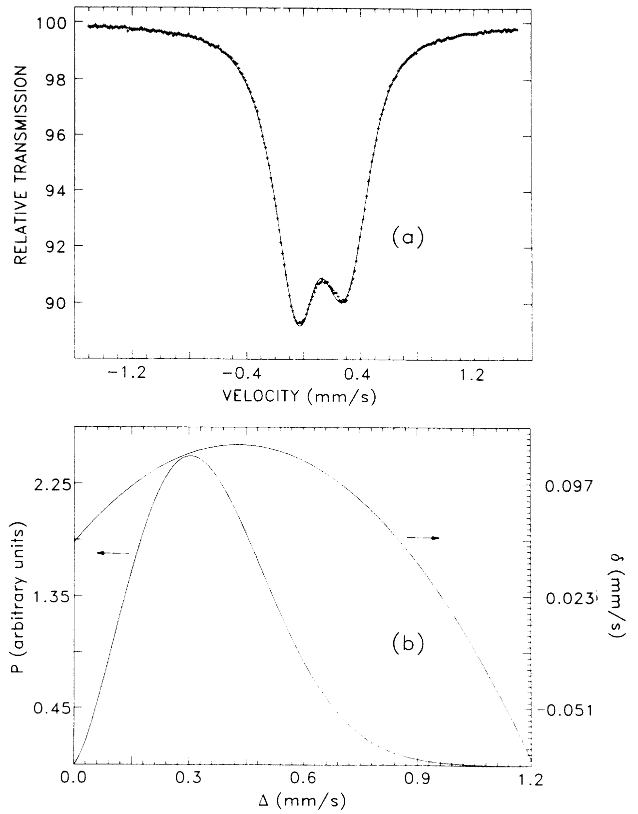

FIG. 3. (a) ^{57}Fe Mössbauer spectrum of the thermodynamically stable $Al_{65}Cu_{20}Fe_{15}$ icosahedral phase fitted (solid line) to a shell model. (b) The distribution function $P(\Delta)$ and the δ-Δ correlation obtained from the fit.

broad lines, nevertheless fits the experimental spectra well. In other words, although the δ and Δ values of each of the two component doublets separately are physically meaningless (Table I), their weighted averages are close to the correct average values. However, the average values of δ and Δ obtained from the one-site model (model *a*, Table I) are, respectively, overestimated and underestimated.

The data in Table II show that within the experimental error the $\overline{\Delta}$ values are the same for thermodynamically stable and metastable samples, whereas the $\overline{\delta}$ value for the former is smaller than the $\overline{\delta}$ value for the latter. The difference in the $\overline{\delta}$ values for these two samples can be correlated with the difference in the values of their lattice constant a_R (Sec. III A). The decrease of a_R for the thermodynamically stable sample means a decrease of the effective volume associated with the lattice "unit cells." Since isomer shift is known to decrease with a decrease in volume for both crystalline[51] and amorphous[52,53] alloys, one would expect a smaller $\overline{\delta}$ value for the thermodynamically stable sample as compared to the $\overline{\delta}$ value of the metastable one, as is observed here (Table II).

D. Duality versus multiplicity of transition-metal sites in icosahedral materials

The main conclusion of this paper is that the continuous distribution of quadrupole splittings in both thermodynamically stable and metastable phases of the novel icosahedral alloy $Al_{65}Cu_{20}Fe_{15}$ is indicative of the continuous distribution of Fe sites, and that the claim of two distinct sites[24,30] is unfounded. Our conclusion of a multiplicity of sites agrees with the inference based on another ^{57}Fe MS study[32] of the icosahedral alloy $Al_{86}(Fe_{0.02}Mn_{0.98})_{14}$. It also finds support in the results of several ^{55}Mn and ^{27}Al NMR studies[54–57] of Al-Mn-based icosahedral materials. These studies clearly show a broad distribution of electric field gradients, consistent with a continuous distribution of sites, and find no evidence for a small number of distinct sites.

Multiplicity of sites of transition-metal atoms in icosahedral materials means a distribution of local environments around these atoms, i.e., the presence of a significant disorder similar to the one inherent in amorphous materials. One could then expect that there may be some similarity between icosahedral and amorphous systems. Such a similarity seems to be shown by the similarities in the ^{57}Fe Mössbauer spectra discussed above and in Ref. 32, in magnetic behavior,[58] or in the calculated structure of the density of states.[59]

The continuous distribution of local environments around Fe atoms found in this study cannot be due mainly to the presence of quenched strains because the $P(\Delta)$ distribution is practically the same for both thermodynamically metastable and stable phases, in spite of the fact that there is much less strain in the latter than in the former, as shown by the widths of the x-ray diffraction lines. Such a distribution appears to be an intrinsic property of icosahedral materials. This seems to be confirmed by high-resolution x-ray studies[60] on large grains of thermodynamically stable icosahedral Al_6Li_3Cu alloy which clearly demonstrate a high degree of atomic disorder.

The existence of the icosahedral alloy $Al_{65}Cu_{20}Fe_{15}$ in a thermodynamically stable phase shows that the IG model, for which metastability is an inherent feature, cannot be used as a structural model of this alloy. It seems that the structure of this alloy can be thought of in terms of the distorted (in Bak's sense[21]) IQ model. Bak[21] asserts

TABLE II. Parameters determined from the shell-model fit. The meaning of the symbols α, β, χ^2, $\overline{\delta}$, $\overline{\Delta}$, and m is the same as in Table I. Other symbols are described in the text. The parameters σ, Γ, δ_0, $\overline{\delta}$, and $\overline{\Delta}$ are in units of mm/s. The units of a and b are, respectively, $(mm/s)^{-1}$ and $(mm/s)^{-2}$.

Sample	n	σ	Γ	δ_0	a	b	$\overline{\delta}$	$\overline{\Delta}$	m	χ^2
α	2.417(2)	0.256(2)	0.247(1)	0.058(1)	0.298(8)	−0.347(10)	0.111(1)	0.359(3)	8	2.70
β	2.299(46)	0.267(4)	0.234(3)	0.087(2)	0.230(12)	−0.296(17)	0.122(2)	0.364(4)	8	1.95

that the frustration in icosahedral crystals, caused by the inability of the "natural" unit cell to fill space, leads to the unit cell adjusting to the local environment by distorting it. This distortion can then lead to multiplicity of sites, as observed in this study.

Zero-field Mössbauer spectra indicate the high degree of disorder in icosahedral materials, but one cannot distinguish on the basis of these spectra alone specific arrangements of atoms. This can be done only by combining MS experiments performed in high (≥ 100 kOe) external magnetic fields (in order to obtain additional information of the predominant sign of the electric-field-gradient distribution) with theoretical calculations of the electric field gradients for specific IQ models, and with the results from other structure sensitive techniques.

IV. SUMMARY

Room-temperature ^{57}Fe Mössbauer spectra of a novel icosahedral alloy $Al_{65}Cu_{20}Fe_{15}$, which can be produced in both thermodynamically stable and metastable phases, show a continuous distribution of quadrupole-splitting magnitudes in both phases. This indicates the presence of a multiplicity of Fe sites which seems to be an intrinsic property of icosahedral materials. Critical review of an analysis of Mössbauer spectra of icosahedral materials with one- and two-site models, together with other published experimental studies, shows that the claim of the presence of two distinct transition-metal sites is unjustified. It is suggested that the structure of $Al_{65}Cu_{20}Fe_{15}$ can be thought of in terms of the distorted-icosahedral quasicrystal model rather than in terms of the icosahedral glass model.

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