Magnetic properties of icosahedral alloys: The case of Al$_{65}$Cu$_{20}$Fe$_{15}$

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Various magnetic properties of a novel, thermodynamically stable, icosahedral alloy Al$_{65}$Cu$_{20}$Fe$_{15}$, have been studied at low temperatures with ^{57}Fe Mössbauer spectroscopy and ac susceptibility. It is found that Fe atoms bear no magnetic moment down to 1.5 K. The presence of a multiplicity of Fe sites in this alloy is demonstrated. It is argued that this reflects the intrinsic disorder in this system. The analysis of Mössbauer spectra of icosahedral alloys used in the literature in terms of two doublets or singlets with unphysically broad lines is shown to be incorrect, and consequently the assertion based on such analysis of there being two distinct transition-metal sites is unfounded. A critical review of published experimental data on the magnetic properties of icosahedral alloys has been performed. Arguments are presented which indicate that the presence or absence of local magnetic moments on transition metals in icosahedral alloys results from the intrinsic disorder rather than from icosahedral symmetry.

I. INTRODUCTION

There has been increasing interest in recent years in the properties of icosahedral quasicrystals.[1] Although much of the published work has been aimed at understanding the structure of these complex materials, this still remains something of an open question. One of the basic problems that needs to be answered is whether icosahedral symmetry induces any special and distinctive features in the physical properties of quasicrystals. Furthermore, since quasicrystals may be regarded as materials situated between regular crystals and completely disordered systems, their fundamental physical properties are expected to exhibit exotic features found neither in crystalline nor in amorphous materials.

While electronic-structure calculations performed for one-dimensional[2] and two-dimensional[3,4] Penrose lattices indeed indicate some special features, for the more realistic three-dimensional case conflicting predictions have appeared. Smith and Ashcroft[5] conclude that there are special features in the density of states (DOS), while Marcus[4] suggests that the DOS is relatively featureless, similar to that expected in amorphous alloys. Also, electronic-structure calculations performed for icosahedral Al and Al-Mn clusters suggest distinctive DOS features resulting directly from local icosahedral symmetry.[6−8] However, such calculations performed for Co icosahedral clusters[9] showed no peculiarities of the DOS which could be directly related to icosahedral symmetry. Thus, with few exceptions,[4,9] most theoretical approaches conclude that there are unique features in the electronic structure induced by icosahedral symmetry, and consequently in the physical properties which depend on the electronic structure.

A majority of experimental studies infer a close simi-

larity between icosahedral and either amorphous or crystalline alloys. Specifically, local probes such as NMR (Refs. 10 and 11) and Mössbauer spectroscopy (MS) (Refs. 12 and 13) clearly demonstrate the existence of a broad distribution of local environments in icosahedral alloys, reminiscent of the distribution in amorphous alloys. Similarly, measurements of the specific heat,[14−16] thermal conductivity,[17] and inelastic neutron scattering[18] have been interpreted as indicating comparable properties in icosahedral and amorphous materials. By contrast, results based on electron-energy-loss spectroscopy (EELS),[18] specific heat,[19,20] sound velocity,[21] and soft-x-ray emission[20] indicate similarities between icosahedral materials and crystalline ones. The only strong experimental argument for the presence of physical properties unique to icosahedral symmetry, which is substantiated theoretically,[5] is based on the plasmon line broadening observed in the EELS spectra of icosahedral Al-Mn alloys.[22]

The possible influence of icosahedral symmetry on the physical properties of quasicrystals has been intensively studied by investigating their magnetic behavior. Table I presents a compilation of such data for several series of icosahedral alloys as well as for some decagonal, crystalline, and amorphous alloys of composition close to the composition of icosahedral alloys. Fits of data on the temperature-dependent susceptibility to a Curie-Weiss law, $\chi = \chi_0 + C/(T - \Theta)$, yielded estimates for the temperature-independent susceptibility χ_0, the paramagnetic Curie temperature Θ, and the effective magnetic moment μ_{eff} (from the Curie constant C). Several characteristics are evident from Table I. For alloys containing U, μ_{eff} is similar for icosahedral, amorphous, and crystalline structures,[23] while spin-glass behavior has been observed in icosahedral and amorphous alloys.[24] In the ex-

TABLE I. Magnetic parameters for icosahedral (i) and decagonal (d) quasicrystals and amorphous (a) and crystalline (c) alloys derived from the susceptibility fits to the Curie-Weiss law $\chi = \chi_0 + C/(T - \Theta)$. T_{SG} is the spin-glass temperature as determined from the position of the peak in the $\chi(T)$ dependence. μ_{eff} is per U atom for U-containing alloys and unless indicated otherwise per Mn atom for Mn-containing alloys.

Comp.	μ_{eff} (μ_B)	$-\Theta$ (K)	χ_0 10^{-6} emu/g	T_{SG} (K)	Ref.
i-Pd$_{60}$U$_{20}$Si$_{20}$	2.31	10	1.88		23
i-Pd$_{58.8}$U$_{20.6}$Si$_{20.6}$		13.5		~5.5[a]	24
a-Pd$_{60}$U$_{20}$Si$_{20}$	2.29	7	8.20		23
a-Pd$_{58.8}$U$_{20.6}$Si$_{20.6}$		11.3		~4.3[a]	24
c-Pd$_3$U	~2.63		~6.32		23
i-Al$_{86}$Mn$_{14}$	0.5[b]	8.7			25
i-Al$_{86}$Mn$_{14}$	0.51[b]		4	1.1[a]	26,27
i-Al$_{86}$Mn$_{14}$	0.50(5)[a]	0	4.0(1)	1.0[a]	28
c-Al$_{86}$Mn$_{14}$	0[b]				25
c-Al$_{86}$Mn$_{14}$	0.20(5)[a]	0	1.0(2)		28
i-Al$_{85.7}$Mn$_{14.3}$	0.747[b]	4.77	7.42		29
i-Al$_{85.7}$Mn$_{14.3}$	0.56[a]	2.5			30
i-Al$_{85.7}$Mn$_{14.3}$	0.56[a]	1.6	0.252		31
c-Al$_{86.7}$Mn$_{14.3}$	0[b]				29
c-Al$_{85.7}$Mn$_{14.3}$	0.28[a]	6.3			30
c-Al$_6$Mn	0[b]				32
a-Al$_{85}$Mn$_{15}$	0.22(5)[b]	0.9(1)			16
i-Al$_{84}$Mn$_{16}$	0.62[b]	5			25
i-Al$_{84}$Mn$_{16}$	0.75[a]	4		<1.0[a]	25
i-Al$_{82.5}$Mn$_{17.5}$	0.79[a]	2.8	0.778		31
i-Al$_{82}$Mn$_{18}$	0.75[b]	5			25
i-Al$_{82}$Mn$_{18}$	0.97[a]	4		1.5[a]	25
i-Al$_{81.5}$Mn$_{18.5}$	0.91[a]	5.1	0.032		31
i-Al$_{80}$Mn$_{20}$	1.06[b]	4			25
i-Al$_{80}$Mn$_{20}$	1.12[a]	1		3[a]	25
i-Al$_{80}$Mn$_{20}$	1.27[b]	5.92	9.82		29
i-Al$_{80}$Mn$_{20}$	1.16(1)[b]	3.90(5)	9.98		33
i-Al$_{80}$Mn$_{20}$	1.12[b]	1.4	1.43		34
i-Al$_{80}$Mn$_{20}$	1.18[a]	4.5	0.203	3.3[a]	31
c-Al$_{80}$Mn$_{20}$	0.617[b]	3.76	45.44		29
c-Al$_{80}$Mn$_{20}$	0				33
i-Al$_{78.5}$Mn$_{21.5}$	1.45[a]	8.1	1.1	4[a]	31
d-Al$_{78}$Mn$_{22}$	1.64[b]	1.5	1.5	7.8[b]	35
i-Al$_{77.5}$Mn$_{22.5}$	1.53[b]	5.0	18.2	8.5[a]	30,31
c-Al$_{77.5}$Mn$_{22.5}$	0.72[a]	6.6	6.21		30
i-Al$_{78}$Mn$_{16}$Si$_6$	1.00[a]	4.5		2.5[a]	25
i-Al$_{77}$Mn$_{20}$Si$_3$	1.28[a]	3.0		3.5[a]	25
i-Al$_{75}$Mn$_{20}$Si$_5$	1.0[a]		46(3)	4.7[a]	26,27
i-Al$_{75}$Mn$_{20}$Si$_5$	1.3(1)[a]	4	35(5)	4.7[a]	28
i-Al$_{74}$Mn$_{20}$Si$_6$	1.27[b]	3.6	1.98	~4.0[b]	36
i-Al$_{74}$Mn$_{20}$Si$_6$	1.28[b]	3.8	4.1		37
i-Al$_{74}$Mn$_{20}$Si$_6$	1.13[b]	9	2.4		38
c-Al$_{75}$Mn$_{20}$Si$_5$	0.20(5)[a]	0	10(1)		28
c-Al$_{74}$Mn$_{20}$Si$_6$	0.63[b]	3.5	2.41		7,36
i-Al$_{73}$Mn$_{21}$Si$_6$	1.25(10)[a]	2.5(5)		5.2(1)[a]	39
i-Al$_{73}$Mn$_{21}$Si$_6$	1.23(3)[b]	5(1)			39
i-Al$_{72}$Mn$_{22}$Si$_6$	1.55[a]	11		3.5[a]	25
i-Al$_{72}$Mn$_{22}$Si$_6$	1.17[b]	10			25
i-Al$_{72}$Mn$_{22}$Si$_6$	1.45	16.8	2.97		40
i-Al$_{72}$Mn$_{22}$Si$_6$	1.27[b]	3.6	1.98		7
a-Al$_{72}$Mn$_{22}$Si$_6$	1.41[a]	2.3		6[a]	25
i-Al$_{74}$Mn$_{12.5}$Fe$_{7.5}$Si$_6$	1.32[b,c]	12	0.9		41
i-Al$_{74}$Mn$_{13}$Fe$_7$Si$_6$	1.33[b,c]	10	0.5		41

TABLE I. (Continued).

Comp.	μ_{eff} (μ_B)	$-\Theta$ (K)	χ_0 10^{-6} emu/g	T_{SG} (K)	Ref.
i-Al$_{74}$Mn$_{15}$Fe$_5$Si$_6$	1.27^{b,c}	10	0.7	~4.2^b	41
i-Al$_{72}$Mn$_{16.5}$Fe$_{5.5}$Si$_6$	1.50^c	12.6	0.91		40
i-Al$_{74}$Mn$_{17.5}$Fe$_{2.5}$Si$_6$	1.30^{b,c}	10	0.6		41
i-Al$_{74}$Mn$_{19.98}$Fe$_{0.02}$Si$_6$	1.36^{b,c}	13	0.9		41
i-Al$_{72}$Mn$_{21.78}$Fe$_{0.22}$Si$_6$	1.45^c	14.1	2.76		40
i-Al$_{74}$Mn$_8$V$_{12}$Si$_6$	0.21^{b,c}	3	1.0		38
i-Al$_{74}$Mn$_{12}$V$_8$Si$_6$	0.32^{b,c}	6	1.1		38
i-Al$_{74}$Mn$_{14}$V$_6$Si$_6$	0.47^{b,c}	6	1.2		38
i-Al$_{74}$Mn$_{16}$V$_4$Si$_6$	0.67^{b,c}	5	1.2		38
i-Al$_{74}$Mn$_{18}$V$_2$Si$_6$	0.91^{b,c}	7	1.7		38
i-Al$_{74}$Cr$_{20}$Si$_6$	0^b				37
i-Al$_{74}$Mn$_3$Cr$_{17}$Si$_6$	0.40^b	1.3	0.37		37
i-Al$_{74}$Mn$_6$Cr$_{14}$Si$_6$	0.45^b	0.5	0.69		37
i-Al$_{74}$Mn$_{10}$Cr$_{10}$Si$_6$	0.65^b	2.5	0.4		37
i-Al$_{74}$Mn$_{15}$Cr$_5$Si$_6$	0.89^b	3.2	0.7		37
i-Ti$_{56}$Ni$_{28}$Si$_{16}$	0.078^{b,d}	3.5	1.5		42
i-Ti$_{56}$Ni$_{18}$Fe$_{10}$Si$_{16}$	0.144^{b,e}	2.4	14.2		42
i-Ti$_{56}$Ni$_{13}$Fe$_{15}$Si$_{16}$	0.224^{b,e}	7.9	14.4		42

$^a\chi_{ac}$ data.
$^b\chi_{dc}$ data.
$^c\mu_{\text{eff}}$ per transition metal.
$^d\mu_{\text{eff}}$ per Ni atom.
$^e\mu_{\text{eff}}$ per Fe atom.

tensively studied Al-Mn system, the most striking feature is the nonzero value of μ_{eff}, which increases with Mn concentration for icosahedral alloys, as opposed to zero or much reduced μ_{eff} values for crystalline or crystallized alloys of similar compositions. Single measurements for amorphous[16] and decagonal[35] Al-Mn alloys indicate smaller and similar values of μ_{eff}, respectively, in comparison to the μ_{eff} values of corresponding icosahedral alloys. Icosahedral Al-Mn alloys, in contrast to crystalline or crystallized ones, exhibit spin-glass behavior, and their spin-glass transition temperatures, T_{SG} seem to increase with Mn concentration. The values of Θ and χ_0 show rather large scatter for alloys of similar compositions, which may be connected with different sample preparation techniques, although the negative sign usually found for Θ indicates predominantly antiferromagnetic Mn-Mn exchange interaction. Essentially similar characteristics are observed for Al-Mn-Si alloys. A comparison between icosahedral and amorphous Al$_{72}$Mn$_{22}$Si$_6$ alloys shows that they have similar values of μ_{eff}. Such similarities between icosahedral and amorphous Al-Mn and Al-Mn-Si alloys have been interpreted[10] as evidence of the inherent disorder present in icosahedral alloys. Thus, the appearance of the local magnetic moment at Mn sites in icosahedral alloys may result from the intrinsic disorder present in these alloys and not from their icosahedral symmetry.

Soon after the discovery of a local magnetic moment associated with Mn atoms in Al-Mn and Al-Mn-Si

icosahedral alloys,[25] it was suggested by Warren et al.[10] that the moment is carried by some subset of the Mn atoms, so that there is a fraction of Mn atoms which do not contribute to the bulk paramagnetism. This suggestion was based on the observation of a decrease in the intensity of the ^{55}Mn NMR line with an increase in μ_{eff} for icosahedral alloys, and the observation of the same line position in both quasicrystal and nonmagnetic crystalline phases. Warren et al.[10] argued that the observed ^{55}Mn NMR line is due to nonmagnetic Mn atoms alone. The notion of two classes of Mn atoms distinguished by the possession or absence of a local magnetic moment was further developed by Edagawa et al.[40] and Eibschütz et al.,[41] who performed susceptibility and in-field ^{57}Fe MS measurements on Al-Mn-Si icosahedral alloys in which a fraction of Mn atoms was substituted by Fe atoms. These authors found that this substitution left the value of μ_{eff} per transition metal (TM) (i.e., per Mn and Fe) virtually unchanged. This is contrary to what is expected if all Mn atoms carry a magnetic moment. Furthermore, the hyperfine magnetic field, H_{hf} (determined from the ^{57}Fe Mössbauer spectra in an external magnetic field H_{ext}) turned out to be equal to H_{ext}. This can happen only for Fe atoms with no local magnetic moment. It was thus concluded[40,41] that Fe atoms substitute for only one class of Mn atoms—the class with zero moment. In a subsequent study, Eibschütz et al.[38] performed susceptibility measurements on Al$_{74}$Mn$_{20-x}$V$_x$Si$_6$ ($0 \leq x \leq 12$) icosahedral alloys; from the decrease of μ_{eff} per TM (see

Table I) it was concluded that V atoms preferentially substitute at the magnetic Mn sites and that the fraction of magnetic Mn atoms is about 60%. The idea of magnetic and nonmagnetic Mn atoms present simultaneously in icosahedral alloys also seems to be supported by a combination of susceptibility and high-field magnetization measurements.[39,43] The latter showed that the saturation magnetization extrapolated from high-field data is much smaller than the μ_{eff} values obtained from the fits of the $\chi(T)$ data, which was interpreted as evidence for the presence of two classes of Mn atoms. However, the estimate of the fraction of magnetic Mn atoms [12–25 % for $\text{Al}_{73}\text{Mn}_{21}\text{Si}_6$ (Ref. 39) and 0.9–3.6% for Al-Mn icosahedral alloys[43]] is much smaller than that found by Eibschütz et al.[38] Specific-heat data have also been interpreted as indicating that only a few percent of Mn atoms are magnetic.[16,26–28]

Apart from these significant discrepancies in estimating the fraction of magnetic Mn atoms, there are experimental arguments which question the validity of the duality model itself, and more importantly, the existence of a localized moment on Mn atoms belonging to icosahedral alloys containing Mn. As mentioned above, the idea of two classes of Mn atoms introduced by Warren et al.[10] was based on a correlation between the decrease of the ^{55}Mn NMR line intensity and the increase of susceptibility, from which it was concluded that the observed ^{55}Mn NMR signal is due solely to nonmagnetic atoms. However, Bennett et al.[44] showed that for nonmagnetic crystalline Al_4Mn there is no observable ^{55}Mn NMR line, contrary to what might be expected from the correlation mentioned previously. Furthermore, the argument that Fe atoms substitute exclusively for nonmagnetic Mn atoms[40,41] and that V atoms substitute exclusively for magnetic atoms,[38] although not impossible, seems, nevertheless, very unusual. There are no examples of crystalline or amorphous alloys in which such a preferential substitution takes place. The argument which questions the idea of a local magnetic moment associated with Mn atoms belonging to the icosahedral Al-Mn structure is based on the observation of the quadratic dependence of μ_{eff} on the Mn concentration.[25] Such a quadratic dependence is closely followed for μ_{eff} data in $\text{Al}_{74}\text{Cr}_{20-x}\text{Mn}_x\text{Si}_6$ icosahedral alloys,[37] for which it has been speculated[37] that the $\mu_{\text{eff}}-x$ dependence can be fitted assuming the presence of only magnetic Mn atoms of two types, with moments of $0.43\mu_B$ and $1.76\mu_B$. Such a quadratic dependence may be caused by clustering of Mn atoms, and thus might not reflect an intrinsic property of icosahedral alloys. The possibility of Mn clustering is indirectly supported by the interpretation of high-field magnetization measurements on icosahedral $\text{Al}_{80}\text{Mn}_{20}$ (Ref. 34) and decagonal $\text{Al}_{78}\text{Mn}_{22}$.[35] From fits of the magnetization curves to the Brillouin function, it was concluded that large-moment clusters are present [with moments of $11\mu_B$ for approximately every 100 Mn atoms in $\text{Al}_{80}\text{Mn}_{20}$ (Ref. 34) and of $25.6\mu_B$ for approximately every 240 Mn atoms in $\text{Al}_{78}\text{Mn}_{22}$ (Ref. 35)]. The observed $\chi(T)$ dependence in Mn-containing icosahedral alloys may also be connected with the presence of a small amount of another magnetic phase or with the presence of a magnetic "interface phase,"[44] not seen in the x-ray-diffraction spectra.

To further elucidate the problem of magnetic properties of icosahedral alloys, we present results of low-temperature susceptibility and ^{57}Fe MS measurements on a novel icosahedral alloy, $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$. This alloy, as opposed to most icosahedral alloys so far studied, is thermodynamically stable, i.e., it exhibits an endothermic peak alone in a differential-thermal-analysis spectrum corresponding to fusion, and can be produced in the same way that stable crystalline alloys are produced. More importantly, it contains a significant amount of Fe, so one might expect the occurrence of enhanced paramagnetism. Furthermore, since Fe atoms are an integral part of this alloy, ^{57}Fe MS measurements can be performed directly on the sample, thus avoiding uncertainties connected with Fe substitution for TM atoms in icosahedral alloys containing TM atoms other than Fe. If there are two classes of Fe atoms in this alloy, as has been suggested for Mn-containing icosahedral alloys, this should be seen clearly in low-temperature ^{57}Fe Mössbauer spectra.

II. EXPERIMENT

An alloy of $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ was prepared by arc melting in an argon atmosphere of high-purity Al, Cu, and Fe. It was vacuum annealed at 1000 K for 48 h.

The alloy was examined by x-ray diffraction using a Siemens D500 diffractometer with Cu $K\alpha$ radiation. ^{57}Fe MS measurements were performed at 4.2 K using a Wissel MSII Mössbauer spectrometer. The spectrometer was calibrated with a 12.7-μm-thick Fe foil,[45] and the spectra were folded. The Mössbauer absorber used was the same as the one used previously for room-temperature Mössbauer studies [the surface density of the absorber was 1.9 (mg Fe)/cm^2].[13] The susceptibility measurements were made on a 0.2-g parallelopiped of the alloy using a phase-locked susceptometer operating at 2.4 kHz with a driving field of 50 mOe rms. The temperature range covered was 1.5–77 K. Throughout the course of these measurements, the sample was suspended in a bundle of fine copper wires in the tail section of a glass Dewar system, around which the susceptometer sensing coil was suspended. The copper wires supporting the sample were soldered at their upper end to a cone-shaped copper block onto which a heater was wound. The latter enabled warming rates of about 0.2 K/min to be achieved between 4.2 and 77 K, temperatures being measured with either a calibrated Ge thermometer (Cryocal Inc. CR2500H), or (about 25 K) a AuFe-versus-Chromel thermocouple placed in good thermal contact with the sample. While this technique is well suited to investigate various types of magnetic order in disordered systems (as might be expected in a sample with substantial Fe content), it is not an ideal method for measuring the response of weakly magnetic alloys (as discussed below).

III. RESULTS AND DISCUSSION

A. X-ray-diffraction and ^{57}Fe Mössbauer data

The lines of the x-ray-diffraction pattern could be indexed[13] to the icosahedral structure, whose "lattice constant" a_R (the edge length of the rhombic dodecahedron cells that make up the three-dimensional Penrose tiling[46]) is 4.452 Å, which is in excellent agreement with the value given by Tsai *et al.*[47]

In order to detect a Zeeman pattern due to possible magnetic Fe atoms, the ^{57}Fe Mössbauer spectrum was measured at 4.2 K in a large velocity range (Fig. 1). As this figure clearly demonstrates, a Zeeman pattern is not present. This proves that at 4.2 K and above all Fe atoms in icosahedral $Al_{65}Cu_{20}Fe_{15}$ are nonmagnetic. The two asymmetric lines (Fig. 1) are due to the electric-quadrupole interaction; these will be discussed later in this section.

B. Susceptibility data

To look for possible magnetic ordering in $Al_{65}Cu_{20}Fe_{15}$ at lower temperatures, ac-susceptibility measurements were carried out from 1.5 to 77 K. Over this temperature interval the sample exhibited a weak magnetic response, a behavior which the susceptometer is not ideally suited to evaluate accurately. Specifically, the specimen modified the background signal from the susceptometer (arising predominantly from the copper wires used to suspend the sample) by less than 10%. Nevertheless, we can state that this icosahedral sample is diamagnetic, but with a susceptibility less than -2×10^{-5} emu/g. No significant changes in the sample's susceptibility were detectable below 77 K (within the admittedly substantial experimental uncertainty for such a weakly magnetic system). We thus conclude that Fe atoms in icosahedral $Al_{65}Cu_{20}Fe_{15}$ do not carry a magnetic moment, at least above 1.5 K. This is an important result since it shows that an icosahedral alloy with a significant amount of Fe atoms is nonmagnetic, contrary to what is observed for icosahedral alloys with a similar concentration of Mn atoms.

C. Magnetic moments and disorder in icosahedral alloys

The formation of a magnetic moment on Mn atoms in icosahedral alloys and the presence of two classes of Mn atoms in particular, has been discussed qualitatively in the literature[38] using arguments based on theories describing magnetic behavior of diluted alloys, i.e., the systems of $3d$ TM impurities in simple metals. Even here though it should be remembered that Mn in Al is closer to the Hartree-Fock criterion for establishing a local moment than Fe. However, since the Mn content in icosahedral alloys is at least 14 at. % (Table I), it seems more appropriate to discuss their magnetism using arguments based on theories for concentrated alloys. It is known from calculations using first-principles total-energy band theory that transition metals,[48] and most probably their alloys as well, favor a magnetic state at large volumes (where there are peaks in the DOS) and a nonmagnetic state at low volumes (where the DOS is smeared in energy). Thus, one can expect that a site may or may not carry a magnetic moment, depending on the volume associated with a given atom in an alloy, which is directly related to a typical length in a crystal structure (e.g., the Wigner-Seitz radius or the lattice constant a_R characteristic for icosahedral alloys). If one accepts the structural model for Al-Mn-Si icosahedral alloys put forward by Eibschütz *et al.*[41] which suggests two classes of Mn atoms (those in large and those in small Al "cages"), then indeed these two classes could be characterized by the presence and absence of a local magnetic moment, respectively. However, there is presently no direct, unambiguous, structural proof of the presence of two such distinct Al cages.

The two classes of Mn atoms, however, do not necessarily imply the existence of two unique structural environments. As indicated in Sec. I, many physical properties of icosahedral alloys have characteristics very similar to those of amorphous alloys. This indicates that the disorder is an intrinsic property of icosahedral systems. Such a view of icosahedral alloys is also supported by theoretical work[49] which showed that the presence of continuously varying "unit cells" is possible in these alloys, leading to the presence of a continuous distribution of interatomic distances. Since magnetic interactions depend crucially on interatomic distances,[48] the distribution of the latter may lead to the occurrence of both magnetic and nonmagnetic atoms simultaneously in a given icosahedral system, as seems to be the case for Mn atoms in Al-Mn and Al-Mn-Si icosahedral alloys. Thus, one does not need to invoke the presence of two specific Al cages to explain the occurrence of magnetic and nonmagnetic atoms. The latter would result from the presence of intrinsic disorder. Such a situation could also be interpreted as evidence against the distinct influence of local symmetry on magnetism in icosahedral alloys.
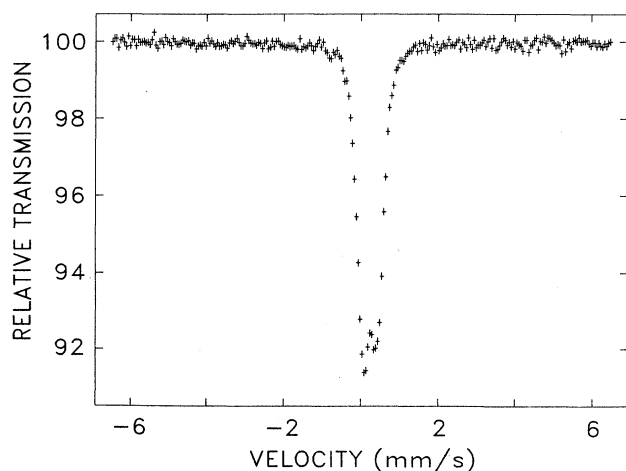

FIG. 1. ^{57}Fe Mössbauer spectrum of icosahedral $Al_{65}Cu_{20}Fe_{15}$ at 4.2 K. The velocity scale is relative to the ^{57}Co(Rh) source.

The above discussion, based on first-principles-theory calculations[48] indicates that the presence or lack of magnetism is a consequence of the distribution of interatomic distances, which results from disorder intrinsic to icosahedral alloys. There have also been theoretical studies, based on cluster calculations, which claim that the Mn magnetic moment is induced by the icosahedral symmetry alone.[7,8] Apart from the approximations inherent in cluster calculations, they were performed for icosahedral Al-Mn clusters in which Mn atoms were assumed to be at their centers. Such an assumption is at variance with experimental structural studies,[50] which indicate that TM atoms are situated at the *vertices* of icosahedra. It is not clear therefore how relevant such calculations are for real icosahedral systems.

D. Analysis of ^{57}Fe Mössbauer data

In order to check whether there is any structure in the shape of the ^{57}Fe Mössbauer spectrum of $Al_{65}Cu_{20}Fe_{15}$ at 4.2 K, it was remeasured for a smaller velocity range [Fig. 2(a)]. Analysis of the shape of ^{57}Fe Mössbauer spectrum is certainly useful since it may reveal the presence or absence of distinct structural environments around Fe atoms, and is thus relevant for discussions of magnetism in icosahedral alloys. In our previous study[13] of structur-
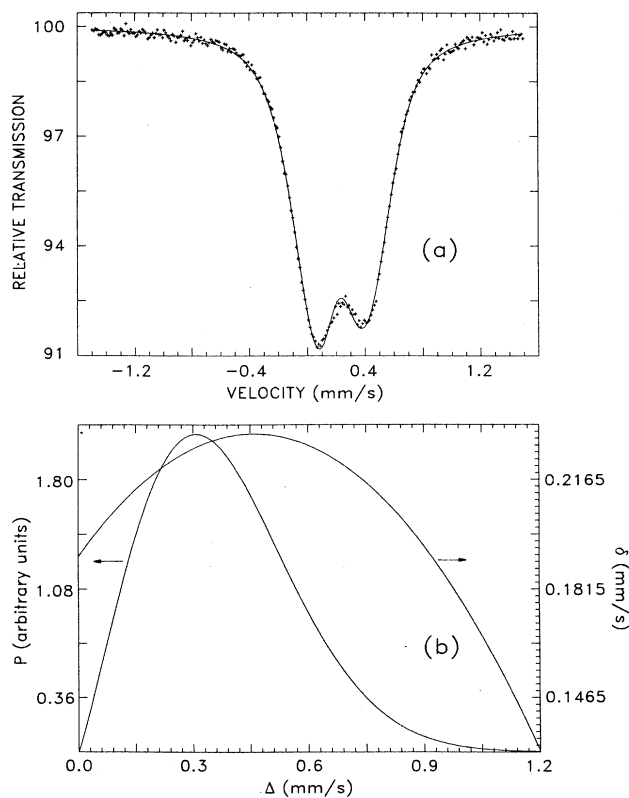

FIG. 2. (a) ^{57}Fe Mössbauer spectrum of icosahedral $Al_{65}Cu_{20}Fe_{15}$ at 4.2 K fitted (solid line) to a shell model. The velocity scale is relative to the ^{57}Co(Rh) source. (b) The distribution function $P(\Delta)$ and the δ-Δ correlation are obtained from the fit.

al properties of icosahedral $Al_{65}Cu_{20}Fe_{15}$, based on analysis of room-temperature ^{57}Fe Mössbauer spectra, we presented arguments that the two-site analysis of Mössbauer spectra in icosahedral alloys is incorrect. Here we perform detailed analyses of the 4.2-K ^{57}Fe Mössbauer spectrum using several fitting models to further elucidate the question of the possibility of two distinct TM sites in icosahedral alloys.

The 4.2-K ^{57}Fe Mössbauer spectrum was fitted using a one-site model (fit with an asymmetric doublet—model a) and two-site model (fit with two symmetric doublets). A fit with two symmetric doublets can be performed in two ways: either by fitting two doublets with significantly different values of isomer shift δ and similar values of quadrupole splitting Δ (model b),[51] or by fitting two doublets with similar δ values and significantly different Δ values (model c).[52] The latter fit is physically more justifiable, since it is well known from ^{57}Fe MS studies of various crystalline materials (with distinct crystallographic sites around Fe ions of a given oxidation state) that the range of changes in δ is much narrower than the range of changes in Δ. The parameters obtained from fits based on models a–c are given in Table II. For models b and c, the average values $\bar{\delta}$ and $\bar{\Delta}$ were calculated using δ_i and Δ_i $(i=1,2)$ values for the component doublets, with the relative areas of the doublets (Table II) as their weighting factors.

To judge the importance and validity of models a–c, particularly for Mössbauer spectra showing no apparent structure, one has to consider not only the quality of fit as measured by χ^2 (Table II), but also the physical soundness of the values of parameters derived from that fit. For unresolved ^{57}Fe Mössbauer paramagnetic spectra analyzed in terms of a discrete number of inequivalent Fe sites, it is of fundamental importance to analyze the values of a full linewidth at half maximum (Γ) obtained from the fits. As discussed in detail in Ref. 13, the Γ value of component lines at room temperature should not differ significantly from about 0.24 mm/s, and at 4.2 K this value would increase to about 0.25 mm/s (other experimental conditions being the same, the Γ increase is solely due to the increase of the absorber Debye-Waller factor with decreasing temperature, which in turn induces the increase of the effective absorber thickness[53]). As can be seen from Table II, although the fits to models b and c give significantly smaller values of χ^2 compared to the fit to model a, the fits to all three models nevertheless give Γ values which are much larger than the value of 0.25 mm/s. We conclude, therefore, that parameters derived from such fits have no physical meaning. Similar significant broadening of component lines was found in other icosahedral alloys by using either model b (Ref. 51) or model c (Ref. 52). Furthermore, the fitting of broad structureless single-line room-temperature ^{57}Fe Mössbauer spectra of Ti-Ni-Fe-Si icosahedral alloys[42] with two-component single lines resulted in linewidths significantly larger than the expected value of 0.24 mm/s. The inadequacy of the two-site fits of ^{57}Fe Mössbauer spectra of icosahedral alloys has also been discussed in Ref. 12. An attempt to fit broad, unresolved ^{57}Fe quadrupole Mössbauer spectra with three or more distinct quad-

TABLE II. Parameters determined from the fits of the 4.2-K ^{57}Fe Mössbauer spectrum to the models a, b, and c described in the text. δ_i [relative to the ^{57}Co(Rh) source], 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 ith line for model a, and the relative area of the ith doublet for models b and c $(A_1+A_2=1)$. χ^2 is defined as $[\sum_{i=1}^{k}(y_i^{\text{expt}}-y_i^{\text{theor}})^2/y_i^{\text{expt}}]/(k-m)$, where k and m are, respectively, the number of experimental points and the number of fitted parameters.

Model	δ_1	δ_2	Δ_1	Δ_2	Γ_1	Γ_2	A_1	$\bar{\delta}$	$\bar{\Delta}$	m	χ^2
a	0.237(4)		0.357(3)		0.385(11)	0.365(12)	0.543(18)			7	4.07
b	0.144(11)	0.282(8)	0.347(5)	0.371(3)	0.301(15)	0.294(74)	0.422(40)	0.224(40)	0.361(57)	9	1.59
c	0.216(3)	0.231(2)	0.182(26)	0.457(18)	0.269(50)	0.314(12)	0.323(113)	0.226(53)	0.368(92)	9	1.85

rupole doublets is a futile exercise. Such fits, apart from using many fitting parameters, require that some of these parameters be fixed at *ad hoc* values; otherwise good fits are obtained for unacceptable values of fitting parameters. This is a natural consequence of the experimental ^{57}Fe Mössbauer spectra of icosahedral alloys showing no structure. The broadening of component lines (Γ) observed here (Table II) and reported elsewhere in the literature[42,51,52] is a consequence of a distribution of Δ values. This, in turn, is due to the presence of a multiplicity of TM sites in icosahedral alloys. Indeed, as will be shown below, the only physically meaningful parameters derived from two-site model fits are the average values $\bar{\delta}$ and $\bar{\Delta}$.

It should be emphasized here that paramagnetic ^{57}Fe Mössbauer spectra of amorphous alloys containing Fe can also be fitted perfectly well with two doublets,[54−56] the linewidths of which are much larger than the 0.24 mm/s expected for typical Mössbauer absorbers under standard experimental conditions. It would be incorrect, however, to claim on the basis of such mathematically good fits that there are two crystallographically distinct Fe sites in amorphous alloys (although such conclusions had been drawn[56]).

As previously mentioned, some physical properties of icosahedral alloys are very similar to those of amorphous alloys. In particular, paramagnetic ^{57}Fe Mössbauer spectra of both types of alloys exhibit two broad structureless lines.[12] Consequently, the spectra of icosahedral alloys can be successfully fitted[12,13] to a shell model, which was introduced originally[57] to describe the distribution of Δ values in amorphous alloys. The distribution function in this model $P(\Delta)=\Delta^{n-1}/\sigma^n\exp(-\Delta^2/2\sigma^2)$ is determined by two parameters alone: n and σ. This model has been used here to fit the 4.2-K spectrum of Al$_{65}$Cu$_{20}$Fe$_{15}$ [Fig. 2(a)]. An asymmetry evident in this spectrum is due to the correlation between δ and Δ, and was taken into account by using a quadratic relation $\delta=\delta_0+a\Delta+b\Delta^2$, where δ_0, a, and b are fitted parameters. One linewidth parameter (Γ) was used in the fit. The 4.2-K spectrum of Al$_{65}$Cu$_{20}$Fe$_{15}$ fitted with the shell model, together with the resulting $P(\Delta)$ distribution and the δ-Δ correlation, are shown in Fig. 2. The parameters obtained from the fit, $n=2.128(72)$, $\sigma=0.290(7)$ mm/s, $\Gamma=0.252(6)$ mm/s, $\delta_0=0.192(3)$ mm/s, $a=-0.171(17)$ (mm/s)$^{-1}$, and $b=-0.185(22)$ (mm/s)$^{-2}$, gave $\chi^2=1.52$, $\bar{\delta}=0.223(2)$ mm/s, and $\bar{\Delta}=0.378(5)$ mm/s. The superiority of the multiple-site model fit over the two-site model fit (Table II) is clearly demonstrated by both the

smaller value of χ^2 obtained for smaller number of fitted parameters $(m=8)$] and by the physically justifiable value of Γ. Our conclusion is that the above analysis shows unambigously the presence of a multiplicity of Fe sites in icosahedral Al$_{65}$Cu$_{20}$Fe$_{15}$.

The $\bar{\delta}$ and $\bar{\Delta}$ values calculated from the two-site model fit (Table II) and those obtained from the shell-model fit are in reasonably numerical agreement. This somewhat surprising result is due to the fact that the fits based on the two-site model, although leading to unphysically broad component lines, nevertheless reproduce the spectra well (in the sense that χ^2 is small). Thus, although the δ and Δ values of each of the two component doublets have no physical meaning, their weighted average is close to the correct average values obtained from the multiple-site model fits.

The temperature changes of $\bar{\delta}$ and $\bar{\Delta}$ between 295 K (Ref. 13) and 4.2 K are -3.85×10^{-4} and -0.48×10^{-4} mm/s K, respectively. The decrease of $\bar{\delta}$ with temperature is due to the second-order Doppler effect, whereas the small decrease of $\bar{\Delta}$ is caused by complex temperature dependences of lattice and valence-electron contributions to the electric-field gradient.

It should be stressed that thermodynamically stable icosahedral Al$_{65}$Cu$_{20}$Fe$_{15}$ alloy is regarded as the most perfect icosahedral alloy presently known, with no presence of phason strains. This has been shown recently by means of high-resolution electron microscopy.[58] We therefore interpret the presence of a multiplicity of Fe sites in this alloy as clear evidence for intrinsic disorder associated with this icosahedral alloy.

We emphasize that the possibility of two classes of Mn atoms (with and without magnetic moment) in Al-Mn and Al-Mn-Si icosahedral alloys, as suggested by interpretation of various experiments, does not necessarily require the existence of two distinct Mn environments. Such moment variations could be a consequence of a continuous distribution of interatomic distances, resulting from intrinsic disorder in icosahedral systems.

IV. SUMMARY

Various magnetic properties of a novel thermodynamically stable icosahedral alloy Al$_{65}$Cu$_{20}$Fe$_{15}$ have been studied with ^{57}Fe Mössbauer spectroscopy and ac susceptibility. The results show that Fe atoms do not possess a local magnetic moment down to 1.5 K. It has also been demonstrated that the two-site analysis of the 4.2-K Mössbauer spectrum of Al$_{65}$Cu$_{20}$Fe$_{15}$ leads to unphysical-

ly broad component lines, which excludes the possibility of two crystallographically distinct Fe sites in this alloy. We conclude that a multiplicity of Fe sites exists in this alloy, which reflects intrinsic disorder present in this icosahedral system (the most perfect so far studied).

A review of the magnetic properties of icosahedral alloys has been presented, from which it has been argued that the presence or absence of local magnetic moments in these alloys is the result of intrinsic disorder rather than of icosahedral symmetry. The existence of such mo-

ments can be related to characteristic structural parameters of the alloys using predictions of the first-principles total-energy band theory.

ACKNOWLEDGEMENTS

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