

## Site preference of Fe in magnetically ordered Al-Mn-Cu-Ge icosahedral alloys

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X-ray-diffraction, magnetization, and  $^{57}\text{Fe}$  Mössbauer-spectroscopy measurements on  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  icosahedral alloys with  $x=0, 0.06,$  and  $3$  have been performed. The previously reported high value of the Curie temperature,  $T_C$ , is due to the presence of a small amount of ferromagnetic AlGeMn impurity. It is argued that  $T_C$  must be below 100 K. A continuous distribution of Fe atoms with no magnetic moment among a multiplicity of sites is found at room temperature. For the  $x=0.06$  composition, Fe atoms enter randomly the magnetic and nonmagnetic class of transition-metal sites in an icosahedral structure at 4.2 K. However, for the  $x=3$  composition, they enter preferentially the magnetic class of sites. The existence of the two classes of transition-metal sites in magnetically ordered icosahedral alloys is discussed in terms of intrinsic disorder present in these alloys and using arguments based on modern band-structure calculations.

### I. INTRODUCTION

The notion of two *classes* of sites in paramagnetic icosahedral alloys (IA's) was first suggested by Warren, Chen, and Espinosa.<sup>1</sup> It was based on a NMR observation that the  $^{55}\text{Mn}$  resonance in paramagnetic Al-Mn IA's occurs at essentially the same position as in the corresponding crystalline phases and that the  $^{55}\text{Mn}$  line intensity decreases as the magnetic susceptibility increases. It was argued<sup>1</sup> that part of the Mn atoms, which does not contribute to the NMR signal, is located in magnetic sites which are favorable for magnetic-moment formation, whereas the other part, which contributes to the NMR signal, resides in nonmagnetic sites which inhibit the moment formation. Although the interpretation of Warren, Chen, and Espinosa<sup>1</sup> was questioned by Bennett *et al.*,<sup>2</sup> who found no observable  $^{55}\text{Mn}$  NMR line in hexagonal  $\text{Al}_4\text{Mn}$  which shows a small magnetic susceptibility, the notion of two classes of sites was later supported by other experiments.

Edagawa *et al.*<sup>3</sup> and Eibschütz *et al.*<sup>4</sup> combined magnetic susceptibility and in-field  $^{57}\text{Fe}$  Mössbauer-spectroscopy (MS) measurements on Al-Mn-Si IA's in which a fraction of Mn atoms was substituted by Fe atoms. They showed<sup>3,4</sup> that the effective magnetic moment per transition metal (TM), i.e., per Mn and Fe, is essentially independent of Fe concentration. This is at variance with what one expects if all Mn atoms carry a magnetic moment. They also showed that the hyperfine magnetic field  $H_{\text{hf}}$ , as determined from the  $^{57}\text{Fe}$  Mössbauer spectra measured in an external magnetic field  $H_{\text{ext}}$ , is equal to  $H_{\text{ext}}$ . This can only occur if the Fe atoms carry no local magnetic moment. This led to the conclusion<sup>3,4</sup> that Fe substitutes only for Mn atoms located in a nonmagnetic class of sites. Using a structural model based on interconnected Mackay icosahedra,

Eibshütz *et al.*<sup>4</sup> hypothesized that the sites in a nonmagnetic class of sites are more compact, whereas those in magnetic class of sites are more expanded. This hypothesis was shown to be correct in a subsequent study<sup>5</sup> of the composition dependence of magnetic susceptibility of the paramagnetic icosahedral series  $\text{Al}_{74}\text{Mn}_{20-x}\text{V}_x\text{Si}_6$ . Vanadium, being larger in equivalent environments than manganese, is expected to replace manganese in larger sites of a magnetic class, thus leading to the decrease of the effective magnetic moment per TM atom. This was indeed observed,<sup>5</sup> and a distribution of Mn magnetic-moment magnitudes was also determined.<sup>5</sup>

As has been often emphasized in the literature,<sup>1,4-6</sup> the notion of two classes of TM sites in IA's does not imply the existence of two well-defined structural environments. It implies the presence of two distributions of sites that span a whole range of local environments. This is strongly supported by the results of measurements using local probes, such as NMR (Refs. 1 and 7-9) and MS.<sup>6,10-14</sup> These measurements clearly demonstrate a continuous distribution of the hyperfine interaction parameters, which results from the distribution of TM sites. Previous analyses<sup>15-17</sup> of  $^{57}\text{Fe}$  Mössbauer spectra of IA's in terms of two distinct TM crystallographic sites (the so-called two-site model) were shown<sup>6,10-14</sup> to be methodologically incorrect. In addition, the notion of two distinct TM sites in IA's, which is based on the simplest interpretation of the three-dimensional Penrose tiling, is incompatible with the notion of a quasicrystal which by its very nature has an infinite number of distinct crystallographic sites.<sup>18</sup>

The first direct evidence for the presence of two classes of TM sites in magnetically ordered IA's was presented in a recent  $^{57}\text{Fe}$  Mössbauer study.<sup>19</sup> It was shown that complex Mössbauer spectra of Al-Mn(Fe)-Ge and Al-Mn-Cu(Fe)-Ge IA's at 4.2 K can be described in terms of a nonmagnetic and a magnetic component. Thus the two

separate classes of TM sites are present both in paramagnetic and magnetically ordered IA's.

As mentioned above, Fe atoms, being smaller than Mn atoms in equivalent environments, were shown<sup>3,4</sup> to replace the latter dominantly at the sites belonging to a nonmagnetic class of Mn sites in paramagnetic Al-Mn-Si IA's. In a recent study Eibschütz *et al.*<sup>20</sup> confirmed, using magnetic-susceptibility measurements, an earlier suggestion, based on x-ray-absorption fine-structure studies,<sup>21</sup> that *very small* amounts of Fe atoms substitute randomly for Mn atoms; i.e., they enter into both the magnetic and nonmagnetic class of sites. Thus whether Fe atoms enter preferentially the magnetic or nonmagnetic class of Mn sites in paramagnetic IA's seems to depend upon the concentration of Fe. For very small Fe concentrations, Fe atoms enter both the magnetic and nonmagnetic class of sites, whereas for larger Fe concentrations, they preferentially enter the nonmagnetic class of sites. It is the purpose of this study to investigate whether this picture is also valid in magnetically ordered IA's.

## II. EXPERIMENT

Ingots of an icosahedral series  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  ( $x = 0, 0.06, \text{ and } 3$ ) and crystalline alloys  $\text{AlGeMn}_{1-x}\text{Fe}_x$  ( $x = 0 \text{ and } 0.005$ ) were prepared by arc melting of high-purity elemental constituents under an argon atmosphere. For the compositions  $x = 0.06$  of the first series and  $x = 0.005$  of the second series, the iron metal used was enriched to 95% in the  $^{57}\text{Fe}$  isotope. The icosahedral and crystalline samples were produced according to a procedure described elsewhere.<sup>19</sup>

Room-temperature x-ray-diffraction (XRD) measurements were done on a Siemens D500 scanning diffractometer using  $\text{Cu } K\alpha$  radiation. The contribution to the spectra from the  $\text{Cu } K\alpha_2$  radiation was subtracted. X-ray scans were carried out with a  $2\theta$  step of  $0.05^\circ$  and a time per step of 5 s. The alloys were gently powdered for XRD measurements.

$^{57}\text{Fe}$  MS measurements were performed at room temperature and at 4.2 K using a Wissel MSII Mössbauer spectrometer operating in a sine mode. The spectrometer was calibrated with a  $12.7\text{-}\mu\text{m}$  Fe foil,<sup>22</sup> and the spectra were folded. The surface densities of the  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{9.94}\text{Fe}_{0.06}\text{Ge}_{25}$  and  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_7\text{Fe}_3\text{Ge}_{25}$  Mössbauer absorbers were  $4.0 \times 10^{-3}$  and  $7.5 \times 10^{-3}$  mg  $^{57}\text{Fe}/\text{cm}^2$ , respectively. The source used was  $^{57}\text{Co}(\text{Rh})$ .

The temperature dependence of the magnetization in the field of 4 kOe was measured for the  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{9.94}\text{Fe}_{0.06}\text{Ge}_{25}$  and  $\text{AlGeMn}$  samples using a vibrating sample magnetometer.

## III. RESULTS AND DISCUSSION

### A. X-ray-diffraction data

The  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  IA's studied so far could not be produced as 100% single phase. This is illustrated in Fig. 1, where one can clearly see weak lines in the XRD spectrum of  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_7\text{Fe}_3\text{Ge}_{25}$  due to a small fraction

of crystalline  $\text{AlGeMn}_{1-x}\text{Fe}_x$  present as a second phase. This phase was demonstrated to be unavoidably present also for other compositions of Al-Mn(Fe)-Ge and Al-Mn-Cu(Fe)-Ge IA's.<sup>19</sup> As we discuss elsewhere,<sup>19</sup> other unidentified minor second phases, giving rise to a rounded maximum centered at  $2\theta \approx 43^\circ$  [Fig. 1(a)], might be also present. Claims made in the literature<sup>23,24</sup> that the studied  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  IA's were single phase are at variance with the corresponding XRD spectra (Fig. 1 in Ref. 23 and Fig. 1 in Ref. 24) containing clearly visible lines which are not due to an icosahedral structure and which were ignored.<sup>23,24</sup> Thus, already an analysis of the XRD spectra of the  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  IA's

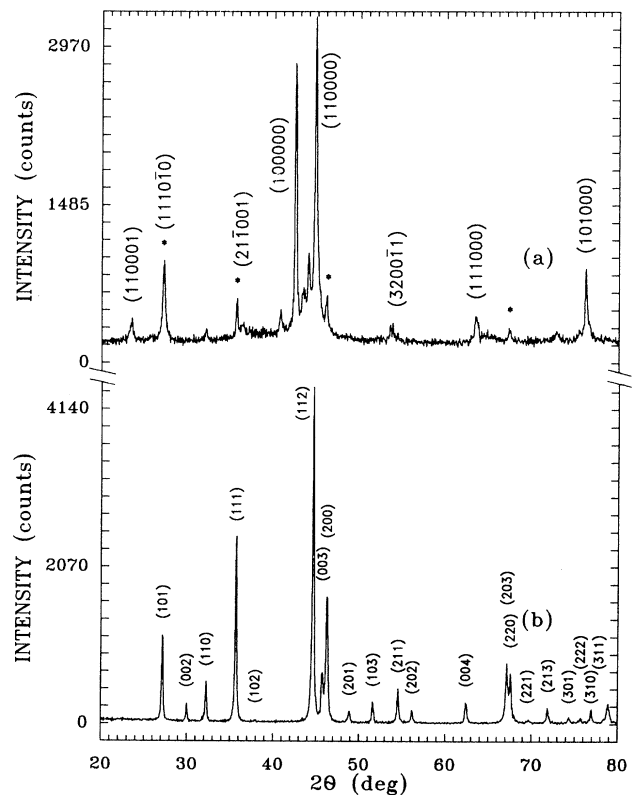


FIG. 1. X-ray diffraction patterns obtained with  $\text{Cu } K\alpha_1$  radiation of (a) icosahedral  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_7\text{Fe}_3\text{Ge}_{25}$  and (b) crystalline  $\text{AlGeMn}_{0.995}\text{Fe}_{0.005}$  alloys. The indexing of icosahedral lines in (a) is according to the scheme of Bancel *et al.* (Ref. 35), whereas the lines in (b) are indexed on the basis of a tetragonal cell (Ref. 36). The quasilattice constant (Ref. 37)  $a_R = 4.504(2)$  Å and the positions of all icosahedral lines indicated were calculated (Ref. 17) from the position of the (100 000) line. The centers of the labels of the icosahedral Miller indices, except the labels (100 000) and (110 000), correspond to the calculated position. The values of the lattice constants  $a$  and  $c$ , obtained from a least-squares fit of the observed line positions in (b), are  $3.919(1)$  and  $5.946(2)$  Å, respectively. The centers of the symbols \* in (a) correspond to the positions of the (101), (111), and (200) lines and to the average position of the (203) and (220) lines from (b). The position of the (112) line coincides with the position of the (110 000) line.

performed here and elsewhere<sup>19</sup> shows that the high value of the ordering temperature  $T_C$  (about 500 K) reported<sup>25</sup> for  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10}\text{Ge}_{25}$ , and assumed<sup>23,24</sup> to be also so high for  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  IA's, is due to the presence of the small amount of ferromagnetic<sup>26</sup>  $\text{AlGeMn(Fe)}$  crystalline alloy as a second phase. This, combined with the very small value of the magnetization, strongly suggests that  $T_C$  associated with magnetic ordering in this system must be substantially smaller than 500 K.

### B. Magnetization data

A comparison of temperature dependences of magnetization of icosahedral  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{9.94}\text{Fe}_{0.06}\text{Ge}_{25}$  and crystalline  $\text{AlGeMn}$  (Fig. 2) shows that the apparent  $T_C$  of the former is practically the same as the  $T_C$  of the latter. More importantly, the shape of the  $M(T)$  dependence for both alloys is very similar in the temperature range from about 100 to 618 K (Fig. 2). This constitutes an additional evidence for the presence of the ferromagnetic  $\text{AlGeMn(Fe)}$  second phase. Below about 100 K, there is a significant nonlinear increase of  $M$  of  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{9.94}\text{Fe}_{0.06}\text{Ge}_{25}$  [Fig. 2(b)], whereas there is a minute increase of  $M$  of  $\text{AlGeMn}$  [Fig. 2(a)] expected for a ferromagnet with a high  $T_C$ . This indicates that the true  $T_C$  of  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{9.94}\text{Fe}_{0.06}\text{Ge}_{25}$  must be below about 100 K. A small rise of  $M$  of  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{9.94}\text{Fe}_{0.06}\text{Ge}_{25}$  above 618 K [Fig. 2(a)] has been observed also for other compositions of the  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  series. It is probably due to the crystallization of an unknown and very weakly magnetic second phase.

### C. $^{57}\text{Fe}$ Mössbauer effect data

The analysis presented above shows that there is a small amount of a crystalline ferromagnet  $\text{AlGeMn(Fe)}$

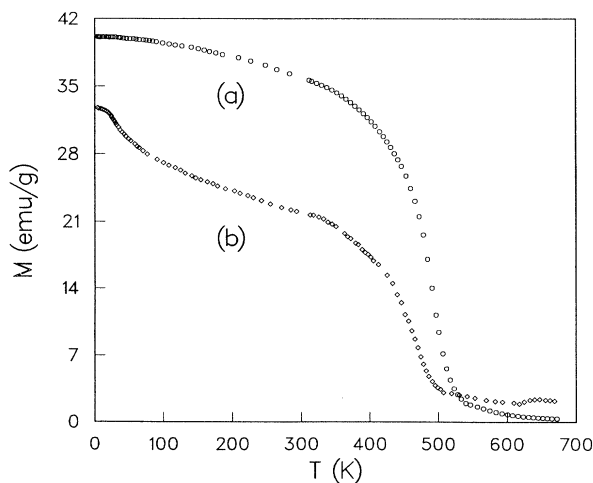


FIG. 2. Temperature dependence of magnetization measured in a field of 4 kOe of (a) crystalline  $\text{AlGeMn}$  and (b) icosahedral  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{9.94}\text{Fe}_{0.06}\text{Ge}_{25}$ . The values of  $M$  corresponding to  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{9.94}\text{Fe}_{0.06}\text{Ge}_{25}$  were multiplied by a factor of 10.

in the samples of  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  IA's. This explains a surprisingly high value of their  $T_C$ . Since the real value of  $T_C$  must be below 100 K,  $^{57}\text{Fe}$  Mössbauer spectra were measured significantly above and below that temperature in order to detect the presence of the weak hyperfine dipole magnetic interaction  $M1$ , which is expected to be comparable in strength with the electric quadrupole interaction  $E2$ .

Usually, the presence of a magnetic impurity hinders the interpretation of Mössbauer spectra. The ferromagnetic impurity  $\text{AlGeMn}_{1-x}\text{Fe}_x$  is unusual from the Mössbauer point of view since, for small  $x$ , its  $^{57}\text{Fe}$  Mössbauer spectrum below its  $T_C$ , contrary to what one could expect, exhibits the presence of only  $E2$  (Fig. 6 in Ref. 19).<sup>27</sup> Thus, in spite of the presence of an  $\text{AlGeMn}_{1-x}\text{Fe}_x$  impurity in  $\text{Al}_{40}\text{Mn}_{25}\text{Fe}_x\text{Cu}_{10-x}\text{Ge}_{25}$  IA's, its contribution to a Mössbauer spectrum will be in the form of a quadrupole doublet only. This means that the presence of a Zeeman pattern below  $T_C$  due to  $M1$  in Mössbauer spectra of these IA's would originate from these alloys and not from the impurity.

#### 1. Room-temperature $^{57}\text{Fe}$ Mössbauer spectra

Room-temperature  $^{57}\text{Fe}$  Mössbauer spectra of the  $x=0.06$  and 3 samples of the icosahedral series  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  (Fig. 3) clearly show a doublet structure, typical for Fe-containing IA's,<sup>3,4,6,10-14,19</sup> which is due to  $E2$ . The full linewidth at half maximum,  $\Gamma$ , of two Lorentzian lines obtained from a fit with an asymmetric doublet are 0.389(2) and 0.412(3) mm/s for the  $x=0.06$  sample and 0.456(9) and 0.418(1) mm/s for the  $x=3$  sample. Such broad lines, compared to the natural linewidth 0.194 mm/s, prove the presence of a distribution of quadrupole splittings,  $\Delta$ .<sup>3,4,6,10-14,19</sup> This distribution has been taken into account by fitting the spectra to a shell model. The details of the fitting procedure have been described elsewhere.<sup>6,19</sup> An attempt to include in the fit a quadrupole doublet subspectrum due to an  $\text{AlGeMn(Fe)}$  impurity resulted in zero intensity of this spectrum, which indicates that the content of this impurity is below the sensitivity of  $^{57}\text{Fe}$  MS. The distribution function  $P(\Delta)$  [Fig. 3(c)] obtained from the fit gave the average values of isomer shift,  $\delta$ , and  $\Delta$  equal to 0.159(2) and 0.426(5) mm/s for the  $x=0.06$  sample and 0.149(5) and 0.419(6) mm/s for the  $x=3$  sample. The  $\Gamma$  values obtained from the fits are, respectively, 0.211(11) and 0.207(10) mm/s and agree with the values one expects for the very thin absorbers<sup>28</sup> used in this study. The values of  $\Delta$  are practically the same for both samples, with the  $P(\Delta)$  distribution wider for the  $x=3$  sample than for the  $x=0.06$  sample [Fig. 3(c)], which is in accordance with a larger degree of disorder expected for higher substitution of Cu for Fe. The presence of a distribution for  $\Delta$  observed here and in other icosahedral alloys<sup>3,4,6,10-14,19</sup> is evidence for a continuous distribution of TM sites in these alloys, which reflects the intrinsic disorder of IA's. The quadrupole spectra in Fig. 3 prove that Fe atoms at room temperature do not carry a magnetic moment, which is consistent with the earlier conclusion that  $T_C$  of the studied system must be below 100 K.

It should be emphasized that a particular model used here (the shell model) to fit the distribution of  $\Delta$  is not the only possible model. Other models providing slightly different shapes of  $P(\Delta)$  fit the spectra equally well. It is not the purpose of this study to determine which model is better, which cannot be decided without measuring the spectra in a strong external magnetic field. Rather, the

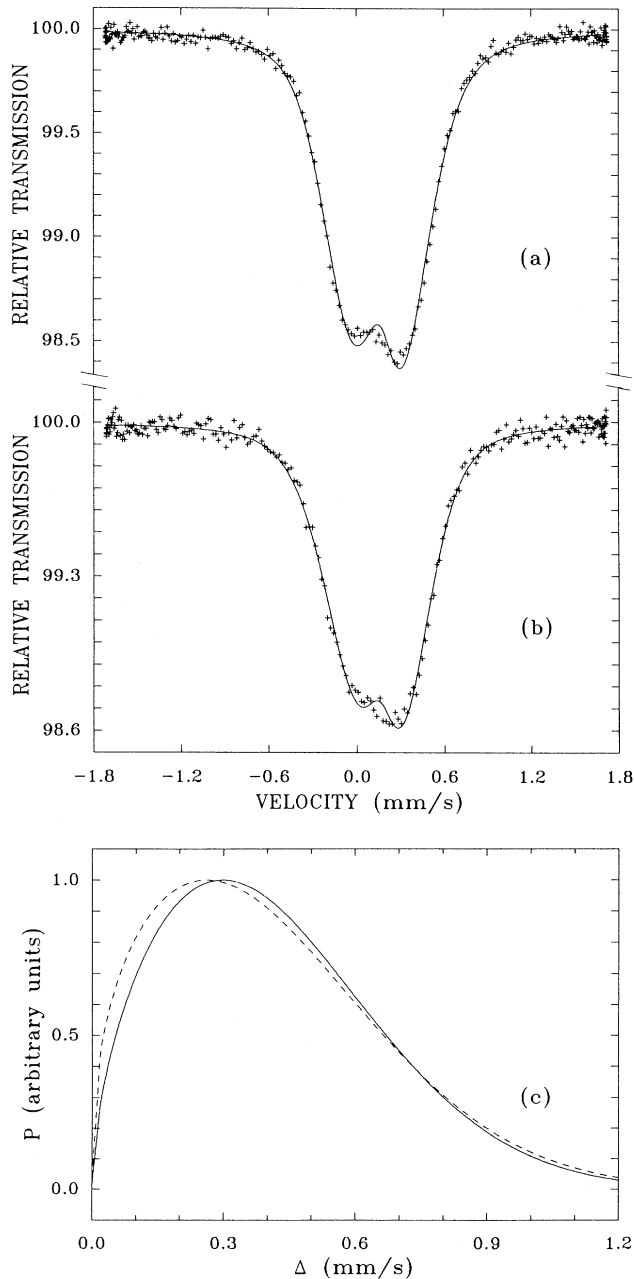


FIG. 3. Room-temperature  $^{57}\text{Fe}$  Mössbauer spectra of icosahedral (a)  $\text{Al}_{40}\text{Mn}_{25}\text{Fe}_{0.06}\text{Cu}_{9.94}\text{Ge}_{25}$  and (b)  $\text{Al}_{40}\text{Mn}_{25}\text{Fe}_3\text{Cu}_7\text{Ge}_{25}$  fitted (solid line) to a shell model. The velocity scale is relative to the  $^{57}\text{Co}(\text{Rh})$  source. (c) The resulting distribution function  $P(\Delta)$  corresponding to fits in (a) (solid line) and (b) (dashed line).

shell model is used to demonstrate the presence of the distribution of  $\Delta$  and, consequently, the presence of a continuous distribution of TM sites. This, in turn, is evidence for the intrinsic disorder present in the IA's.<sup>1,6-14</sup>

$^{57}\text{Fe}$  Mössbauer spectra of the  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  IA's with  $x = 3, 6,$  and  $10$  measured at room temperature<sup>23,24,29</sup> and at  $110\text{ K}$  [for the composition  $x = 3$  (Ref. 23)] were analyzed with a Zeeman pattern and with a distribution of hyperfine magnetic fields  $H_{\text{hf}}$  using first-order perturbation theory. The criticism of such an analysis is presented in Ref. 19.

#### 2. 4.2-K $^{57}\text{Fe}$ Mössbauer spectra

The 4.2-K Mössbauer spectra of the  $x = 0.06$  and  $3$  samples (Fig. 4) show a significant broadening compared to the room-temperature spectra (Fig. 3). Because of the very thin absorbers used in this study, the broadening due to the increase of the Debye-Waller factor<sup>28</sup> is smaller than  $0.003\text{ mm/s}$  and is therefore negligible. The observed broadening is thus due to the appearance of  $M1$ . In addition to a doublet structure, similar to the one observed for room-temperature spectra (Fig. 3), present in the central part of the 4.2-K spectra, they clearly exhibit a feature at the right wing (Fig. 4). This constitutes an additional evidence for the presence of  $M1$ . Because  $E2$

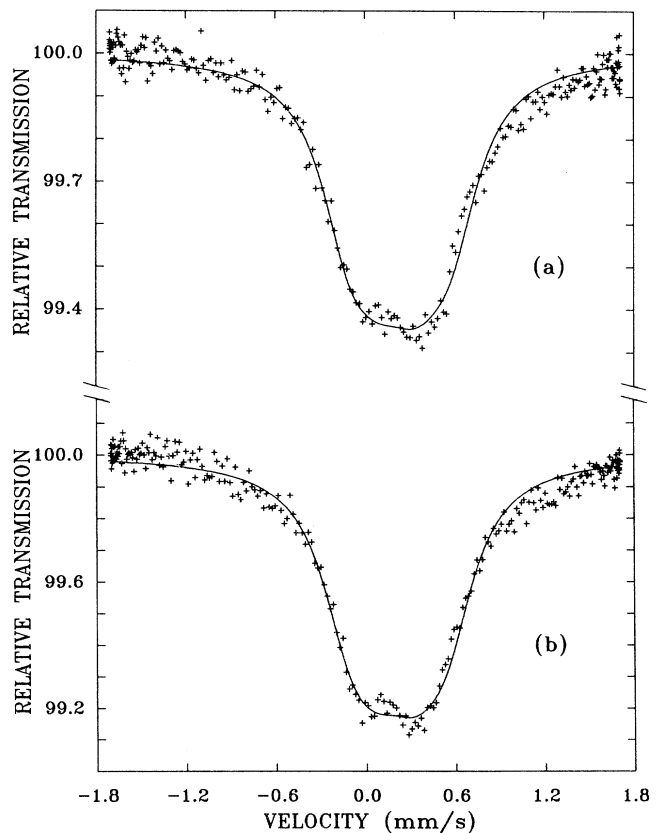


FIG. 4. 4.2-K  $^{57}\text{Fe}$  Mössbauer spectra of icosahedral (a)  $\text{Al}_{40}\text{Mn}_{25}\text{Fe}_{0.06}\text{Cu}_{9.94}\text{Ge}_{25}$  and (b)  $\text{Al}_{40}\text{Mn}_{25}\text{Fe}_3\text{Cu}_7\text{Ge}_{25}$ . The velocity scale is relative to the  $^{57}\text{Co}(\text{Rh})$  source. The fits (solid lines) are explained in the text.

and  $M1$  are of comparable magnitudes, the spectra must be treated using the exact Hamiltonian.

The presence of the disorder in the studied alloys was taken into account by assuming that there is no correlation between the electric-field-gradient (EFG) principal axes and the direction of  $H_{\text{hf}}$ . We employed the algorithm given by Blaes, Fischer, and Gonser,<sup>30</sup> which is suitable for such a case. The fitting routine provides  $\delta$ ,  $H_{\text{hf}}$ , the quadrupole coupling constant  $\Delta_{\text{QS}} = eQV_{zz}/2$  ( $e$  is the magnitude of the electron charge,  $Q$  is the quadrupole moment of the  $^{57}\text{Fe}$  nucleus, and  $V_{zz}$  is the principal component of the EFG tensor),  $\eta$  (the asymmetry parameter), and  $\alpha$  (the angle between the gamma ray and direction of  $H_{\text{hf}}$ ). Since, in reality, all the above parameters exhibit some distribution, their values obtained from such a one-site fit can be treated as the average values, much as one can treat a quadrupole splitting  $\Delta$  obtained from an asymmetric doublet fit of a spectrum exhibiting a distribution of  $\Delta$  values.<sup>6,11</sup> Because of the smallness of  $M1$  manifested in the broadening of 4.2-K Mössbauer spectra, it is impossible to fit such spectra using the distribution of various parameters. This distribution has been taken indirectly into account by fixing the value of  $\Gamma$  in the fits to the weighted average of linewidths of two-component lines obtained from the fits of the room-temperature spectra in Fig. 3 to an asymmetric doublet. These values are 0.416 mm/s for the  $x = 0.06$  sample and 0.438 mm/s for the  $x = 3$  sample. Attempts to improve the fits by including an additional quadrupole doublet subspectrum due to AlGeMn(Fe) impurity resulted in zero intensity of such a spectrum. This shows that in the 4.2-K spectra the amount of the impurity is also below the resolution of  $^{57}\text{Fe}$  ME technique. The parameters obtained from the fit for the  $x = 0.06$  sample [Fig. 4(a)] are  $\delta = 0.234(4)$  mm/s,  $H_{\text{hf}} = 11.8(5)$  kOe,  $\Delta_{\text{QS}} = -0.438(6)$  mm/s,  $\eta = 0.1(1)$ , and  $\alpha = 90(20)^\circ$ . The corresponding parameters from the fit of the  $x = 3$  sample [Fig. 4(b)] are 0.211(3) mm/s, 11.0(4) kOe,  $-0.424(5)$  mm/s, 0.1(1), and  $90(19)^\circ$ . The fits are very sensitive to the values of  $\delta$ ,  $H_{\text{hf}}$ , and  $\Delta_{\text{QS}}$ , but only marginally sensitive to  $\eta$  and  $\alpha$ . Therefore, the values of  $\eta$  and  $\alpha$  are only estimates.

It is evident from Fig. 4 that the fit using the procedure described above is not satisfactory. Neither the doublet structure in the center of the spectra nor the feature at the right wing is accounted for properly. This suggests the necessity of including a second component in the fit. The persistence of the doublet structure in the center of the spectra indicates that there must be a significant fraction of Fe atoms which do not participate in the  $M1$  interaction, i.e., that they do not bear a magnetic moment. On the other hand, the appearance of the feature at the right wing and a significant broadening of the wings indicates that a fraction of Fe atoms must be subjected to the  $M1$  interaction; i.e., they carry a magnetic moment. We therefore refitted the 4.2-K spectra with two subspectra. In one subspectrum  $H_{\text{hf}}(1) = 0$  is set, which corresponds to the assumption that at 4.2 K some of Fe atoms are nonmagnetic, and other parameters, except  $\delta_1$  and the subspectrum relative area  $A_1$ , are set to the values obtained from an asymmetric doublet fit of room-temperature spectra. This is justified since the tempera-

ture dependence of the quadrupole splitting is very small.<sup>6</sup> All parameters of the second subspectrum, i.e.,  $\delta_2$ ,  $H_{\text{hf}}(2)$ ,  $\Delta_{\text{QS}_2}$ ,  $\eta_2$ ,  $\alpha_2$ , and  $A_2$ , are fitted. Similarly to the fits in Fig. 4, the value of  $\Gamma_2$  is fixed. The fits shown in Fig. 5 account well for the features at the wings and in the central part of the experimental spectra. Attempts to include the third subspectrum due to the AlGeMn(Fe) second phase failed to produce a better fit. The fraction of this subspectrum was below 1% and was not statistically meaningful. This reconfirms that the AlGeMn(Fe) content is below the resolution of  $^{57}\text{Fe}$  Mössbauer spectroscopy. The parameters obtained from the fit for the  $x = 0.06$  sample [Fig. 5(a)] are  $\delta_1 = 0.195(5)$  mm/s,  $A_1 = 0.54(1)$ ,  $\delta_2 = 0.289(10)$  mm/s,  $H_{\text{hf}}(2) = 28.7(7)$  kOe,  $\Delta_{\text{QS}_2} = -0.355(25)$  mm/s,  $\eta_2 = 0.01(1)$ ,  $\alpha_2 = 90(20)^\circ$ , and  $A_2 = 0.46(1)$ . The corresponding parameters for the  $x = 3$  sample [Fig. 5(b)] are 0.197(4) mm/s, 0.71(1), 0.288(13) mm/s, 45.0(2.5) kOe,  $-0.281(93)$  mm/s, 0.0(1),  $90(25)^\circ$ , and 0.29(1). Freeing  $H_{\text{hf}}(1)$  in the fit resulted in a value which was practically zero, which justifies the assumption made. The fits were effectively insensitive to the values of  $\eta_2$  and  $\alpha_2$ . Therefore, the values of these parameters should be treated only as estimations.

The hyperfine parameters are practically the same for both samples studied. The predominant negative sign of

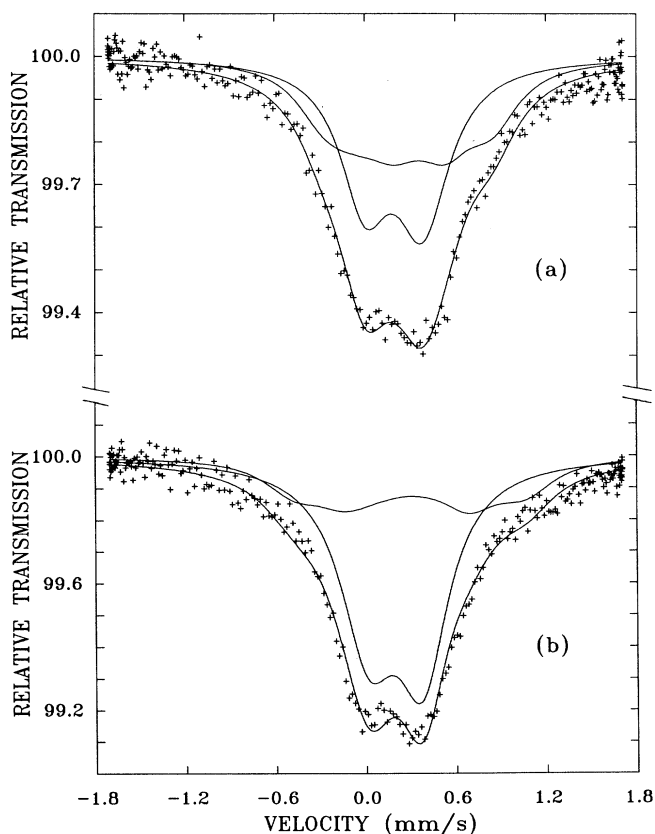


FIG. 5. Same spectra as in Fig. 4 fitted (solid line) with two subspectra, which are also shown (solid lines). The fits are explained in the text.

$\Delta_{QS}$  is consistent with the same predominant sign of  $\Delta_{QS}$  obtained from in-field  $^{57}\text{Fe}$  Mössbauer spectra of paramagnetic Al-Mn-based IA's.<sup>10,12,13</sup> It indicates that the local environment around Fe atoms in the studied IA's must be similar to the corresponding environment in the paramagnetic Al-Mn-based IA's. Thus one can expect the presence of the two classes of sites also in the studied magnetically ordered IA's. Because of the lack of structural studies of the local environment of TM atoms in the IA's studied here, it is not possible at present to associate the  $\Delta_{QS}$  value with a particular local atomic structure model. From the values of  $H_{\text{hf}}(2)$  and using the hyperfine constant of  $142 \text{ kOe}/\mu_B$  found for many alloys,<sup>31</sup> we estimate that the values of  $\mu_{\text{Fe}}$  are  $0.20\mu_B$  and  $0.32\mu_B$  for the  $x=0.06$  and 3 samples, respectively. Such small values of  $\mu_{\text{Fe}}$  are expected for a system with  $T_C$  below 100 K.

If one assumes that in the studied alloys the local environment of TM atoms is similar to the corresponding environment in paramagnetic Al-Mn(Fe) and Al-Mn(Fe)-Si IA's (the negative sign of  $\Delta_{QS}$  indicates that such an assumption is justified), then one can interpret the two-component fit (Fig. 5) in terms of two classes of TM sites. Of special importance here is the fraction of nonmagnetic Fe atoms,  $A_1$ . It increases from 54(1)% for the  $x=0.06$  composition [Fig. 5(a)] to 71(1)% for the  $x=3$  composition [Fig. 5(b)]. This means that for the very small Fe concentration, Fe atoms enter randomly both the nonmagnetic and magnetic class of TM sites. However, for larger Fe concentration, Fe atoms enter preferentially the nonmagnetic class of TM sites. The presence of a few percent of impurity in the samples studied, which could not be taken into account in the fits, cannot change significantly the observed dependence of  $A_1$  upon Fe concentration.

We thus conclude that the two classes of TM sites are present, not only in paramagnetic IA's,<sup>1,3-5,20,21</sup> but also in magnetically ordered IA's. Similarly to paramagnetic IA's, in magnetically ordered IA's Fe atoms enter randomly the nonmagnetic and magnetic class of TM sites for very small Fe concentration, whereas for larger Fe concentration they enter preferentially the nonmagnetic class of TM sites.

#### D. Two classes of TM sites and band calculations

A qualitative explanation for the existence of two classes of TM sites in paramagnetic Al-Mn-Si IA's was given in the literature<sup>4,5</sup> using arguments based on theories describing the behavior of diluted TM atoms inserted into a metallic matrix. Since the concentration of TM atoms in the magnetically ordered  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  IA's is much above the diluted limit, it is more appropriate to justify qualitatively the existence of two classes of TM sites in these alloys, applying arguments based on the results of theories developed for concentrated alloys.

It is now well established through self-consistent parameter-free total-energy-band calculations that, in general, TM atoms either in metals<sup>32</sup> or their alloys<sup>33</sup> favor a magnetic state at large volumes, where the densi-

ty of states tends to exhibit peaks. However, at low volumes, they favor a nonmagnetic state, where the density of states becomes smeared in energy. One can therefore expect that a given crystalline system will undergo a transition from one state to another when the volume changes. This is indeed predicted by theoretical calculations.<sup>32,33</sup> If one makes not an unrealistic assumption that a similar volume dependence of TM magnetism exists in magnetically ordered IA's, then the following qualitative explanation can be offered. As mentioned earlier, the results of measurements with local probes<sup>1,6-14</sup> clearly show the presence of disorder in IA's, even in the most perfect ones,<sup>6,11</sup> i.e., with the least amount of phason strain. This disorder is interpreted as the direct manifestation of the icosahedral structure seen as a continuous distribution of "unit cells."<sup>34</sup> In other words, this disorder reflects the fact that there is an infinite number of sites in a quasicrystal structure which are not exactly equivalent.<sup>18</sup> This naturally implies the distribution of interatomic distances (volumes) which are crucial for the formation of a magnetic moment on a given TM atom. Thus the existence of two classes of TM sites is the consequence of the topological disorder inherent to icosahedral systems. This interpretation leads also to the conclusion that it is disorder rather than icosahedral symmetry which is more important in determining physical properties of IA's.

#### IV. SUMMARY

Magnetic properties of the icosahedral system  $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}$  ( $x=0, 0.06$ , and 3) and crystalline  $\text{AlGeMn}_{1-x}\text{Fe}_x$  ( $x=0$  and 0.005) have been studied with XRD, magnetization, and  $^{57}\text{Fe}$  MS. It has been shown that the apparent high value of  $T_C$  of these IA's is an artifact caused by the presence of a small amount of ferromagnetic AlGeMn(Fe) impurity. Experimental data indicate that the upper limit of  $T_C$  is about 100 K. It has been found that Fe atoms do not possess a magnetic moment at room temperature. The occurrence of a distribution of Fe sites has been interpreted as evidence for disorder intrinsic to all icosahedral alloys. It has been shown that Fe atoms at 4.2 K bear a small magnetic moment. They substitute randomly the nonmagnetic and magnetic class of TM sites for very small Fe concentration. For higher Fe concentration, they enter preferentially the nonmagnetic class of sites. The existence of two classes of TM sites in magnetically ordered icosahedral alloys has been justified by combining intrinsic disorder present in icosahedral alloys with the predictions of first-principles total-energy-band calculations.

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