Mixed hyperfine interactions in the ferromagnetic quasicrystals $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ (x=3, 5 or 10)

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Mixed hyperfine interactions in the ferromagnetic quasicrystals $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ ($x = 3$, 5 or 10)

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Abstract. Mössbauer effect measurements of the ferromagnetic quasicrystals $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ with $x = 3$, 6 or 10 are reported both above ($T = 553$ K) and below ($T = 100$ K) the Curie temperature T_C. Below T_C, the spectra are best fitted to a model which involves a combined magnetic and quadrupole Hamiltonian. These fits yield the mean hyperfine parameters: hyperfine field $H = 9$ kOe and quadrupole splitting $\Delta = -0.33$ mm s^{-1}. These results are essentially independent of Fe content for $3 \leqslant x \leqslant 10$ and suggest that the localized Fe moment is small. Above T_C the spectra are suitably fitted to a distribution of quadrupole interactions with a mean value $|\Delta|$ of 0.36 mm s^{-1}. This is consistent with the value obtained below T_C.

1. Introduction

The magnetic properties of quasicrystals have been studied extensively over the past few years [1]. While the earliest reports showed quasicrystalline alloys to be weak paramagnets [2], subsequent studies revealed that some quasicrystalline alloys show a spin glass freezing at low temperatures [3]. Within the past year or so, several quasicrystalline alloys have been reported [4–6] that appear to exhibit ferromagnetic order. While several studies of these ferromagnetic properties have been reported [7–11], a number of questions concerning this behaviour have not yet been answered. Among the unusual and as yet unexplained properties of ferromagnetic quasicrystals are the following:

(i) relatively high values of the Curie temperature T_C but very small values of the measured saturation magnetization compared with conventional ferromagnets,
(ii) a sizable coercivity and
(iii) the apparent superposition of ferromagnetic and spin-glass behaviour at low temperatures.

While certain recent measurements have suggested the possibility that the so-called ferromagnetic phase is, in fact, a concentrated spin glass [10], other measurements [12] have shown that some of these alloys exhibit behaviour that is not unlike typical strong ferromagnetic alloys. In particular the $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ system has yielded some interesting results. Magnetization studies have shown that these alloys possess

(1) large coercivities (up to about 2 kOe [5]),
(2) large magnetizations (up to 35 emu g^{-1} [9, 12]) and

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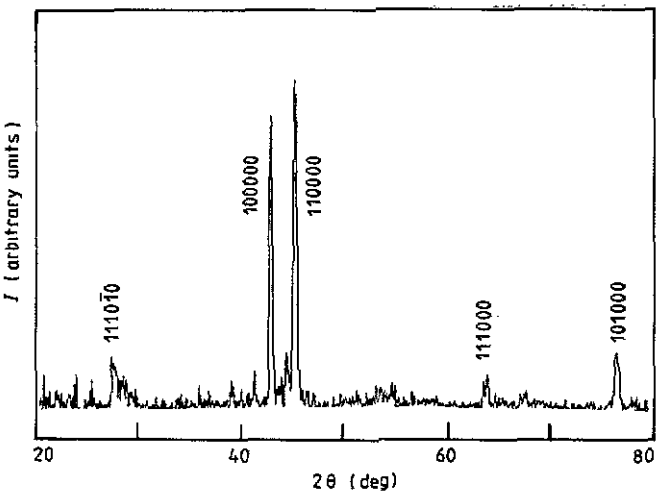

Figure 1. Room-temperature Cu Kα x-ray diffraction pattern of icosahedral $Al_{60}Mn_{25}Fe_{10}Ge_{25}$. The indices for the quasicrystalline diffraction phase are indicated [13].

(3) high Curie temperatures (up to 500 K [5]).

These results imply that these Al–Mn–Cu–Fe–Ge quasicrystals are predominantly ferromagnetically ordered. In order to understand the behaviour of these alloys better, we have recently reported preliminary Mössbauer effect measurements [8] on Fe containing ferromagnetic quasicrystals. In the present work we have extended our Mössbauer studies and we report measurements both above and below T_C for ferromagnetic Al–Mn–Cu–Fe–Ge quasicrystals.

2. Experimental methods

Samples of $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ with x varying from 0 to 10 at.%, were prepared by arc melting high-purity elemental components. Single-phase icosahedral quasicrystals were prepared by melt spinning onto a single copper roller with a surface velocity of 60 m s^{-1}. The resulting samples were characterized using a Siemens D-500 x-ray diffractometer. ^{57}Fe Mössbauer effect studies were performed at various temperatures using a room-temperature **Pd**–^{57}Co source and either a Wissel system II (for low-temperature data) or an Austin ASA S600 spectrometer (for high-temperature data) operating in the constant-acceleration mode. In both cases, natural iron was used for calibration and the intrinsic linewidth (full width at half maximum (FWHM)) was observed to be 0.24 mm s^{-1}. The low-temperature Mössbauer data were obtained using a cold-finger-type liquid-nitrogen cryostat and the high-temperature data were obtained using a Ricor high-temperature furnace with a temperature accuracy of 1 K.

3. Results and discussion

X-ray diffraction studies showed all samples to be essentially single-phase icosahedral quasicrystalline alloys. A typical x-ray diffraction pattern is illustrated along with the indexing scheme of Bancel *et al* [13] in figure 1. It has been a concern in the past that the

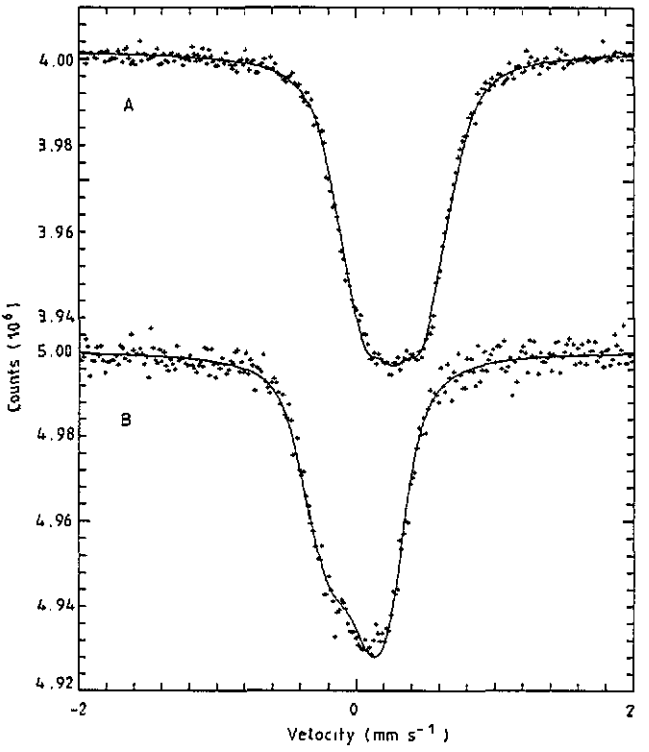

Figure 2. ^{57}Fe Mössbauer effect spectrum of icosahedral $Al_{40}Mn_{25}Fe_{10}Ge_{25}$ at 100 K (spectrum A) and 553 K (spectrum B). For the spectrum at 100 K the full curve line represents a fit to the exact Hamiltonian method of Brand and coworkers [20]. For the spectrum at 553 K the full curve is a fit to a distribution of quadrupole splittings using the method of Le Caer and Dubois [16] and a linear relationship between isomer shift and quadrupole splitting to account for the spectral asymmetry.

ferromagnetism in these alloys is not an intrinsic property of the quasicrystalline phase but rather that it is the result of a small quantity of crystalline ferromagnetic precipitate. While a small quantity of a crystalline precipitate might not be detected in x-ray measurements and would explain the saturation magnetization and Curie temperature of most Al–Mn–Si-based ferromagnetic quasicrystals, recent measurements [12] of saturation magnetization of up to about 35 emu g^{-1} in Al–Mn–Cu–Fe–Ge quasicrystals would seem to rule out this possibility. As further evidence for the association of the ferromagnetism with the quasicrystalline phase, recent electron microprobe analyses on a variety of single-phase ferromagnetic quasicrystals [14] have shown that there are no measurable compositional variations within grains, between grains or at grain boundaries.

Mössbauer effect spectra of icosahedral $Al_{40}Mn_{25}Fe_{10}Ge_{25}$ obtained at $T = 100$ K and 553 K are illustrated in figure 2. Dunlap *et al* [12] have shown that the Curie temperature T_C of these alloys is in the vicinity of 410 K for $x = 0$ and drops to the vicinity of 300 K for $x = 10$. Thus the two measurements shown in figure 2, spectra A and B, represent the situation well below and well above T_C, respectively. The measured crystallization temperature of this alloy is around 650 K [14]. We would, therefore, not expect that annealing at 553 K for the duration of the Mössbauer experiment would

Table 1. Results of fits using the method of Le Caer and Dubois [16] to the ^{57}Fe Mössbauer spectrum obtained in the paramagnetic region for $Al_{40}Mn_{25}Fe_{10}Ge_{25}$. δ is the isomer shift relative to α-Fe, Δ is the mean splitting and $\Gamma(\Delta)$ is FWHM of the distribution. The velocities are ± 0.005 mm s^{-1}.

Temperature (K)	δ (mm s^{-1})	Δ (mm s^{-1})	$\Gamma(\Delta)$ (mm s^{-1})
508	0.129	0.360	0.219
528	0.112	0.354	0.223
553	0.099	0.354	0.196

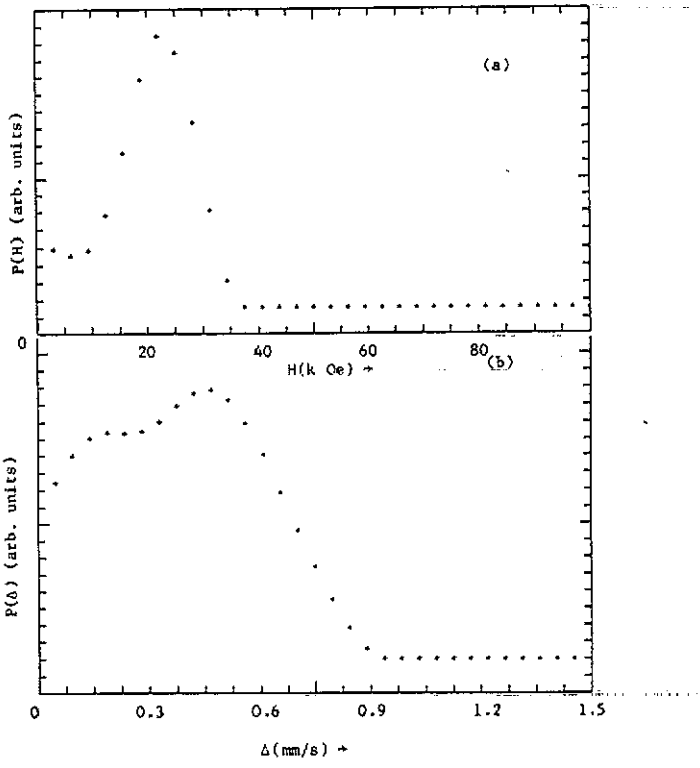

Figure 3. (*a*) Hyperfine field distribution for icosahedral $Al_{40}Mn_{25}Fe_{10}Ge_{25}$ at 100 K and (*b*) quadrupole splitting distribution of the same alloy at 553 K both obtained using the method of Le Caer and Dubois [16].

detrimentally affect the sample. In fact, the x-ray diffraction of a sample annealed at 553 K for several days was identical with that of the as-quenched sample. The broad Mössbauer spectra above T_C were fitted to a distribution of quadrupole splittings $P(\Delta)$ as has been used for other paramagnetic quasicrystals [15, 16]. Results of these fits are given in table 1 and a typical $P(\Delta)$ curve is illustrated in figure 3. As is typical of these materials [15], the quadrupole splitting distribution shows a non-zero component as

$\Delta \rightarrow 0$. This suggests that specific quadrupole distribution models which require that $P(0) = 0$, such as the shell model, are not appropriate for spectra of this type.

The Mössbauer spectra below T_C are observed to be similar in shape but broader than those obtained above T_C. This broadening could be due to the presence of a magnetic component. In earlier work we tried various fitting procedures and showed that a suitable fit could be obtained for other ferromagnetic Al–Mn–Cu–Fe–Ge quasicrystals below T_C by using a distribution of hyperfine fields [8]. More recently Stadnik and Stroink [11] reported similar experimental results but fitted their data to a distribution of quadrupole doublets such as they have previously used for diamagnetic quasicrystals. They have attributed the resulting misfit of the calculated spectrum to the presence of magnetic interactions. However, we believe that it is rather ambiguous to fit a Mössbauer effect spectrum of a ferromagnetic material below T_C to a distribution of quadrupole doublets and as indicated by Stadnik and Stroink [11] this does not allow for an estimate of the magnitude of magnetic component of the spectrum. The results of the distribution of hyperfine field fits (method 1 in table 2) are summarized in table 2 and a typical field distribution is shown in figure 3. In cases such as this where the Zeeman splitting is small, a more thorough analysis requires the inclusion of mixed quadrupole and magnetic dipole interactions. The implementation of such an approach is not straight forward and we have, in fact, approached the problem in several ways and we show here that these give consistent results.

Firstly we have taken the results of the fits above T_C as an indication of the magnitude of the quadrupole interaction in these materials. We see from table 1 that this is about 0.35 mm s^{-1} and shows no significant temperature variation. Using this value, we have generated Mössbauer effect spectra for different values of the magnetic hyperfine field on the basis of numerical solution to the Hamiltonian for a mixed interaction [17]. Results for simulated spectra are illustrated in figure 4. The general shape of the measured spectrum below T_C as seen in figure 2, spectrum A, can be reproduced for a hyperfine field of about 9.0 kOe.

A second approach to the analysis of spectra of this type is to apply the superoperator formalism proposed by Blaes *et al* [18] (method 2 in table 2). This method assumes an isotropic distribution of both magnetic hyperfine and electric quadrupole interactions. This means that the angle between the magnetic field direction and the principal axis of the electric field gradient is chosen to be the 'magic angle', 54.7°, as suggested by Grenche and Varret [19] for magnetically textured samples. The results for different fits to the room temperature $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ spectra are given in table 2 and a typical spectrum showing the fitted curve is given in figure 5.

The final method which we have employed is the exact Hamiltonian method proposed by Brand [20] (method 3 in table 2). This fit yields the mean hyperfine field, quadrupole splitting, linewidth and asymmetry parameter η, as given in table 2. On a statistical basis it is difficult to distinguish between the fits to a distribution of magnetically split sextets and that to combined quadrupole and hyperfine interactions. An analysis of the physical characteristics of the system, however, suggests that the latter is more reasonable.

The method of dealing with combined quadrupole and hyperfine magnetic interactions which have been described above have yielded consistent results which can be summarized in the following way.

(1) The quadrupole and magnetic hyperfine parameters are essentially independent of Fe content in the series of icosahedral alloys $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$.

(2) The internal hyperfine field is about 9 kOe.

Table 2. Fitting parameters for icosahedral $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ Mössbauer spectra at 100 K. Results are given for a distribution of magnetic splittings using the method of Le Caer and Dubois [16] (method 1), the method of Blaes *et al* [18] (method 2) and the exact Hamiltonian method [20] (method 3). For method 1 the linewidth was fixed at the intrinsic spectrometer linewidth of 0.24 mm s^{-1} (FWHM).

	Method 1			Method 2				Method 3				
x	δ (mm s^{-1})	$\bar{H}$ (kOe)	$\langle H \rangle$ (kOe)	δ (mm s^{-1})	H (kOe)	Δ (mm s^{-1})	Γ (mm s^{-1})	δ (mm s^{-1})	H (kOe)	Δ (mm s^{-1})	Γ (mm s^{-1})	η
3	0.328	20.33	13.12	0.304	7.20	−0.367	0.326	0.301	9.40	−0.303	0.303	0.946
6	0.335	20.15	12.47	0.316	9.68	−0.367	0.306	0.316	10.56	−0.335	0.307	0.503
10	0.351	17.98	7.33	0.332	9.73	−0.351	0.304	0.332	10.26	−0.338	0.303	0.241

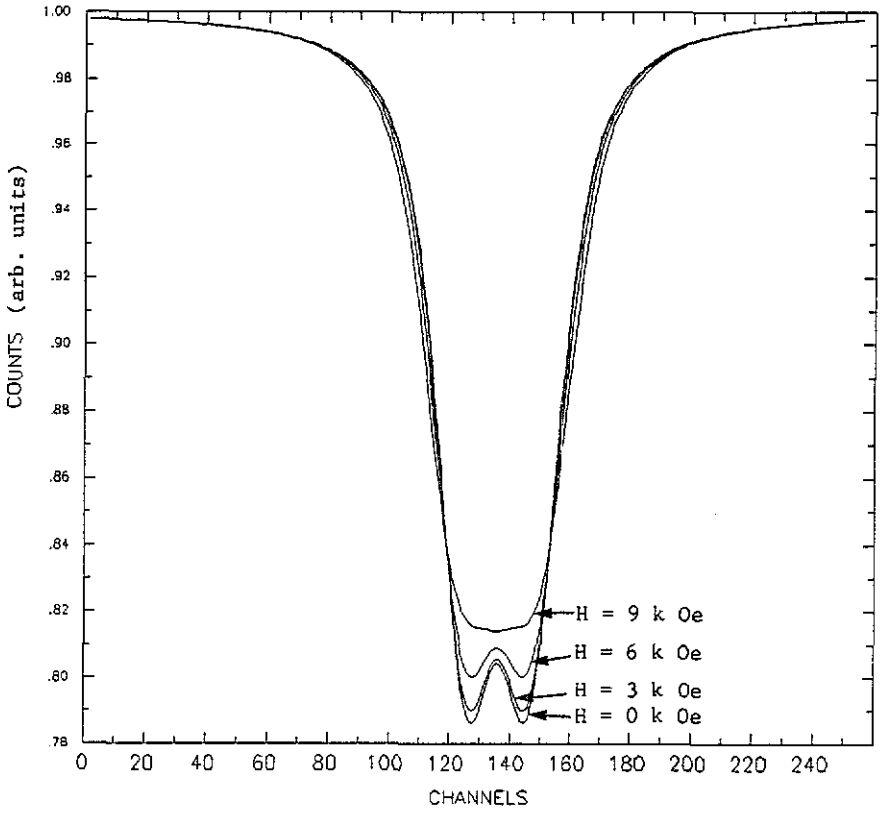

Figure 4. Simulated Mössbauer spectra for $\Delta = 0.35$ mm s^{-1} and different values of the internal magnetic field.

(3) The quadrupole splitting is about 0.33 mm s^{-1}.
(4) The sign of the quadrupole interactions is negative.

The magnitude of the quadrupole splitting obtained for fits to the ferromagnetic spectrum is consistent with the value obtained from fits to the spectra in the paramagnetic region. Also, the sign of the quadrupole splitting is the same as that obtained on the basis of previous in field Mössbauer measurements on paramagnetic quasicrystals [21]. It is interesting, however, that the mean hyperfine field found from this fit, 9.2 kOe, is significantly less than that obtained from the fit to the magnetically split spectrum without quadrupole interactions. This is expected since, in the former case, part of the broadening of the resonance peak was accounted for by the quadrupole interaction while, in the latter case, it must be accounted for entirely by the magnetic interaction.

A final interesting point has to do with the composition dependence of the Mössbauer parameters for these alloys. The hyperfine field at an Fe probe is given as the sum of two contributions: firstly a local contribution due to any magnetic moment carried by the Fe atom and secondly a transferred contribution due to the polarization of the conduction band by ferromagnetically coupled neighbouring moments. Since the Fe magnetic field does not change as Fe is substituted for Cu in the $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ series, it is reasonable to assume that the Fe hyperfine field in these materials is primarily due to

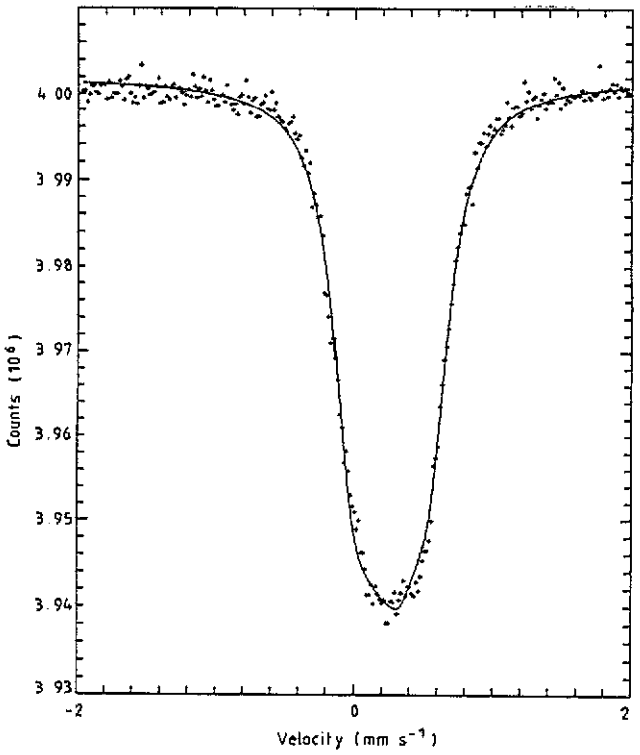

Figure 5. ^{57}Fe Mössbauer effect spectrum of icosahedral $Al_{40}Mn_{25}Fe_{10}Ge_{25}$ at 100 K showing the least-squares fit (——) to combined quadrupole and magnetic interactions using the method of Blaes *et al* [18] for an angle θ of 54.7°.

the transferred contribution, in this case from moments residing on ferromagnetically coupled Mn. In other words, it is likely that the local Fe moment is small or non-existent. In fact a calculation of the local Fe moment on the basis of the usual moment-to-field relationship for ferromagnetically coupled Fe atoms gives a local moment in these alloys of about $0.06\mu_B$. This concept of non-magnetic Fe sites in these ferromagnetic quasicrystals is consistant with the picture of non-moment-carrying Fe in paramagnetic Al-based quasicrystals proposed by Eibschutz *et al* [22].

It is informative to compare the present results with those obtained for analogous crystalline materials. In this case tetragonal AlMnGe shows magnetic behaviour which is similar to that of its icosahedral counterpart. Mössbauer effect studies on this crystalline alloy have been reported [23, 24] and these show a broadening of the spectral line at low temperatures indicative of weak ferromagnetic behaviour. However, the linewidths for the crystalline alloy are much smaller than those for the quasicrystalline alloys and this can be understood on the basis of intrinsic disorder in the icosahedral materials.

The present results can be summarized as follows.

(1) Mössbauer effect measurements show a small hyperfine field at Fe sites in the present series of samples.

(2) Mössbauer spectra are satisfactorily fitted to a distribution of quadrupole doublets above T_C and to combined magnetic and quadrupole interactions below T_C.

(3) The magnitude of the Fe hyperfine field and the lack of composition dependence of these results suggest that Fe atoms in these alloys do not carry a magnetic moment.

The presence of a transferred component of the hyperfine field at Fe sites in these alloys below T_C indicates that there is a net spontaneous spin alignment in the so-called ferromagnetic region. It is possible that competing interactions result from the inherent disorder of the quasicrystalline phase to produce a small apparent ferromagnetic moment. It would seem that this effect is present to a greater extent in ferromagnetic Al–Mn–Si quasicrystals which show behaviour which in many ways [10] is characteristic of principally spin-glass ordering and to a lesser extent in the more strongly ferromagnetic Al–Mn–Ge-based quasicrystals.

Acknowledgments

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