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Structural relaxation in icosahedral $Al_{65}Cr_{10}Fe_{10}Ge_{15}$

D Bahadur†, V Srinivas and R A Dunlap
Department of Physics, Dalhousie Uniersity, Halifax, Nova Scotia B3H 3J5, Canada

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Abstract. Rapidly solidified $Al_{65}Cr_{10}Fe_{10}Ge_{15}$ is found to be of the quasi-crystalline structure with icosahedral symmetry. ^{57}Fe Mössbauer effect measurements suggest a disordered arrangement of transition-metal atoms in the as-quenched alloy. Thermal analysis measurements indicate a structural relaxation at approximately 700 K, and x-ray and Mössbauer effect measurements suggest that this represents primarily changes in the chemical short-range order of the alloy, yielding a more ordered structure.

1. Introduction

Since the icosahedral structure was first reported in a rapidly quenched Al–Mn alloy (Shechtman *et al* 1984), a number of attempts have been made to understand the reasons for preferential broadening of the x-ray diffraction lines (Bancel and Heiney 1986, Goldman and Stephens 1988, Socolar and Wright 1987). These features, which are due to some inherent disorder in quasi-crystals, have been explained in terms of phason and phonon strains (Goldman and Stephens 1988, Socolar and Wright 1987, Lubensky *et al* 1986). Thermal measurements, differential thermal analysis (DTA) or differential scanning calorimetry may, in principle, indicate the relaxation of some types of disorder (if they are not very stable) by the presence of small endothermic and/or exothermic peaks in addition to the crystallisation exotherm. Generally, such behaviour has not been reported in quasi-crystals. Recently, however, there have been reports of such endothermic and/or exothermic peaks before the crystallisation temperature (Luck *et al* 1986, Inoue *et al* 1988), and these have been attributed to relaxation phenomena similar to those found in rapidly quenched metallic glasses (Greer 1982). Although structural relaxation cannot be easily demonstrated through direct structural techniques in metallic glasses, its observation could be more straightforward in quasi-crystals, where well defined sharp diffraction lines are observed in the x-ray and electron diffraction patterns. Mukhopadhyay *et al* (1987) have recently studied structural relaxation in Al–Mn quasi-crystals through electron diffraction techniques, and Chen *et al* (1985) have studied similar phenomena using specific heat and Young's modulus measurements. Very recently, Inoue *et al* (1988) have reported enthalpy relaxation behaviour in Al–Cr–Si quasi-crystals using calorimetry.

In this paper, we report the results of a detailed study of structural relaxation in the icosahedral alloy $Al_{65}Cr_{10}Fe_{10}Ge_{15}$, using x-ray diffraction and Mössbauer effect measurements.

† Permanent address: Advanced Centre for Materials Science, Indian Institute of Technology, Kanpur, India 208016.

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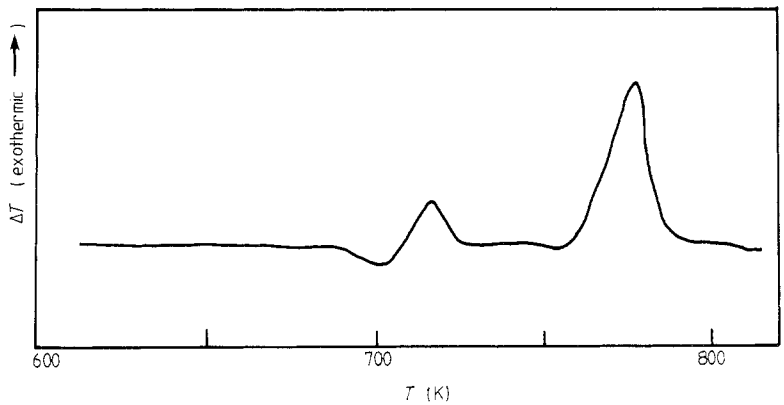

Figure 1. The DTA of quasi-crystalline $Al_{65}Cr_{10}Fe_{10}Ge_{15}$ obtained at a heating rate of 20 K min^{-1}.

2. Experimental methods

A single-phase quasi-crystalline $Al_{65}Cr_{10}Fe_{10}Ge_{15}$ alloy has been prepared by rapid quenching using the method of McHenry *et al* (1988) for other Al-based icosahedral alloys. The DTA measurement has been performed on a Fisher 260F thermal analyser using a heating rate of 20 K min^{-1}. X-ray diffraction measurements were performed on a Siemens scanning diffractomer, using Cu Kα radiation. Room-temperature ^{57}Fe Mössbauer effect measurements were made using a $Pd^{57}Co$ source and a Wissel System II spectrometer with an intrinsic ^{57}Fe linewidth of 0.23 mm s^{-1}.

3. Results and discussion

The DTA scan of the $Al_{65}Cr_{10}Fe_{10}Ge_{15}$ quasi-crystal illustrated in figure 1 exhibits a small endothermic peak with a minimum near 700 K, a small exothermic peak with a maximum near 715 K and a large exothermic peak, due to crystallisation, with a maximum at 775 K. It may be pointed out that these extra peaks have been found for all the samples of the series $Al_{65}Cr_{20-x}Fe_xGe_{15}$ ($0 \leqslant x \leqslant 17.5$). The presence of such peaks is uncommon in quasi-crystals, and, analogous to the situation in amorphous materials, it could indicate relaxation of some type of disorder (Luck *et al* 1986, Inoue *et al* 1988). This DTA feature was investigated by annealing the sample at 700 K for 15 min. This is the temperature of the endothermic position of the DTA feature prior to the crystallisation peak.

The x-ray diffraction and Mössbauer effect measurements of the annealed sample exhibit interesting changes. Figure 2 illustrates the x-ray diffraction pattern of the as-quenched and annealed $Al_{65}Cr_{10}Fe_{10}Ge_{15}$ samples. The indexing scheme of Bancel *et al* (1985) has been used to identify the Miller indices of the icosahedral reflections. Table 1 gives the q-values, indices and intensities of the various diffraction lines. We observe that annealing produces significant changes in the x-ray diffraction patterns. These are as follows.

(i) A few additional diffuse lines appear.
(ii) The line positions shift to lower q-values after annealing.
(iii) There are small changes in the relative intensities of the lines.

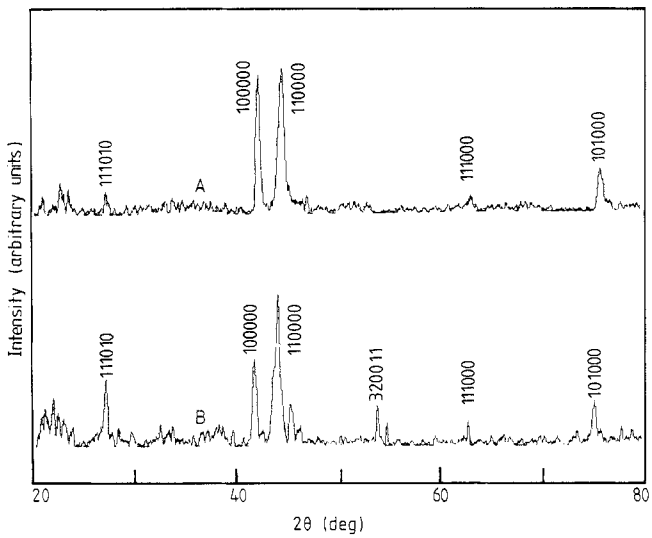

Figure 2. X-ray diffraction patterns of quasi-crystalline $Al_{65}Cr_{10}Fe_{10}Ge_{15}$: curve A, as quenched; curve B, annealed at 700 K for 15 min.

Table 1. q-values and relative intensities for the major icosahedral reflections in as-quenched and annealed $Al_{65}Cr_{10}Fe_{10}Ge_{15}$.

	As quenched		Annealed	
Indices	q (nm^{-1})	I (relative units)	q (nm^{-1})	I (relative units)
111010	19.10	16	19.12	44
100000	29.28	95	29.04	59
110000	30.80	100	30.56	100
111000	42.43	10	42.30	15
101000	49.76	29	49.48	28

Mukhopadhyay *et al* (1987) also observed some weak diffuse spots in the electron diffraction patterns of Al–Mn quasi-crystals when annealed at 600 K (considerably below the crystallisation temperature). They have attributed these to short-range order in the icosahedral phase prior to crystallisation. However, they did not observe any change in the positions of the diffraction spots nor in their intensities. We, also, did not find any shift in the x-ray line positions when we recently annealed icosahedral $Al_{74}Mn_{20}Si_6$ at about 50 K below the crystallisation temperature for about 40 min (Bahadur *et al* 1988). For the present samples, however, an appreciable shift in the x-ray diffraction lines has been found on annealing. Interestingly, this sample exhibited an extra endothermic and exothermic peak in the DTA scan which was not found for the two samples mentioned above (Mukhopadhyay *et al* 1987, Bahadur *et al* 1988). Disorder in the present sample is very evident in terms of the preferential x-ray line broadening. Therefore, it seems likely that the extra peaks in the DTA scans signify structural relaxation involving some type of short-range order. Two kinds of short-range order are known:

(i) Topological short-range order (TSRO) and
(ii) chemical short-range order (CSRO).

The endothermic peak signifies changes in CSRO, whereas the exothermic peak signifies changes in TSRO. Changes in TSRO, which generally follow changes in CSRO, involve

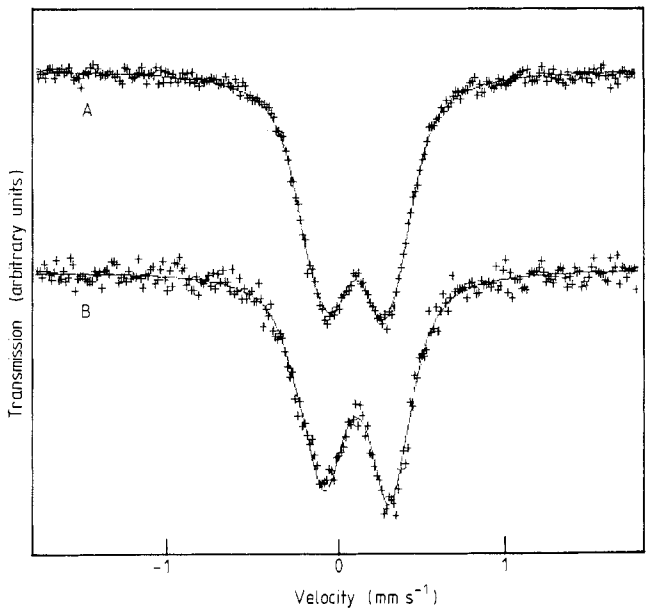

Figure 3. Room-temperature ^{57}Fe Mössbauer effect spectra of $Al_{65}Cr_{10}Fe_{10}Ge_{15}$: curve A as quenched; curve B, annealed at 700 K.

variations in the atomic positions and a reduction in the free volume, if any. This may lead to changes in the structure factor. Changes in CSRO, on the contrary, deal with changes in the local surroundings and may affect the coordination and inter-atomic distances. Since the present sample has been annealed for a short time (15 min) at the onset of the small endothermic peak, it is expected that changes in CSRO may be the important factor. However, changes in TSRO cannot be completely ruled out, as indicated by changes in the x-ray line intensities (i.e. structure factor changes are indicated). A significant shift of line positions to lower q-values would indicate an increase in inter-atomic distances due to CSRO. A similar observation has been made by Egami (1978), while studying structural relaxation in amorphous $Fe_{40}Ni_{40}P_{14}B_6$. Therefore, the development of short-range order is evident from the evolution of a few diffuse weak diffraction lines, from the shift in q-values of the x-ray lines and from the presence of the small endothermic and/or exothermic peaks in the DTA scans prior to the crystallisation temperature. It may be pointed out that the ordering, or relaxation in the present case, is much more significant than that observed, for example, in an Al–Mn quasi-crystal by Mukhopadhyay *et al* (1987). Obviously the disorder or strain introduced during quenching in the former system is much greater than in the latter.

Since changes in the short-range order appear significant in the annealed sample, we utilised the presence of Fe in this alloy by performing Mössbauer effect measurements to obtain more information about the structural relaxation.

^{57}Fe Mössbauer spectra of as-quenched and annealed (structurally relaxed) samples of the composition $Al_{65}Cr_{10}Fe_{10}Ge_{15}$ are shown in figure 3. Both spectra show asymmetric quadrupole split doublets. In order to obtain information concerning average values of the Mössbauer parameters, we have fitted these two spectra to two Lorentzian lines. Results of these fits are given in table 2. It is interesting to note that the spectral asymmetry, indicated by the ratios A_1/A_2 of the areas of the two lines is greater than unity for both as-quenched and annealed samples. While it is customary to observe

Table 2. Mean ^{57}Fe Mössbauer effect parameters obtained by fits to Lorentzian lines. δ is the isomer shift relative to α-Fe, Δ the quadrupole splitting, Γ_i the linewidths and A_i the line areas.

Alloy	δ (mm s^{-1})	Δ (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	A_2/A_2
As quenched	+0.232	0.399	0.392	0.364	1.083
Annealed	+0.223	0.454	0.398	0.310	1.140

$A_1/A_2 < 1$ in icosahedral alloys (see, e.g., Schurer *et al* 1986), this is by no means a universal feature of ^{57}Fe Mössbauer effect spectra as evidenced by the present measurements, as well as by measurements by Stadnik and Stroink (1988) on Al–Fe–Cu. The excessive linewidths in these alloys are characteristic of quasi-crystalline materials and are indicative of more than a single well defined Fe site.

The question of the distribution of quadrupole splittings in quasi-crystals has been considered by a number of researchers (see, e.g., Dunlap *et al* 1988, Eibschütz *et al* 1986, 1987, Swartzendruber *et al* 1985, Schurer *et al* 1986, 1988, van der Woude and Schurer 1987, Stadnik and Stroink 1988). While some workers have suggested an analysis based on two discrete Fe sites, either with similar isomer shifts (see, e.g., Swartzendruber *et al* 1985, Schurer *et al* 1986, 1988) or with similar quadrupole splittings (see, e.g., Dunlap *et al* 1988), others have used a distribution of splittings given by the shell model (Czjzek *et al* 1985), and correlated to an isomer shift distribution (see, e.g., Eibschütz *et al* 1986, Stadnik and Stroink 1988). The excessive linewidths obtained from fits to two discrete lines indicate that, if indeed the spectra are defined by two 'classes' of sites, these classes contain, as a result of disorder, distributions of Δ-values. Rather than assuming *a priori* any form of the quadrupole distribution $P(\Delta)$, we have implemented the method of LeCaer and Dubois (1979), which expands $P(\Delta)$ as a discrete series in Δ. This distribution has been correlated to an isomer shift distribution by a linear relationship

$$\delta = \delta_0 + \alpha\Delta. \tag{1}$$

This method avoids difficulties caused by unphysical features in $P(\Delta)$ sometimes encountered when using Fourier expansion methods based on that of Window (1971).

Figure 4 illustrates $P(\Delta)$ obtained for the as-quenched and annealed samples. Using 32 discrete steps between $\Delta = 0$ and 1.0 mm s^{-1} has been found to yield good results. The intrinsic linewidth of the component spectra has been fixed to be 0.23 mm s^{-1} (FWHM). As can be seen in the figure, the as-quenched sample yields a $P(\Delta)$ bimodal structure. Although the details of this $P(\Delta)$ are somewhat sensitive to the fixed parameters of the fit, it is a general feature of fits obtained for this spectrum that $P(\Delta)$ is highly structured with well defined peaks. On annealing at a temperature which produces structural relaxation, however, the major peak in $P(\Delta)$ shifts to larger Δ and the distinction between the peaks of the bimodal distribution becomes lost. Parameters from the fits given in equation (1) are given in table 3. This single peaked $P(\Delta)$ is a feature common to all fits, regardless of fixed parameter values, for this spectrum. The most significant feature of these fitted parameters is a significant increase in α caused by annealing. This is obvious as well from the increased spectral asymmetry seen in figure 3.

While the distribution in figure 4(*b*) for the annealed sample may be closely approximated by a shell-model-like function, the distribution for the as-quenched alloy, as shown in figure 4, clearly cannot.

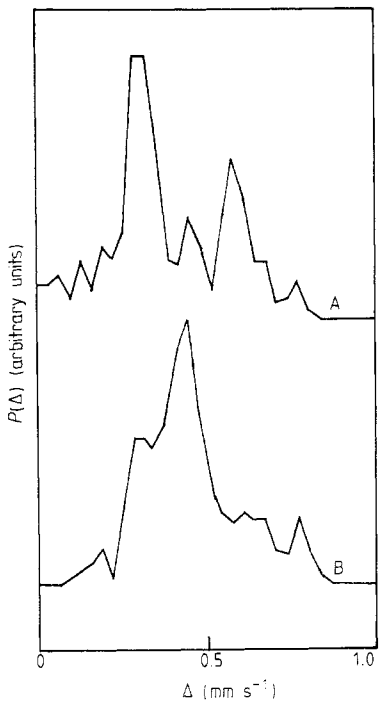

Figure 4. Quadrupole splitting distributions $P(\Delta)$ obtained as described in the text, for quasi-crystalline $Al_{65}Cr_{10}Fe_{10}Ge_{15}$: curve A, as quenched; curve B, annealed at 700 K.

Table 3. Mössbauer parameters obtained from the analysis of icosahedral $Al_{65}Cr_{10}Fe_{10}Ge_{15}$ spectra using the method of LeCaer and Dubois (1979).

Sample	δ_0 (mm s^{-1})	α
As quenched	+0.206	−0.044
Annealed	+0.195	−0.122

The bimodal nature of $P(\Delta)$ in figure 4 curve A, is consistent with fits of other quasi-crystal Mössbauer spectra which here suggest the existence of more than one distinct class of site. The widths of the peaks in the $P(\Delta)$ distribution, as well, are consistent with the broadened lines observed in the conventional two-site analysis. A comparison of the distributions in figure 4 suggests that generalisations concerning appropriate fitting methods for ^{57}Fe Mössbauer spectra of quasi-crystals can be dangerous. It is, however, not surprising to find significant differences between the $P(\Delta)$ for as-quenched and structurally relaxed samples of the same alloy. Since thermal and x-ray measurements have indicated the existence of CSRO changes, as a result of structural relaxation in this alloy, modifications in the distribution of Fe neighbour environments, and hence in $P(\Delta)$, are not unexpected. The reasons for two classes of transition-metal sites in quasi-crystals, on the basis of atomic-size effects, has recently been discussed in detail by Eibschütz *et al* (1988) and Lawther *et al* (1988). These models propose that the two classes of transition-metal sites are distinguished, at least in part, on the basis of size. The present results are consistent with a model in which the CSRO of the as-quenched alloy contains Fe atoms on both small and large transition-metal sites. Changes in the CSRO which results from structural relaxation yield a more ordered structure where Fe primarily occupies only a single (the smaller) class of transition-metal site.

The present analysis indicates that as-quenched quasi-crystalline $Al_{65}Cr_{10}Fe_{10}Ge_{15}$ is disordered and that, on heating to approximately 700 K, results in changes in the CSRO and possibly the TSRO as well, which produces a more ordered structure. This interpretation is consistent with $P(\Delta)$ obtained from Mössbauer measurements and structural models based on two classes of transition-metal sites, as proposed by Eibschütz *et al* (1988) and Lawther *et al* (1988).

Acknowledgments

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