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A positron annihilation study of vacancy-type defects in Al–Cu–Fe quasicrystals

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Abstract. A positron annihilation study of the icosahedral Al–Cu–Fe alloy system has been carried out using both Doppler broadening and lifetime measurement techniques. Isochronal annealing studies show that a nearly unchanged two-component lifetime spectrum is obtained up to the highest annealing temperature of 450 °C used in the present work, indicating the stability of the structure and the defect state in this quasicrystalline phase up to this annealing temperature. The vacancy defect concentration is about 8 ppm which is higher than that observed in our earlier study on icosahedral Al–Mn–Si, though the vacancy size is lower—approximately a monovacancy size on average in Al–Cu–Fe against a divacancy size in Al–Mn–Si. The existence of such a high concentration of vacancy defects even in quasicrystalline Al–Cu–Fe, which has little phason disorder, should be significant from the point of view of developing a structural model for quasicrystals. It appears that a two-component positron lifetime spectrum indicative of a high concentration of vacancy-type defects is characteristic of the icosahedral quasicrystalline phase. The possibility of a central hole in the icosahedral building block in this phase is ruled out from our positron annihilation experiments.

1. Introduction

The icosahedral point group symmetry exhibited by rapidly solidified alloy systems like Al–Mn [1], Al–Mn–Si [2], Al–Zn–Mg [3] etc and some others like Al–Cu–Li [4] produced by slow ingot casting can be interpreted with varying degrees of success by more than one structural model. Pauling [5] has felt that the long-range icosahedral order found in quasicrystals can be interpreted in terms of icosahedrally twinned grains of ordinary crystals. The 'icosahedral quasicrystal' model of Levine and Steinhardt [6] is based on the Penrose tiling model. In the 'icosahedral glass' model of Stephens and Goldman [7] icosahedral clusters of atoms are randomly packed, but neighbouring clusters share their symmetry axes in such a way that the clusters are oriented parallel to one another. In our earlier positron annihilation study of the icosahedral Al–Mn–Si alloy system [8], we showed the existence of approximately divacancy-sized vacancy clusters with a concentration of about 3 ppm which disappear on transformation by heating to the crystalline phase. It could be concluded from this study that space-filling models based

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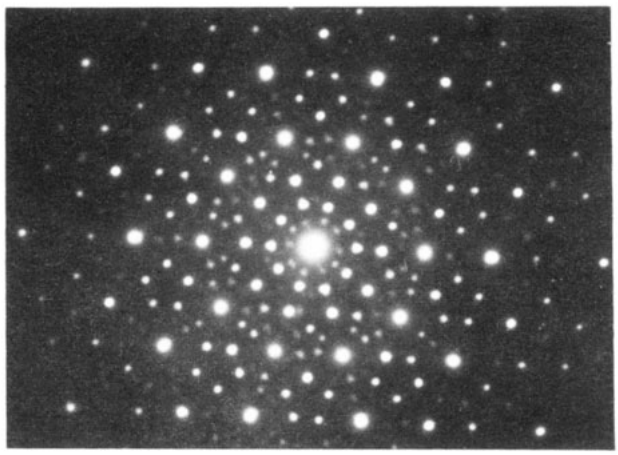

Figure 1. The electron diffraction pattern of the Al–Cu–Fe sample taken in a Philips TEM operating at 120 kV, showing fivefold symmetry (taken by S Raghunathan).

either on twinning or on Penrose tiling cannot easily explain the existence of these vacancy-type defects.

A new class of quasicrystals based on the Al–Cu–Fe alloy system has been discovered more recently [9] and has been found to be nearly free of phason disorder [10]. From EXAFS measurements [11], it has been shown that the local structure in Al–Cu–Fe is different from that in other quasicrystals and that the Fe and Cu atoms do not occupy the same sites at random. The same conclusion is drawn from electron channelling experiments [12]. This phase has a direct-space lattice which is a face-centred icosahedral (FCI) lattice [9] in contrast to the simple icosahedral (SI) lattice observed in other quasicrystals. However, it has been suggested recently [13] that the FCI quasicrystals can be interpreted in terms of superlattice ordering in SI quasicrystals. The strange behaviour of the Al–Cu–Fe alloy system [14] on annealing around 600 °C, as indicated by an increase in diffraction peak widths and a subsequent decrease on annealing at higher temperatures etc, is intriguing though an attempt has been made to explain similar results in terms of what the author calls 'dynamical phasons' [15].

It was felt that it would be interesting to carry out a positron annihilation study of the defect state in Al–Cu–Fe quasicrystals in order to see how the near-absence of phason disorder influences the size and concentration of vacancy-type defects.

2. Experimental details

The quasicrystalline ribbon samples (of width 3 mm and thickness about 30 μm) of the alloy of starting ingot composition $Al_{65}Cu_{20}Fe_{15}$ made of high purity constituents, were obtained by Dr V S Raghunathan (Indira Gandhi Centre for Atomic Research, Kalpakkam) by melt spinning in an argon atmosphere. The quasicrystalline character of the ribbons was verified by electron diffraction (see figure 1) though there are some small quantities of co-existing crystalline phases [16]. Raghunathan *et al* [16] also carried out microchemical analysis of the quasicrystalline phase using a LINK Analytical 10/85 S EDX system attached to the Philips EM400T transmission electron microscope and

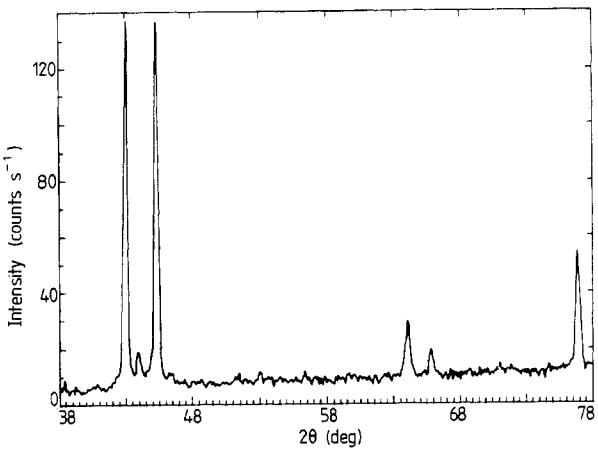

Figure 2. The x-ray diffraction pattern of the Al–Cu–Fe sample taken with Cu Kα radiation from a rotating anode x-ray generator with graphite monochromator. The observed values of q defined as $2\pi \sin\theta/\lambda$ are 1.491, 1.521, 1.561, 2.16, 2.214 and 2.535; these match well with published patterns in the literature.

found the approximate final composition to be $Al_{61}Cu_{23}Fe_{16}$. The sample which was powdered from the ribbons and used in our experiments is mostly quasicrystalline as seen from the x-ray diffraction pattern shown in figure 2. The experimental techniques for the Doppler broadening and lifetime measurements and the data analysis procedures are identical to those described earlier [8] for our study of the icosahedral Al–Mn–Si alloy system. The isochronal annealing of the samples was done from 100 °C up to 450 °C at intervals of 50 °C in an argon atmosphere (400 mm of Hg). The annealing was carried out alongside the positron source (in the form of NaCl) in order to have a stable source specimen geometry [17]; annealing beyond 450 °C was not carried out in view of possible sublimation of NaCl. The annealing time was 10 minutes at each temperature and the sample was then slowly cooled. All the positron annihilation measurements were done at room temperature.

3. Results and discussion

The variations of the S parameter and the mean positron lifetime τ_m as functions of the isochronal annealing temperature are shown in figure 3. The S parameter is defined as the ratio of the area under the central channels in the Doppler-broadened spectrum to the total area under the annihilation curve. In our earlier studies on Al–Mn–Si [8], and on Al–Mn [17], the S parameter showed a smooth and continuous fall from an annealing temperature of 200 °C or so, and then stabilised out as the crystallization process was completed. On the contrary, it can be seen from figure 3 that, in the case of Al–Cu–Fe, the variation in the S parameter is much smaller (less than 1%) over the annealing temperature range up to 450 °C. The constancy of the S parameter implies a constancy in the electron momentum distribution and thus confirms the stability of the quasicrystalline phase over the temperature range.

The lifetime spectra are shown in figure 4. There is very little difference between the lifetime spectrum of the as-grown quasicrystals and the spectra for the various annealing

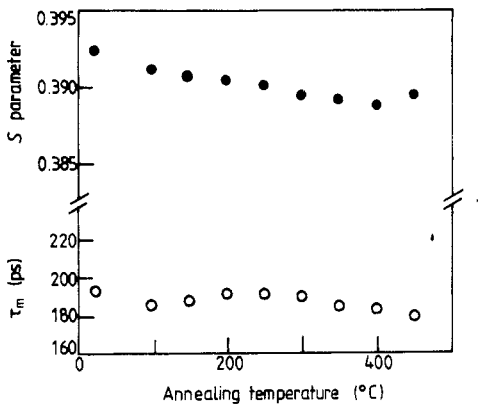

Figure 3. The Doppler broadened annihilation lineshape parameter S and the mean lifetime τ_m of i-$Al_{61}Cu_{23}Fe_{16}$ as a function of annealing temperatures. The typical errors in S and τ_m are about 0.0008 and 2 ps respectively.

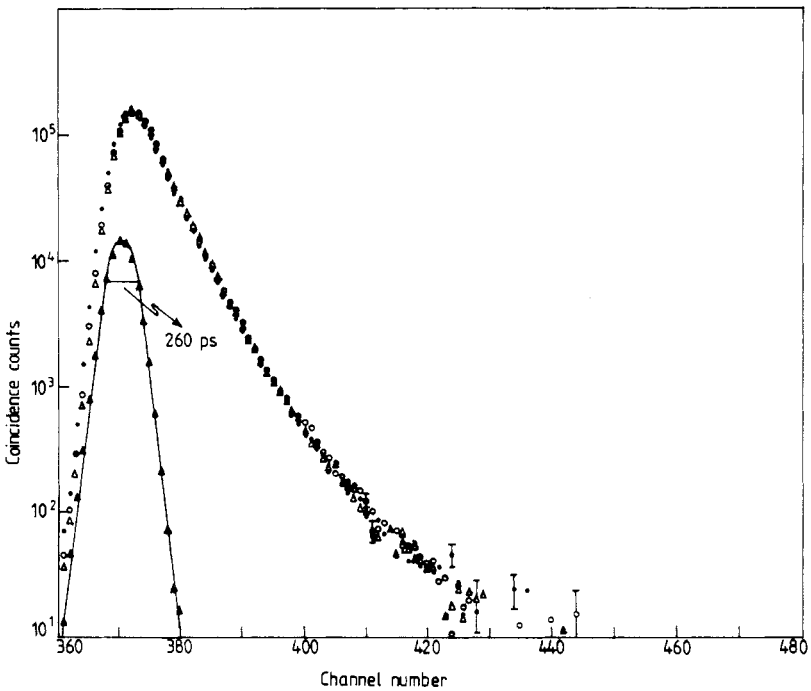

Figure 4. Positron lifetime spectra of i-$Al_{61}Cu_{23}Fe_{16}$: as-grown (●), annealed at 250 °C (○) and annealed at 450 °C (△). The three spectra have been peak-normalized. The prompt time resolution curve taken with ^{60}Co is also shown (▲). (1 channel = 50 ps.)

temperatures. This fact, coupled with the near-constancy of the mean positron lifetime τ_m as seen from figure 3, is indicative of a stability in the electron distribution and the defect state over this range of annealing temperatures.

The lifetime spectra could be analysed in terms of two components τ_1 and τ_2 with relative intensities I_1 and I_2 which are given in table 1 along with values of τ_m and S. It can be seen that the two components persist with approximately the same values of τ_1 and τ_2 and similar relative intensities up to the highest annealing temperature of 450 °C.

Table 1. Results of positron annihilation lineshape and lifetime measurements on the quasicrystalline sample i-$Al_{61}Cu_{23}Fe_{16}$; typical errors are: in τ_1 and $\tau_2 \sim 4$ ps, in I_1 and $I_2 \sim 3\%$, in $\tau_m \sim 2$ ps and in $S \sim 0.0008$. VOF is the variance of fit, which should be unity in the absence of systematic errors.

Annealing temperature (°C)	VOF	τ_1 (ps)	τ_2 (ps)	I_1 (%)	I_2 (%)	τ_m (ps)	S
As-grown	1.01	150	238	50	50	194	0.3924
100	1.03	121	231	41	59	186	0.3913
150	1.29	124	234	42	58	188	0.3907
200	1.26	143	248	53	47	192	0.3903
250	1.30	146	247	55	45	192	0.3901
300	1.00	141	242	51	49	190	0.3895
350	1.07	121	234	44	56	185	0.3892
400	1.10	117	227	40	60	183	0.3888
450	0.97	112	226	40	60	180	0.3896

This should be contrasted with the results on the Al–Mn–Si alloy system [8, 18] where, on crystallization, the lifetime spectrum could be fitted on the basis of a single component.

The second-higher lifetime component indicates the presence of vacancy-type defects in the quasicrystalline phase, as in the Al–Mn–Si alloy. We have ruled out the possibility that the larger lifetime component might arise from surface effects in the powder samples used. For example, Morinaga [19] found from his work on sintering of ultrafine silver particles (about 700 Å mean diameter) that the positron annihilation angular correlation curves become similar to those of bulk silver with increasing degreee of sintering. He estimated from his results that the 'critical diameter' of silver for this to happen would be a few thousand Å. The mean positron diffusion lengths are in the range of 0.1–0.2 μm [20] and it is obvious that particles would have to be about 1 μm or less for surface effects to be significant [21]. In our experiments the particle size is about 30 μm and hence surface effects are not important in the present context.

To calculate the size and concentration of the vacancy clusters in our study of Al–Mn–Si alloys [8], the lifetimes were analysed using the two-state trapping model [22]. In this model, it is assumed that annihilations can only occur from either the positron bulk state (τ_1) or the positron trap state (τ_2), giving rise to a two-component lifetime spectrum. The analysis requires a value for τ_b, the positron lifetime in the defect-free bulk material. In an analysis of the data on the Al–Mn–Si alloy system [8], τ_b was taken as the value of the single-component lifetime observed in the reference crystalline phase. Since in the present Al–Cu–Fe alloy system, the transformation to a crystalline phase does not take place, a reference value for τ_b is not available.

Hence to obtain an approximate value for the vacancy size in the present system, the following procedure was adopted. τ_b and the trapping rate K in the defects can be expressed in terms of the experimentally measured parameters τ_1, τ_2, I_1 and I_2:

$$\tau_b = \tau_1\tau_2/(\tau_1 I_2 + \tau_2 I_1) \tag{1}$$

and

$$K = I_2(1/\tau_1 - 1/\tau_2). \tag{2}$$

Using the average values of $\tau_1 = 131$ ps, $\tau_2 = 236$ ps, $I_1 = 0.46$ and $I_2 = 0.54$ as obtained in our experiments we get

$$\tau_b = 172 \text{ ps} \qquad K = 0.00192 \text{ ps}^{-1}.$$

The average value of $\tau_2 - \tau_b$ is obtained as 64 ps, while the value expected from calculations [23] in Al is 83 ps for a monovacancy. We have seen from our analysis of the Al–Mn–Si data that the above method tends to predict too high a value of τ_b. A similar procedure applied to the Al–Mn–Si data in the quasicrystalline phase gives 177 ps instead of the experimentally observed value of 158 ps in the reference crystalline phase. Hence we tend to believe that the average vacancy size in the quasicrystalline phase of Al–Cu–Fe is approximately that of a monovacancy. Using the calculated value [24] for the specific trapping rate μ of 2.5×10^{14} s^{-1}, the defect concentration $C = K/\mu$ comes out as about 8 PPM.

It has been pointed out by us [8] from our study of the Al–Mn–Si alloy system that the existence of more than one component in the lifetime spectrum rules out the postulated central hole [25] in the icosahedral building block for the quasicrystalline phase. Such a hole with a radius of about 90% of that of a monovacancy would have acted as a saturation trap for positrons and given a single-component lifetime spectrum. For the same reason, and from the fact that we get a two-component lifetime spectrum here, we can again rule out the possibility of a central hole in the icosahedral building block forming the quasicrystalline structure in Al–Cu–Fe.

4. Conclusion

It is very interesting to note that the quasicrystals of Al–Cu–Fe with very little phason disorder also show a two-component positron annihilation lifetime spectrum like the quasicrystalline phases of Al–Mn–Si and Al–Mn. The large vacancy defect concentration of about 8 ppm with a vacancy size approximately that of a monovacancy deduced from our data is more compatible with the icosahedral glass model (with suitable modifications) than with space-filling models like the icosahedral quasicrystal model or the icosatwinning model. It is also interesting—and significant from the point of view of developing an atomic structure model for quasicrystals—that quasicrystalline Al–Cu–Fe shows a higher vacancy concentration compared to quasicrystalline Al–Mn–Si (8 ppm against 3 ppm) though the vacancy size in the former is about half that in the latter. The vacancy defects in the quasicrystalline phase are likely to be in the regions connecting the icosahedral atomic clusters rather than in the clusters themselves.

In any case, it appears that a two-component positron lifetime spectrum indicative of a high concentration of vacancy-type defects is characteristic of the icosahedral quasicrystalline phase. We are carrying out further positron annihilation studies of the anomalous annealing behaviour in the temperature region 600–825 °C.

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