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^{57}Fe Mössbauer and positron lifetime studies of Al–Cu–Fe quasicrystals

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Abstract. $Al_{61\cdot4}Cu_{22\cdot7}Fe_{15\cdot9}$, $Al_{63\cdot2}Cu_{21\cdot8}Fe_{15}$ and $Al_{71}Cu_{14}Fe_{15}$ have been studied by Mössbauer, positron annihilation and X-ray diffraction techniques. The positron lifetime, measured as a function of temperature, in $Al_{61\cdot4}Cu_{22\cdot7}Fe_{15\cdot9}$ shows a two-step increase. This is found to be due to the dynamics of phasons associated with Al and Cu, having activation energies of 0·43 eV and 0·78 eV respectively. In the case of $Al_{71}Cu_{14}Fe_{15}$, a phase transformation from the quasicrystalline–crystalline phase at ≈ 550°C is observed.

Keywords. Quasicrystal; icosahedral phase; Mössbauer spectroscopy; positron annihilation; phasons.

1. Introduction

Despite a large number of studies on quasicrystals (QCs), interest in this class of materials continues to persist. Many questions regarding the atomic positions, degree of phase stability, physical properties etc in these materials are not completely answered. Al–Cu–Fe is a family of ternary alloys that exhibits a complex phase diagram (Bancel 1991). Apart from the various crystalline phases present, there is also an icosahedral QC phase in a narrow range of compositions. In the present work, this phase and the associated phase transformations are investigated through Mössbauer, positron lifetime and XRD measurements.

2. Experimental

Samples of Al–Cu–Fe QC-phase were prepared by the melt-spinning method and were characterized by XRD, TEM and EDX. Mössbauer measurements were carried out on a home-made spectrometer (Chittaranjan *et al* 1993) in the transmission geometry, using a 20 mCi ^{57}Fe source in rhodium matrix. Positron lifetime measurements were conducted on a fast–fast coincidence spectrometer that uses a 5 μCi ^{22}NaCl source. Temperature runs were made with the help of a vacuum furnace.

3. Results and discussion

3.1 $Al_{61\cdot4}Cu_{22\cdot7}Fe_{15\cdot9}$

The as-prepared samples were found from XRD to be purely icosahedral. The composition was determined by EDX to be Al:Cu:Fe :: 61·4:22·7:15·9. Figure 1 shows the room temperature Mössbauer spectra of samples annealed at various temperatures. Very little changes are seen between the spectra of quenched and annealed samples,

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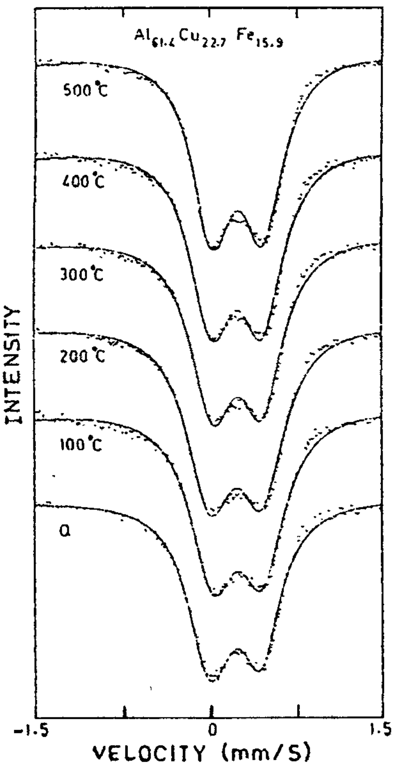

Figure 1. *RT* Mössbauer spectra of $Al_{61.4}Cu_{22.7}Fe_{15.9}$ annealed at various temperatures.

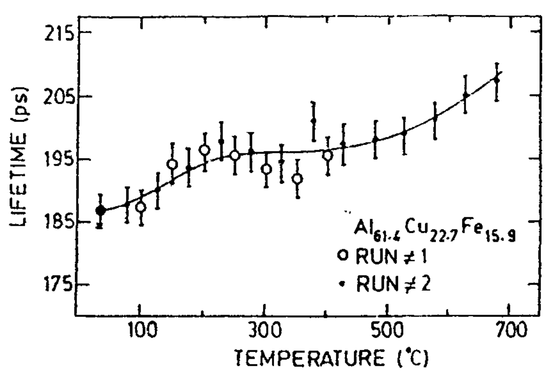

Figure 2. Variation of the mean positron lifetime of positrons in $Al_{61.4}Cu_{22.7}Fe_{15.9}$ as a function of temperature.

indicating that this phase is stable at least up to a temperature of 500°C. The temperature variation of the mean positron lifetime τ is shown in figure 2. τ is seen to increase up to 250°C, level off and rise again above 400°C. From the *in situ* Doppler broadening measurements (Lawther and Dunlap 1994) done on samples with slightly different compositions opposite trends are seen in the lineshape parameter as temperature is varied, which cannot be explained on the basis of positron trapping at thermal vacancies. This means the two-step increase in τ is not due to vacancies trapping the positrons. However, it is well known that phason disorders are inherently present in quasicrystals. These disorders may be dynamic in nature with the phasons undergoing a flipping motion which can lead to clustering of oblate rhombohedra, leaving large open regions for positrons to get trapped, thereby increasing their lifetime. An estimation of the activation energies, corresponding to the two steps in figure 2, using the relation $E = 14\,kT_N$, where T_N is the Knee temperature (Hautojarvi 1979) gives 0·43 eV and 0·78 eV respectively. Thus the two steps in the lifetime data can be attributed to positron trapping due to thermally-generated phasons associated with Al and Cu with an activation energy of 0·43 eV and 0·78 eV respectively. This picture is also supported by the recent quasielastic neutron scattering experiments (Codens *et al* 1991; Codens and Bellisent 1993), where the peak broadening above 650°C is attributed to dynamic Cu atom phasons, having an activation energy of 0·75 eV.

3.2 $Al_{71}Cu_{14}Fe_{15}$

When melt-spun ribbons of this alloy were characterized by XRD, they were found to be a mixture of i-phase and crystalline $Al_{13}Fe_4$ (λ-) phase. The powder XRD patterns of samples annealed at various temperatures are shown in figure 3. It is seen from these

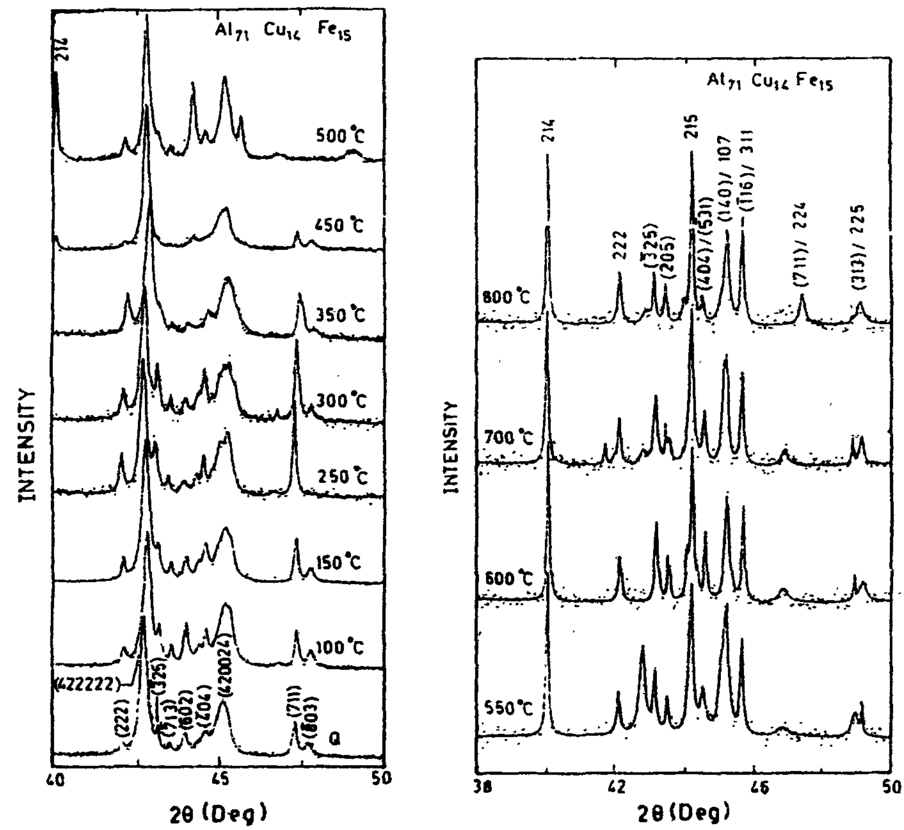

Figure 3. *RT* XRD patterns of $Al_{71}Cu_{14}Fe_{15}$ annealed at various temperatures.

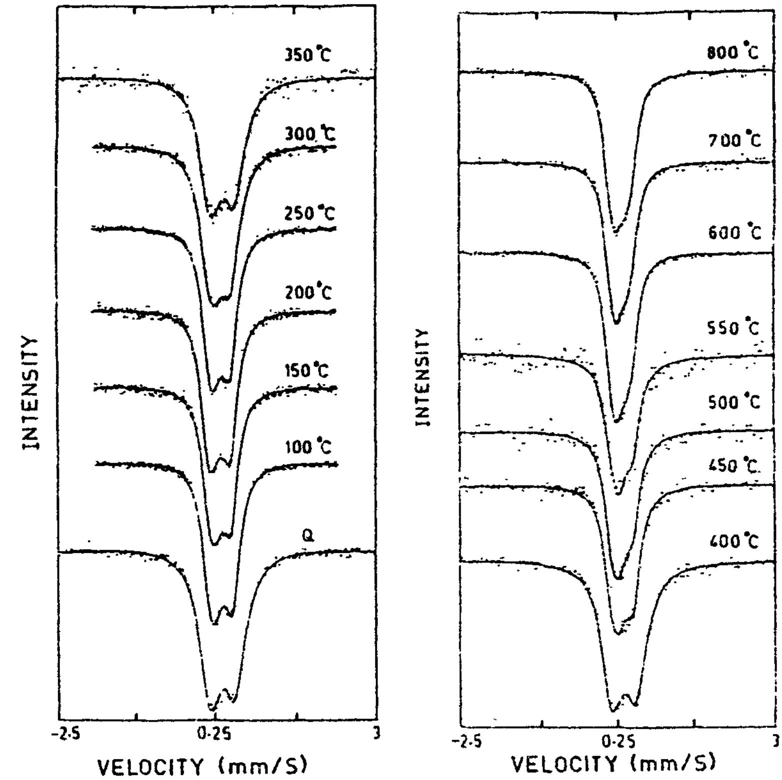

Figure 4. Mössbauer spectra of $Al_{71}Cu_{14}Fe_{15}$ annealed at various temperatures.

that the (422222) peak of the i-phase vanishes above 550°C. Above 350°C, new peaks (e.g. $2\theta \approx 40°$), corresponding to Al_7Cu_2Fe (ω-phase), are seen to evolve and gradually grow in intensity. The decrease in i-phase peak intensity is due to the phase transforming to a rhombohedral approximant. Mössbauer spectra of annealed samples are shown in figure 4. The doublet pattern of the as-quenched sample is seen to turn gradually into a broad singlet for higher annealing temperatures. These changes observed in the Mössbauer spectra are analysed in terms of three components, corresponding to the three phases: (i) a doublet corresponding to the i-phase (Srinivas and Dunlap 1991), (ii) a singlet with an IS of 0·143 mm/s and width of 0·360 mm/s, the characteristic Mössbauer parameters of the ω-phase (Srinivas and Dunlap 1991), and (iii) a component corresponding to the spectrum of $Al_{13}Fe_4$ phase. The evolution or otherwise of percentage fractions of the three phases as a function of annealing temperature are shown in figure 5. In figure 6, variations of IS, QS and the linewidth of the doublet, corresponding to the QC phase, are plotted as a function of the annealing temperatures. The decrease seen in the QS and linewidth values are indicative of the phase transformation. The positron lifetime variation with temperature is shown in figure 7. The large room temperature value of the lifetime (203 ps) is indicative of the presence of quenched-in vacancies and/or phason disorder. However, considering that $Al_{61·4}Cu_{22·7}Fe_{15·9}$, which was also quenched under similar conditions, shows a distinctly smaller value of lifetime (185 ps), the positron traps must be due to phason disorder

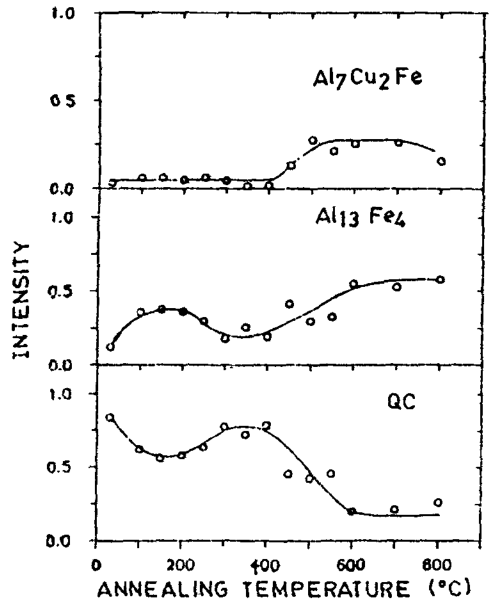

Figure 5. Fractions of ω-, λ- and i-phases for various annealing temperatures.

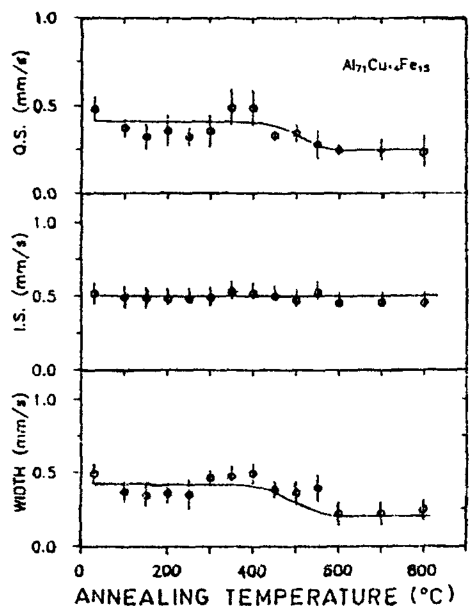

Figure 6. Variation of IS, QS and linewidth as a function of annealing temperature.

rather than vacancies. This is because the quenched-in vacancies are not expected to be different in samples of very nearly the same composition. The presence of phason disorder in $Al_{71}Cu_{14}Fe_{15}$ and its absence in $Al_{61\cdot4}Cu_{22\cdot7}Fe_{15\cdot9}$ can also be inferred from the broader quasicrystalline diffraction peaks in the former. Thus the decrease in lifetime

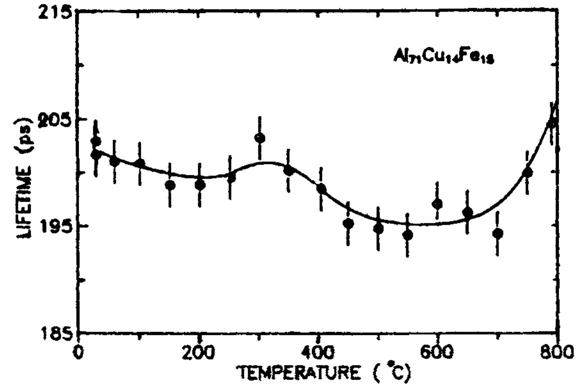

Figure 7. Variation of positron lifetime of $Al_{71}Cu_{14}Fe_{15}$ with temperature.

above 400°C can be attributed to the annealing out of the phason disorder. Another feature of the lifetime data in figure 7 is the increase in lifetime beyond 700°C. This could arise due to melting of the ω-phase, for it is known that the ω phase melts at around 740°C (Bancel 1991).

4. Conclusions

We have effectively used MS and PAS in the case of $Al_{61\cdot4}Cu_{22\cdot7}Fe_{15\cdot9}$ to understand the phason dynamics. Phasons with activation energies of 0·43 eV and 0·78 eV associated with Al and Cu respectively are shown to be responsible for the observed increase in the positron lifetimes. In the case of $Al_{71}Cu_{14}Fe_{15}$, mixed phase was observed. In addition to MS and PAS, powder XRD was also used to track the QC-rhombohedral phase transformation at 550°C in this alloy. From Mössbauer and XRD data it was seen that ω-phase evolved beyond 350°C. The as-quenched alloy has quenched-in phason disorder which was found to get annealed out at around the phase transition temperature.

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