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alloys

LETTER TO THE EDITOR

A positron annihilation study of crystalline, quasicrystalline and amorphous Al–Cu–T (T = Fe,V) alloys

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Abstract. Results of a Doppler broadening positron annihilation study on crystalline, quasicrystalline and amorphous Al–Cu–T (T = Fe,V) alloys are presented. For the first time it is shown that a quasicrystal ($Al_{65}Cu_{20}Fe_{15}$) can be prepared with a positron trapping site concentration below the sensitivity of positron annihilation spectroscopy. The results and those of similar studies previously reported for quasicrystalline Al–Mn–Si and Al–Cu–Li are discussed in conjunction with possible stabilisation mechanisms.

The original diffraction studies [1] on metastable Al-based quasicrystals (QC) and later on the stable icosahedral (i) phase of Al_6CuLi_3 [2] indicated that a certain amount of disorder may be inherent to QC. Recently, however, careful x-ray analyses [3] on a new class of QC in Al–Cu–transition metal (T) alloys have indicated that phason disorder can be eliminated from the i phase for two of its members: Al–Cu–T (T = Fe,Ru).

To date, positron annihilation spectroscopy (PAS) studies on QC [4–6] have been limited to Al–Mn–Si [4–6] and Al–Cu–Li [5] alloys. Doppler broadening and lifetime measurements on i-Al–Mn–Si [4–6] and i-Al–Cu–Li [5] reveal the existence of positron trapping site (PTS) concentrations intermediate to related (i.e. in terms of stoichiometry) crystalline and amorphous phases. Lifetime measurements [5, 6] indicate that such PTS correspond principally to small vacancy clusters which tend to migrate and annihilate upon low-temperature annealing. This is generally associated with dislocations which are synonymous with phason disorder. The observed persistence of such disorder (e.g. slightly elevated Doppler broadening L and S parameter values for the i phase relative to the associated crystalline phase [4,5]) is consistent with the suggestion that disorder may be inherent to i-Al–Mn–Si and i-Al–Cu–Li.

In the light of the above, however, this may not be the case for the Al–Cu–T class of QC. In this work, we address this point by presenting the first Doppler broadening PAS study on Al–Cu–T (T = Fe,V) alloys.

All samples were prepared by first arc melting high-purity elemental components under an atmosphere of argon. Amorphous (a) $Al_{75}Cu_{15}V_{10}$ and i-$Al_{65}Cu_{20}Fe_{15}$ were prepared by rapid quenching onto the surface of a single Cu roller [7]. Alternatively, well ordered i-$Al_{65}Cu_{20}Fe_{15}$ was produced by annealing the as-cast ingot [8]. The i phase in $Al_{75}Cu_{15}V_{10}$ was prepared by annealing the amorphous precursor at 693 K for one hour under argon. Single-phase crystalline (c) $Al_{70}Cu_{20}Fe_{10}$ was prepared by annealing the as-cast ingot under argon for 50 h at 1118 K.

X-ray diffraction analysis of the samples was carried out on a Siemens D500 diffractometer using Cu Kα radiation.

Positron sources were prepared via the $^{63}Cu(n,\gamma)^{64}Cu$ reaction by *in situ* irradiation of natural Cu using a thermal neutron flux of 5×10^{11} cm^{-2} s^{-1}. Before irradiation, the samples were ground into particles a few μm in diameter and enclosed in a thin plastic container. In all cases, samples with a mass of $\sim$260 mg were used. The irradiation times were approximately 20 minutes and resulted in an initial activity $\sim$60 μCi from the decay of ^{64}Cu. Before each experiment, the samples were allowed to cool for several hours so that short-lived activity could die down. A Princeton Gamma Tech planar intrinsic Ge detector with an energy resolution at the annihilation energy of $\sim$ 1.2 keV was used. Further details concerning the experimental apparatus can be found elsewhere [4, 9]. For each sample, data were taken over a period of about one day. However, individual runs were limited to one hour due to (i) the relatively short half life of ^{64}Cu ($t_{1/2} = 12.7$ h), and (ii) the sensitivity of the instrumentation to variations in the count rate.

X-ray analysis before and after irradiation of the samples verified the existence of the desired phase in each sample. No deterioration of the x-ray lines was observed due to the irradiation process. Except for the annealed i-Al$_{65}$Cu$_{20}$Fe$_{15}$, all samples were found to be single phased. In the case of i-Al$_{65}$Cu$_{20}$Fe$_{15}$, precipitation of a small quantity of monoclinic Al$_3$Fe was observed and is consistent with the results of Calvayrac *et al* [3]. However, Doppler broadening PAS should be insensitive to this because the amount of impurity phase was small.

For each experiment, the resulting annihilation spectra were stripped of their background and characterised by the usual lineshape parameters as follows,

$$L = I_v/I_c \tag{1}$$

and

$$S = I_v\left(\int N(E)\,dE\right)^{-1} \tag{2}$$

where $N(E)$ is the number of counts as a function of energy. I_v is taken to be an area around the annihilation peak and I_c is the sum of two areas taken symmetrically on either side of the annihilation peak. Representative L and S values are given in table 1. Figures 1 and 2 show the dependence of these parameters on electronic dead time (D) (i.e. a quantity proportional to the count rate).

Table 1. Results of least-squares fits to expression (3) as described in the text. Note that the values for the L and S parameters at $D = 0$ correspond to the values of A. (an) and (as-q) stand for annealed and as-quenched, respectively.

Sample	L		S	
	A ($\pm$0.01)	B ($\times10^{-4}$)	A ($\pm$0.001)	B ($\times10^{-6}$)
a-Al$_{75}$Cu$_{15}$V$_{10}$	4.51	−1.5	0.295	−6.0
i-Al$_{75}$Cu$_{15}$V$_{10}$	4.35	−1.2	0.292	−5.3
i-Al$_{65}$Cu$_{20}$Fe$_{15}$ (an)	3.96	−1.0	0.281	−4.8
i-Al$_{65}$Cu$_{20}$Fe$_{15}$ (as-q)	3.95	−1.1	0.281	−5.4
c-Al$_{70}$Cu$_{20}$Fe$_{10}$	3.96	−1.1	0.280	−5.3
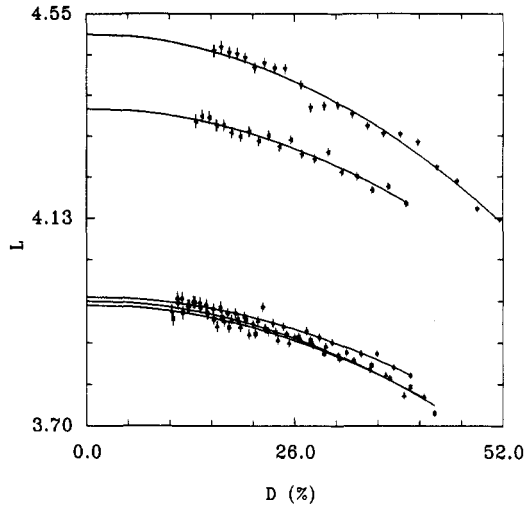
Figure 1. Plots of the L parameter values as a function of D for: ($\blacktriangledown$) a-$Al_{75}Cu_{15}V_{10}$; ($\blacktriangleleft$) i-$Al_{75}Cu_{15}V_{10}$; ($\bullet$) annealed i-$Al_{65}Cu_{20}Fe_{15}$; ($\blacktriangle$) as-quenched i-$Al_{65}Cu_{20}Fe_{15}$; and ($\blacksquare$) c-$Al_{70}Cu_{20}Fe_{10}$. Also included are the fitted curves to expression (3) given in the text.
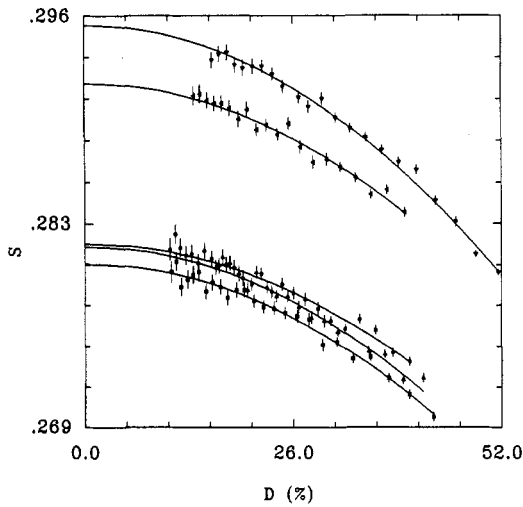
Figure 2. Plots of the S parameter values as a function of D for: ($\blacktriangledown$) a-$Al_{75}Cu_{15}V_{10}$; ($\blacktriangleleft$) i-$Al_{75}Cu_{15}V_{10}$; ($\bullet$) annealed i-$Al_{65}Cu_{20}Fe_{15}$; ($\blacktriangle$) as-quenched i-$Al_{65}Cu_{20}Fe_{15}$; and ($\blacksquare$) c-$Al_{70}Cu_{20}Fe_{10}$. Also included are the fitted curves to expression (3) given in the text.

For high D, there is a significant occurrence of pulse pile-up which tends to distort the annihilation peak resulting in a lowering of the L and S values. It is this distortion which disallows the summation of adjacent one-hour runs as a means of improving the statistics of the spectra. The values presented in table 1 correspond to extrapolations of the data to zero per cent D using a least-squares fit to a second-order polynomial

of the form:

$$F(D) = A + B(D)^2. \tag{3}$$

$F(D)$ is a generalised lineshape parameter (corresponding to either L or S) and D is measured as a percentage.

The insistence that the fit to $F(D)$ does not include a term linear in D is based upon the physical requirement that $\lim_{D \to 0}[dF(D)/dD] = 0$. The validity of such an assumption has been verified via a systematic study of the pile-up effects using a 30 μCi ^{22}Na salt solution. By varying the source to detector distance, the corresponding $F_{Na}(D)$ was determined for $0 < D < 50\%$. Fitting of $F_{Na}(D)$ to a second-order polynomial revealed that the term linear in D was negligible. That is, neither the $D = 0$ extrapolation nor the χ^2 values were significantly altered when a subsequent fit to expression (3) was performed. This also applies for the data collected from the five samples studied here.

In a simple two-state trapping model [10], the lineshape parameters comprise components corresponding to annihilations within PTS, F_t, and bulk states, F_b, respectively. This can be expressed in the form,

$$F = PF_t + (1 - P)F_b \tag{4}$$

where $F \equiv F(D = 0)$ and P is the relative probability that a positron will annihilate from a PTS.

Since all five samples have very similar compositions, it is not expected that F_b would vary significantly from sample to sample. Furthermore, the DB lineshape parameters are not particularly sensitive to the type of PTS formed. Thus F_t will not vary significantly either. Hence the variability of F from sample to sample will be principally associated with differences in P which are, in turn, related to differences in the concentration of PTS, Δn, since [11]

$$n = K/\mu = P\lambda_b/[\mu(1 - P)] \tag{5}$$

where λ_b is the positron annihilation rate in the bulk states, K is the trapping rate and μ is the trapping rate per PTS. Thus the observed variances in F are a direct indication of the relative concentration of PTS.

Although it is difficult to place much significance on the individual L and S values given in table 1 (unfolding of the energy resolution of the detector from the data has not been performed) their differences do reflect the variances in annihilation behaviour. Of particular note is the inability of Doppler broadening PAS to detect differences in the annihilation behaviour among the as-quenched i-$Al_{65}Cu_{20}Fe_{15}$, annealed i-$Al_{65}Cu_{20}Fe_{15}$ and c-$Al_{70}Cu_{20}Fe_{10}$ samples. On the other hand, the a-$Al_{75}Cu_{15}V_{10}$ and i-$Al_{75}Cu_{15}V_{10}$ samples are uniquely characterised.

It is not expected that the two i-$Al_{65}Cu_{20}Fe_{15}$ would possess equal PTS concentrations due to the high probability for quenched-in disorder to result from rapid solidification [5,6]. However, the observed behaviour is justified in the light of the equivalence of these L and S values with those for the c-$Al_{70}Cu_{20}Fe_{10}$ sample. This indicates that all three Al–Cu–Fe samples possess PTS concentrations at or below the minimum value (10^{-7}) for which PAS is sensitive [12]. The PTS concentration for i-$Al_{75}Cu_{15}V_{10}$, on the other hand, is significantly higher and is intermediate to those for the c-Al–Cu–Fe and a-Al–Cu–V samples.

According to Janot and co-workers [13], the structures of QC are best described in terms of the projection of a decorated six-dimensional (6D) periodic lattice, $\delta(r_6) *$ $A_{3\perp}(r_\perp)$, onto the 3D physical space, $R_{3\parallel}$. δ repesents the familiar Dirac delta function and r_6 the set of 6D vectors defining the lattice. The so-called acceptance function, $A_{3\perp}(r_\perp)$, is associated with the orthogonal 3D space and its convolution with the 6D lattice defines the decoration. The projection onto an irrationally oriented $R_{3\parallel}$ leads to quasi-lattice site occupation probabilities that are distributed (from unity) in accordance with the exact form of $A_{3\perp}(r_\perp)$ (i.e. the 6D lattice decoration).

The results presented in this work on the i-Al–Cu–Fe and i-Al–Cu–V alloys indicate that the relative probability for the formation of atomic site vacancies, even within a specific class of i phase, can be intrinsically different. Presumably this implies that $A_{3\perp}(r_\perp)$ is sensitive to the composition of the alloys. This could arise from such factors as atomic size (pair distances) and incompatible bond angles which would require the imposition of a composition-specific 'chemical modulation' in order to induce stability of the i phase (see, for example, [14]).

In the particular case of i-Al–Cu–Fe and i-Al–Cu–V, the reason for the observed difference in defect structure is by no means well understood. However, the expected similarity in chemical behaviour of Fe and V probably rules out incompatibility of bond angles as a principal contributor. On the other hand, there is considerable experimental evidence [15] to suggest that the 'in-bulk' size of the V atoms compared with that of the Fe atoms in similar i phase environments is larger. A further consideration of this with respect to possible de-stabilisation and defect enhancement of the i phase is warranted.

Furthermore, the suggestion that a Hume-Rothery stabilisation mechanism exists in QC [16] could influence i phase behaviour and hence be of relevance here. The principal motivation for such a suggestion comes from (i) observed correlations between the i phase Fermi surface and strong diffraction peaks [17], and (ii) density of states (DOS) calculations based upon specific heat measurements [18]. In the former case, direct calculation of the conduction electron concentration was restricted to QC not possessing elements with unfilled d orbital configurations. For i-Al–Cu–Fe and i-Al–Cu–V, the valencies of V and Fe are not known. Hence, such experimental evidence for the applicability of a Hume-Rothery stabilisation mechanism in i-Al–Cu–T (T = Fe,V) is indirect. From specific heat measurements, a direct correlation has been observed between the occurrence of a low DOS at the Fermi surface and the existence of a thermodynamically stable i phase in Al–Cu–Li, Al–Cu–Fe and Ga–Mg–Zn alloys. By comparison, similar measurements in metastable i-Al–Cu–V, i-Al–Cu–Mg and i-Al–Mg–Zn alloys reveal DOS near their expected free electron values.

The implication of a Hume-Rothery stabilisation mechanism to defect behaviour is illustrated by substitutional experiments in many binary alloys (e.g. γ-Al–Cu [19]). In such cases, even though a systematic increase in the average electron concentration per atom becomes incompatible with the Hume-Rothery stabilisation mechanism, stability is preserved by the inclusion of vacancies which maintains the average electron concentration per unit cell at the appropriate value.

This is a possible explanation for the high PTS concentration observed for the i-Al–Cu–V alloy compared with the i-Al–Cu–Fe alloy. However, questions remain unanswered. For example, why is it that the inclusion of vacancies in the i-Al–Mn–Si and i-Al–Cu–V alloys is unsuccessful in producing a thermodynamically stable QC whereas it is successful in the i-Al–Cu–Li alloy? We are currently conducting PAS experiments on other QC in order to gain more insight into the relationship between

stability and vacancy formation.

Doppler broadening positron annihilation spectroscopy on Al–Cu–T (T = Fe,V) alloys indicates that vacancy cluster formation is not an intrinsic property of all quasicrystals. The positron trapping site concentration in icosahedral $Al_{65}Cu_{20}Fe_{15}$ is found to be at or below 10^{-7} and, as such, is comparable with that found in well ordered crystalline samples. Conversely, icosahedral $Al_{75}Cu_{15}V_{10}$ is similar to previously investigated quasicrystals in the sense that it possesses a positron trapping site concentration intermediate to crystalline and amorphous phases. It has been argued that, at least in part, the appearance of vacancies in quasicrystals is linked to a Hume-Rothery stabilisation mechanism.

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