Positron annihilation studies of an icosahedral quasicrystal and the cubic *R* phase of Al-Li-Cu

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Positron annihilation lifetime and Doppler-broadening measurements have been performed for Bridgman-grown single-grained icosahedral quasicrystal and cubic *R* phase of Al-Li-Cu. The results are consistent with the existence of triacontahedral clusters with the vacant center in the icosahedral phase as well as in the *R* phase.

Since the discovery of the Al-Mn alloy with a diffraction pattern exhibiting icosahedral point symmetry,[1] several classes of quasicrystals have been produced by rapid solidification of the melt or by other nonequilibrium methods.[2] One of the stable icosahedral phases is the Al-Li-Cu system.[3-5] To determine the atomic structure of an icosahedral phase, it is important to investigate the atomic packing in the crystalline analog. Marcus and Elser[6] have pointed out that the cubic *R* phase consisting of icosahedral clusters is related to icosahedral Al-Li-Cu. Audier *et al.*[7] have constructed icosahedral Al-Li-Cu and the cubic *R* phases by different matching rules using two kinds of triacontahedral clusters. Recently, the structure of the cubic *R* phase has been studied in detail by x-ray and neutron diffractions.[8,9] It has been clarified that the central site of triacontahedral cluster in the cubic *R* phase is vacant. These results suggest that the icosahedral Al-Li-Cu also contains densely triacontahedra with a vacant center. However, it has not been proved experimentally that triacontahedra with vacant centers exist in icosahedral Al-Li-Cu densely.

It is known that positron annihilation methods are very powerful when studying vacancies in solids. In this study, we have performed positron annihilation lifetime and Doppler-broadening measurements for the Bridgman-grown single-grained icosahedral phase and the cubic *R* phase of Al-Li-Cu and have observed structural vacancies in the icosahedral Al-Li-Cu as well as in the *R* phase.

Specimens have been produced in the following way. Using a mother alloy of Al-Li-Cu, pure aluminum and copper, all with purity better than 99.9%, we melted ternary alloys in a boron nitride crucible that was sealed in a quartz ampoule, and then lowered the ampoule in a Bridgman furnace at a speed of 2 mm/h. The composition of the initial melt was $Al_{60.9}Li_{28.9}Cu_{10.2}$ for the growth of the icosahedral phase and $Al_{54.6}Li_{34.0}Cu_{11.4}$ for the cubic *R* phase. After the Bridgman growth, the ingot was found to be composed of large grains, with approximately 1 cm diameter, of the icosahedral or the cubic *R* phase, and fcc aluminum phase which surrounded the large grains. We cut the ingots into 0.4-mm-thick plates with a multiwire saw, etched off completely the surrounding Al phase and used the obtained single-grained quasicrystals or *R* phase crystals for measurements. Figure 1 shows x-ray-diffraction spectra for powdered samples of the two kinds of sliced specimens. It is found that all the diffraction peaks can be indexed either by the cubic *R* phase or the icosahedral phase and that no peak from other phases can be detected. The monocrystalline nature was confirmed by taking Laue photographs at two ends of the specimens, although the Laue spots from quasicrystalline specimens were quite diffuse.

The positron source, 10 μCi ^{22}NaCl sealed in an aluminum thin foil, was set at the center of the specimen. The specimen was sealed in a Pyrex glass tube in a vacuum of 10^{-5} Torr. The isochronal annealing was performed

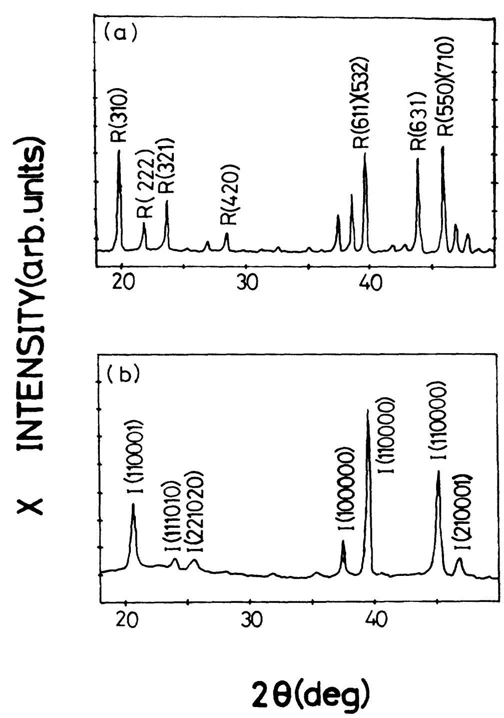

FIG. 1. Powder x-ray-diffraction spectra from *R*-phase specimen, (a) and quasicrystalline specimen, (b).

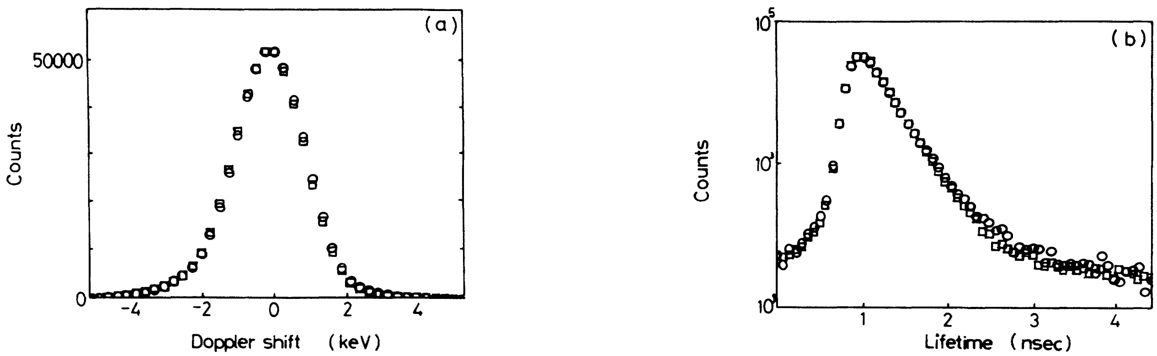

FIG. 2. (a) Open circles and open squares show the raw data for the positron Doppler-broadening spectra of the icosahedral quasicrystal and the cubic *R* phase, respectively. (b) Open circles and open squares show the raw data for the positron lifetime spectra of the icosahedral quasicrystal and the cubic *R* phase, respectively.

from room temperature to 350 °C for 20 min at 50 °C intervals. The measurements of Doppler broadening were carried out at the room temperature by use of a solid-state detector (pure Ge), whose energy resolution was 1.19 keV (FWHM) at 512 keV. The total counts in a spectrum were 1.2×10^6. The positron lifetime spectra were obtained at the room temperature with a fast-fast coincidence system by using Hamamatsu photomultipliers (H3378) and 1×1 in.^{2} BaF_2 scintillators. The time resolution of the system was 230 psec (FWHM) with the use of ^{60}Co. After background subtraction the line-shape parameter *h* was determined by the ratio of the central area over 20 channels to the total area of the spectrum. The line-shape parameter *w* was determined by the ratio of the two wings taken between $\pm$ (15~20 channels) from the center of the peak to the total area. The values of *h* and *w* parameters were normalized by setting the value of the *h* and *w* parameters of a well-annealed Al

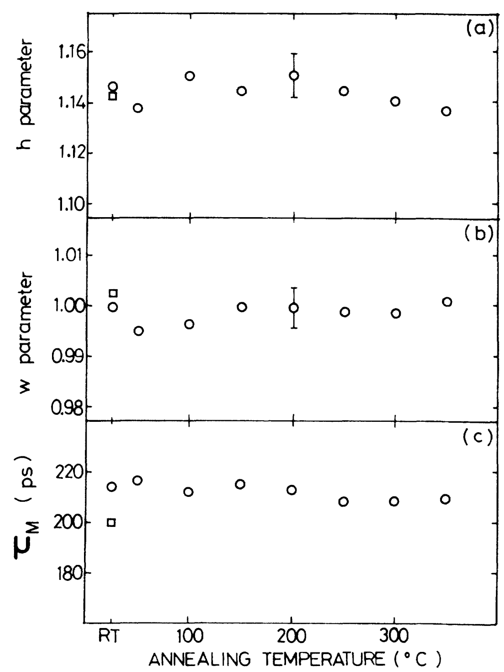

FIG. 3. (a) Open circles show the values of *h* parameter of the quasicrystal after isochronal aging for 20 min from the room temperature to 350 °C. Open square shows the value of *h* parameter of the as-casted *R* phase. (b) Open circles show the values of *w* parameter of the quasicrystal after isochronal aging for 20 min from the room temperature to 350 °C. Open square shows the value of *w* parameter of the as-casted *R* phase. (c) Open circles show the values of the mean lifetime after isochronal aging for 20 min from the room temperature to 350 °C in the quasicrystal. Open square shows the value of the mean lifetime of the as-casted *R* phase.

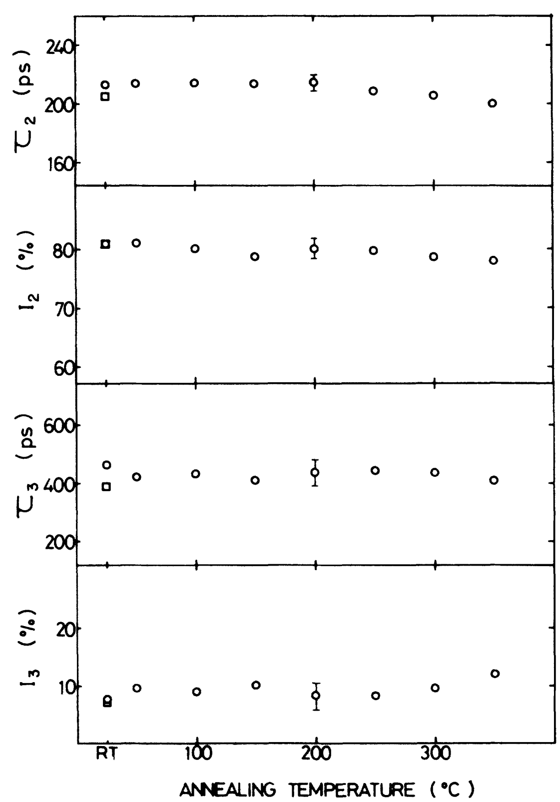

FIG. 4. Open circles show the intensity I_2 and the lifetime τ_2 of component two, and I_3 and τ_3 of component three from the room temperature to 350 °C in the quasicrystal. Open squares show I_2, τ_2, I_3, and τ_3 in the as-casted *R* phase.

(99.9999 wt. %) equal to 1. Positron lifetime spectra were analyzed by POSITRONFIT (Ref. 10) after subtracting the background. Each χ^2/q was below 1.0.

Figure 2(a) shows the raw data for the positron Doppler-broadening spectra and Fig. 2(b) shows the raw data for the positron lifetime spectra in the two phases of Al-Li-Cu at room temperature. Open circles and open squares indicate the values for the quasicrystal and the cubic R phase, respectively. It is seen that the data are quite similar for the two phases. Figures 3(a), (b), and (c) show the values of the h parameter, w parameter, and the mean lifetime of the quasicrystal measured after isochronal aging for 20 min at each temperature. Data for the cubic R phase at the room temperature are also plotted. It seems that the values of the h and w parameters of the quasicrystal are almost constant from room temperature to 350 °C. It is also observed that the values of h and w parameters of the R phase are similar to those of the quasicrystal. The values of the mean lifetime of the quasicrystal are 212±4 psec from room temperature to 350 °C. The value of the mean lifetime of the cubic R phase is 200±4 psec, which is only slightly shorter than those of the quasicrystal. The observed lifetime spectra are well fitted with three lifetime components. The open circles in Fig. 4 show the intensity I_2 and the lifetime τ_2 of component two, and I_3 and τ_3 of component three from the room temperature to 350 °C in the quasicrystal. The open squares in Fig. 4 show I_2, τ_2,I_3, and τ_3 in the cubic R phase. The lifetime τ_2 of component two is in the range 205±4 psec from room temperature to 350 °C in the quasicrystal.

In view of the value τ_2=205±4 psec, it is considered that this component corresponds to that of vacancy-like defects.[11] The intensities I_2 of component two are ~80% from room temperature to 350 °C. The lifetime τ_3 of component three has almost the same value of 430±20 psec on the average from the room temperature to 350 °C in the quasicrystal. The intensities I_3 of component three are ~11% from the room temperature to 350 °C. From the value of 430±20 psec, it seems that component three corresponds to microvoids in the quasicrystal.

It should be noted that the intensity of component two, which is ~80%, is very high in both phases. This means that there exists a dense concentration of vacancy-like defects; in other words, vacancy-like defects exist as a structural defect in both phases. Furthermore, it is very interesting that I_2,τ_2,I_3, and τ_3 in the quasicrystal are similar to those in the cubic R phase. As described previously, x-ray analysis of the structure of the cubic R phase revealed that the center site of the triacontahedral clusters is vacant, meaning that the I_2 and τ_2 in the R phase are due to this vacant site. Therefore, the above results suggest that the Al-Li-Cu icosahedral phase also contains a similar density of the same triacontahedral cluster with vacant center as in the cubic R phase.

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