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2004 J. Phys.: Condens. Matter 16 1899

(http://iopscience.iop.org/0953-8984/16/10/020)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 1899–1905 PII: S0953-8984(04)70629-3

Positron annihilation studies of icosahedral quasicrystals and their approximants in the Al–Cu–Ru–(Si) alloy systems

H Uchiyama[1,4], T Takahashi[1], K Arinuma[1], K Sato[1,5], I Kanazawa[1], E Hamada[2,6], T Suzuki[2], K Kirihara[3,7] and K Kimura[3]

[1] Department of Physics, Tokyo Gakugei University, Koganei, Tokyo 184-0015, Japan
[2] Research Science Centre, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
[3] Department of Advanced Materials Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received 14 October 2003
Published 27 February 2004
Online at stacks.iop.org/JPhysCM/16/1899 (DOI: 10.1088/0953-8984/16/10/020)

Abstract

The positron lifetimes for the icosahedral quasicrystal $Al_{62.4}Cu_{25.4}Ru_{12.2}$ and its cubic approximants (1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$, 1/1-$Al_{68}Cu_7Ru_{17}Si_8$, and 1/0-$Al_{55}Cu_{15}Ru_{20}Si_{10}$), two-detector coincident Doppler broadening for the icosahedral quasicrystal $Al_{62.4}Cu_{25.4}Ru_{12.2}$ and its 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ cubic approximant, and the Doppler broadening obtained by making use of a slow positron beam for the 1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$ cubic approximant have been measured. Structurally intrinsic trapping sites giving rise to saturation trapping were detected by lifetime measurements. The chemical environments of the trapping sites in the icosahedral quasicrystal $Al_{62.4}Cu_{25.4}Ru_{12.2}$ and the 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ cubic approximant were determined by coincident Doppler broadening techniques to be dominantly surrounded by Al atoms. The positron diffusion length in the 1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$ cubic approximant derived from the measured S parameter measured by means of a slow positron beam was $\sim$180 Å, which is clearly too short, probably due to the high concentration of trapping sites as described above. The atomic structures of the icosahedral quasicrystal $Al_{62.4}Cu_{25.4}Ru_{12.2}$ and its variety of approximants are discussed and compared to the present proposed model.

[4] Present address: The Graduate University for Advanced Studies, Department of Materials Structure Science, Oho, Tsukuba, Ibaraki 305-0801, Japan.
[5] Present address: Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.
[6] Present address: Institute for Environmental Sciences, Obuchi, Rokkasho-Mura, Aomori 039-3212, Japan.
[7] Present address: Nanoarchitechtonics Research Centre, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

1. Introduction

The crystal structures of condensed matter have been studied by diffraction experiments, such as single-crystal x-ray structural or Rietveld analyses. The identification of detailed atomic structure becomes more complex in structurally aperiodic systems, such as quasicrystals (QCs), due to a lack of periodicity in the atomic structures. Therefore, approaches making use of the well-known atomic structures of low order crystalline approximants have been extensively employed since they possess clusters similar to these found in QCs and many reports on their structural models are available [1]. Nevertheless, it still has to be said that a reliable quasiperiodic structure has not been sufficiently determined. In this case, positrons yielding specific information on the atomic scale may enable us to derive systematic information on the electron density or momentum from the lowest order of the crystalline approximants up to quasicrystals as a local probe, and may give complementary information to diffraction methods.

We selected the Al–Cu–Ru–(Si) alloy system for this study. In the vicinity of a composition range forming a thermodynamically stable Al–Cu–Ru icosahedral QC [2] in the phase diagram, two different kinds of cubic approximant phases appear. Both are recognized as 1/1 [3] and 1/0 [4] cubic approximants of Al–Cu–Ru icosahedral QCs with lattice constants of 12.38 and 7.7 Å respectively. Both 1/1 [5] and 1/0 [6] cubic approximants also appear with lattice constants of 12.68 and 15.38 Å, as an approximant phase of the Al–Cu–Ru icosahedral QC in a Al–Cu–Ru–Si alloy system. The structural models of these four cubic approximants, determined by diffraction method, are available elsewhere [4, 6–8]. The centre sites of the primitive clusters are vacant for the structural models of 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ [7], but occupied for 1/0-$Al_{71}Cu_7Ru_{22}$ [4], 1/1-$Al_{57.3}Cu_{31.4}Ru_{11.3}$ [8], and 1/0-$Al_{66.3}Cu_{14.6}Ru_{20.2}Si_{10.1}$ [6]. Therefore, an investigation on the atomic scale making use of positrons in terms of the vacancy-type site in the Al–Cu–Ru–(Si) alloy system is of particular interest.

Positron lifetime spectroscopy on icosahedral QCs has revealed structural vacancies at atomic concentrations of about 10^{-3} [9]. Furthermore, positron diffusion experiments have made it feasible to derive qualitative information, such as the structural vacancy density under saturation trapping conditions, as demonstrated for some QCs in our earlier experiments [10–13]. An even more powerful tool becomes available when these techniques are coupled with a coincident Doppler broadening measurement of the electron–positron annihilation photons [14]. This technique is sensitive to the chemical environment of the annihilation site, by probing the core electron momentum densities [15]. In the present paper we focus on systematic studies in the Al–Cu–Ru–(Si) alloy system by a series of positron annihilation techniques.

2. Experimental details

Icosahedral QC $Al_{62.4}Cu_{25.4}Ru_{12.2}$ and three cubic approximants (1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$, 1/1-$Al_{68}Cu_7Ru_{17}Si_8$, and 1/0-$Al_{55}Cu_{15}Ru_{20}Si_{10}$) were prepared by arc melting in an argon atmosphere, and then annealed for 74 h at 1173 K, 96 h at 1023 K, 96 h at 1023 K, and 24 h at 1123 K in vacuum after sealing in a quartz tube. After annealing, a water quench treatment was immediately performed for all samples. The structural quality of the quasicrystalline and approximant phases was confirmed by x-ray diffraction analysis.

The positron lifetimes were measured by a fast–fast coincident spectrometer with a time resolution of 240 ps full width at half-maximum (FWHM) at room temperature. The positron source (^{22}Na, activity about 5 μSv), sealed in a thin Kapton foil, was mounted in a specimen–source–specimen sandwich. For each spectrum at least 1.0×10^6 annihilations were accumulated. The time resolution function was assumed to be composed of two Gaussian

functions. Using this time resolution function, the lifetime in the bulk of well-annealed pure Al (purity 99.9999 wt%) was measured as 166 ± 2 ps. After subtracting the background, the positron annihilation lifetime spectra were analysed using the POSITRONFIT code [16]; each χ^2/q was below 1.2.

Coincident measurements of the Doppler broadening were performed with a collinear set-up of two high purity Ge detectors. When a coincidence measurement of the energies of the two γ-rays is made using two similar detectors, the signal to noise ratio can be improved from about 100–1 to 10^5–1. This allows one to make accurate measurements of both the valence and core electron contributions to the Doppler broadening up to $p_L = (40 \times 10^{-3})m_0c$, where p_L is the momentum component along the direction of the γ-ray emission. Points along the diagonal ($E_1 + E_2 = 2 \times 511$ keV) from the two-dimensional array of about 1×10^6 coincident counts was accumulated. The width of the diagonal integrated by cutting was equal to the FWHM of the resolution function. The FWHM of the energy resolution of the detectors was about 1.8 at 511 keV. Details on the coincident Doppler broadening spectroscopy are given elsewhere [15].

A slow variable monoenergetic positron beam for Doppler broadening measurements was composed of a ^{22}Na positron source (about 5 mCi) and a single W$\langle 100 \rangle$ foil of 1 μm thickness. The foil was annealed at 2273 K in a vacuum of $\sim 10^{-9}$ Torr, and was attached in front of the source to moderate the positrons. A fraction of these energetic positrons emitted from a ^{22}Na source were thermalized through a variety of collision processes in a tungsten moderator and re-emitted from this moderator as monoenergetic slow positrons. The intensity of the slow positron beam was about 1.0×10^4 s^{-1}. The incident positron energy was variable from 0 to 13 keV. Measurements of the Doppler broadening spectra using a slow positron beam were carried out at room temperature by using a solid state detector (pure Ge). The total counts in a spectrum corresponding to each incident positron energy were 8.0×10^4.

In order to estimate the vacancy-type defects in the samples, the S parameter, determined as the ratio of the central area over ± 0.5 keV to the total area of the Doppler broadening spectrum after subtracting the background, was used.

3. Results and discussion

The observed positron lifetime spectra for all of the samples were composed of a single component with a lifetime of τ_2. Table 1 lists the evaluated positron lifetimes with the atomic densities together with those of the single elements. Considering that the atomic densities for four Al–Cu–Ru–(Si) alloys ($\sim 7.90 \times 10^{28}$ m^{-3}), which were estimated from the composition, are in between those of pure Al (6.02×10^{28} m^{-3}) and pure Cu (8.45×10^{28} m^{-3}), significantly high lifetimes were measured (table 1). Here, we have estimated the positron lifetimes in the free state for the QC and cubic approximants, approximating those to be the compositionally weighted averages of the constituent element values ($\tau_{\mathrm{Al}} = 166$ ps, $\tau_{\mathrm{Cu}} = 112$ ps, $\tau_{\mathrm{Ru}} = 90$ ps, and $\tau_{\mathrm{Si}} = 221$ ps). The estimated values are 143, 141, 154, and 148 ps for icosahedral QC $Al_{62.4}Cu_{25.4}Ru_{12.2}$, 1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$, 1/1-$Al_{68}Cu_7Ru_{17}Si_8$, and 1/0-$Al_{55}Cu_{15}Ru_{20}Si_{10}$, respectively, which are clearly shorter than the lifetimes observed here by ~ 30 ps. Therefore, it is unlikely that the positron lifetimes obtained, of 187–205 ps, are due to annihilations in the defect-free region of the samples, and they are concluded to be due to vacancy-type defects.

This effect could be confirmed by the S parameter taken as a function of the positron incident energy for 1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$ obtained by using a slow positron beam (figure 1). The value of the measured S parameter increases rapidly, signifying a dense distribution of the vacancy-type sites, and becomes saturated above 4 keV. This is a quite typical tendency for QCs or crystalline approximants observed earlier [10–13]. From an analysis of the measured

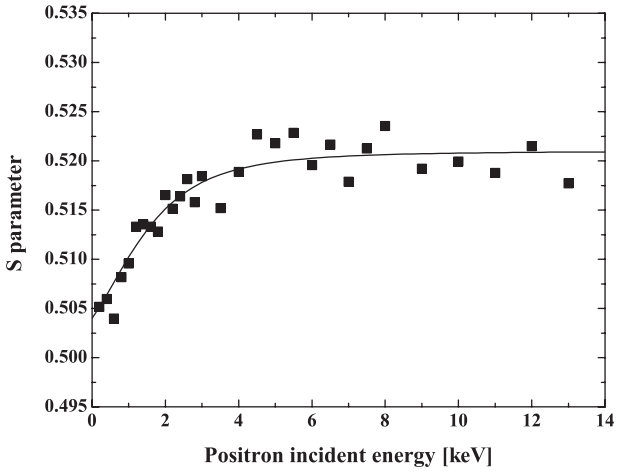

Figure 1. Measured and fitted *S*-parameter data for the 1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$ cubic approximant. The solid curve is a result of a fit, in which the positron diffusion length was determined as to be 180 Å.

Table 1. The positron lifetime component (τ_2) measured on the icosahedral quasicrystal $Al_{62.4}Cu_{25.4}Ru_{12.2}$ and four cubic approximants (1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$, 1/1-$Al_{68}Cu_7Ru_{17}Si_8$, and 1/0-$Al_{55}Cu_{15}Ru_{20}Si_{10}$). The atomic density ($\rho_{at.}$) presented in the table was estimated from the composition and density. The experimental uncertainty is $\Delta\tau = \pm 3$ ps. The positron lifetime (τ_f) in the free state and the positron lifetime (τ_v) in the lattice vacancies of the pure Al, pure Cu, pure Ru, and pure Si are given for comparison.

Specimen	Structure	$\rho_{at.}$ (10^{28} m^{-3})	τ_1 (ps)	τ_2 (ps)
$Al_{62.4}Cu_{25.4}Ru_{12.2}$	Quasicrystal	7.70	—	205
$Al_{58}Cu_{31.5}Ru_{10.5}$	1/1 cubic	7.70	—	193
$Al_{55}Cu_{15}Ru_{20}Si_{10}$	1/0 cubic	7.90	—	187
$Al_{68}Cu_7Ru_{17}Si_8$	1/1 cubic	7.49	—	186
			τ_f (ps)	τ_v (ps)
Al	fcc	6.02	166 [17]	251 [18]
Cu	fcc	8.45	112 [18]	179 [18]
Ru	hcp	14.74	90 [17]	—
Si	Diamond	3.75	218 [19]	266 [20]

S parameter data, the average positron diffusion length was determined as 180 Å, which is lower than those for typical metals by an order of magnitude, as indicated by the solid curve in figure 1. This is because the densely distributed vacancy-type sites mentioned above cause the positron diffusion length to be substantially shortened.

Figure 2 shows the coincident Doppler broadening ratio spectra normalized by pure Al for icosahedral QC $Al_{62.4}Cu_{25.4}Ru_{12.2}$ and 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ cubic approximant together with pure elements. The chemical surroundings of the structural vacancies for QC $Al_{62.4}Cu_{25.4}Ru_{12.2}$ are dominated by Al atoms as demonstrated in the coincident Doppler broadening ratio to pure Al spectra in figure 2 where the curves for $Al_{62.4}Cu_{25.4}Ru_{12.2}$ and 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ are almost identical to that of pure Al in the high momentum range. For the 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ we could not distinguish the difference between pure Al and Si because of the similar electronic states in the periodic table. Therefore it can be concluded at this stage that the chemical surroundings of the trapping sites for 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ are dominated by Al or Si atoms.

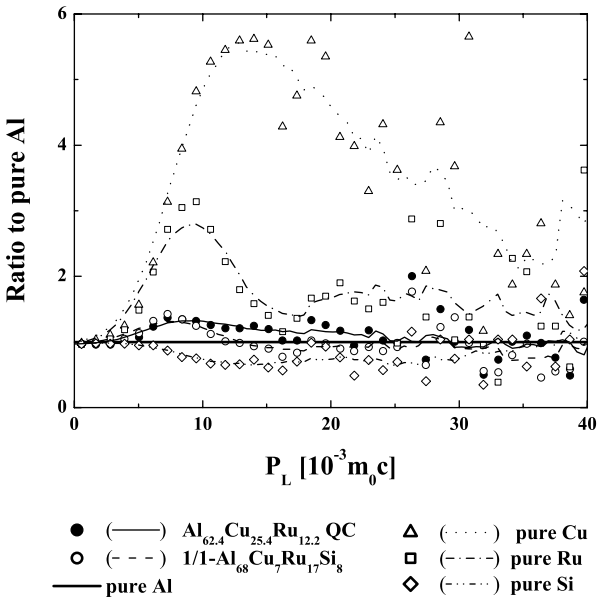

Figure 2. Doppler broadening ratio spectra for the 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ cubic approximant (open circles) and icosahedral quasicrystal $Al_{62.4}Cu_{25.4}Ru_{12.2}$ (full circles) together with those for pure Al (solid line, $Y = 1$), pure Cu (open triangles), pure Ru (open squares), and pure Si (open diamonds). Each spectrum was normalized to the Doppler broadening spectrum of pure Al. For clarity, ten-point averaged data are also shown.

In the case of the 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ cubic approximant, the atomic structure has been determined from the powder x-ray diffraction spectrum using the Rietveld method [7]. It belongs to the space group $Im\bar{3}$ and contains a total of 144 atoms in its unit cell of the bcc structure. The centres of the clusters located at the vertices and centres of the unit cell are vacant. Here, we note that the nearest neighbours of these vacancy sites are Al atoms. As mentioned above, we have observed the chemical environment surrounded by Al or Si atoms at the annihilation sites by coincident Doppler broadening spectroscopy. Following the atomic structure determined by a Rietveld analysis [7], it is likely that this type of vacancy site detected by the present coincident Doppler spectroscopy is dominated by Al atoms. Therefore, it is concluded that the centre sites of MI clusters with the chemical surroundings of Al atoms are specifically detected by the positron annihilation lifetime (see table 1) and the coincident Doppler broadening spectroscopy (see figure 2).

Interestingly, we have observed a chemical environment of Al atoms that is the same as that in icosahedral QC $Al_{62.4}Cu_{25.4}Ru_{12.2}$, as concluded by the coincident Doppler method (see figure 2) with a lifetime of 205 ps, corresponding to the structural vacancy. This may support the notion that the icosahedral QC $Al_{62.4}Cu_{25.4}Ru_{12.2}$ has the same vacancy-type sites surrounded by Al atoms as the 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ cubic approximant, and therefore it is worth mentioning that the structure of the icosahedral QC Al–Cu–Ru may be composed of an MI cluster with a vacant centre surrounded by Al atoms. The slightly longer lifetime of icosahedral QC $Al_{62.4}Cu_{25.4}Ru_{12.2}$ may indicate larger vacancies with respect to those of the 1/1-$Al_{68}Cu_7Ru_{17}Si_8$ cubic approximant.

Recently, Sugiyama *et al* [8] determined the atomic structures of the 1/1-$Al_{57.3}Cu_{31.4}Ru_{11.3}$ cubic approximant by means of single-crystal x-ray diffraction. This study showed that

a Cu-rich double Mackay-like rhombicosidodecahedral cluster and a Ru-rich Mackay-like icosidodecahedral cluster are located at the vertex of the unit cell (1a site) and at the body centre of the unit cell (1b site), respectively. In this model, the central positions in the first shell at both the 1a and 1b sites are occupied by a Ru atom. This is quite different to the α-Al–Mn–Si 1/1 approximant [1], where the centre sites of MI clusters are essentially vacant and are detected by positron annihilation methods [10]. In addition, Sugiyama *et al* have determined the atomic structure of 1/0-$Al_{55.1}Cu_{14.6}Ru_{20.2}Si_{10.1}$ cubic approximant with the same technique [6] and concluded that dodecahedral clusters with icosahedral symmetry and small clusters with cubic symmetry are located at the body centre of a unit cell (8c site) and the vertex of a unit cell (4a and 4b sites), respectively. The centre sites in these two clusters are also occupied. However, it is commonly said that two kinds of primitive clusters are heavily disordered at the first shell in both structural models for 1/1-Al–Cu–Ru and 1/0-Al–Cu–Ru–Si cubic approximants. Judging from the positron lifetimes ($\sim$187 ps), most positrons may be selectively trapped into small cavities or the lower electron density sites created by such a locally disordered state in the clusters. Therefore, slightly shorter positron lifetimes compared to that in the icosahedral QC are considered to be observed in this study. Owing to this kind of trapping site being distributed densely, thermalized positrons in the 1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$ cubic approximant could not diffuse sufficiently, and a very short positron diffusion length may have been observed as a result.

The observed positron lifetimes in this study can be clearly classified into three categories; icosahedral QC $Al_{62.4}Cu_{25.4}Ru_{12.2}$ (205 ps), 1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$ cubic approximant (193 ps), 1/0-$Al_{55}Cu_{15}Ru20Si_{10}$ and 1/1-$Al_{68}Cu_{7}Ru_{17}Si_{8}$ cubic approximants ($\sim$187 ps). We finally discuss why the observed positron lifetimes of the three cubic approximants were measured to be slightly shorter than that of the QC. In the cases of 1/1-AlCuRu and 1/0-AlCuRuSi, thermalized positrons are trapped into the small cavities or the lower electron density sites created by a locally disordered state in the clusters as described above [8]. Since the size of these sites may be smaller than that in the QC, the observed positron lifetimes become slightly shorter. For the 1/1-AlCuRuSi, the same picture may be able to give a plausible explanation for the slightly short lifetime [21] aside from the atomic structure model determined from Rietveld analyses [7]. Furthermore, it may be very interesting to note that the observed lifetimes for 1/1-AlCuRuSi and 1/0-AlCuRuSi become shorter than those for QC and 1/1-AlCuRu due to the addition of the Si element. That is, the size of the vacancy-type defect is decreased by adding the Si element. Further studies are under consideration for obtaining more information on atomic structure and giving satisfactory explanations for these alloy systems.

4. Conclusion

A variety of Al–Cu–Ru–(Si) alloys from lower orders of approximants up to QCs were investigated by a series of positron annihilation techniques. Also, the atomic structures for this alloy system were discussed based on the results from both the positron and diffraction techniques. For the 1/1-$Al_{68}Cu_{7}Ru_{17}Si_{8}$ cubic approximant, the centre site of the MI cluster was specifically detected by a positron lifetime method, and was found to be dominated by the Al atom, as concluded from a coincident Doppler broadening technique. This result is likely to indicate the structural model determined by Mizutani *et al* [7]. For the 1/1-$Al_{58}Cu_{31.5}Ru_{10.5}$ and 1/0-$Al_{55}Cu_{15}Ru_{20}Si_{10}$ cubic approximants, small cavities or the lower electron density sites created by a locally disordered state in the clusters were observed. We revealed a structural vacancy with the chemical environment of Al atoms for icosahedral QC $Al_{62.4}Cu_{25.4}Ru_{12.2}$. This supports the notion that the structure of icosahedral QC Al–Cu–Ru may be composed of MI clusters with a vacant centres surrounded by Al atoms. This structural information, locally

probed by positrons in these studies, should be useful for future investigations of the atomic structure of the Al–Cu–Ru–(Si) alloy system, and is therefore of importance.

Acknowledgments

Helpful discussions with and kind encouragement from Professor H Murakami, Tokyo Gakugei University, and Professor K Sugiyama, Tokyo University, are gratefully acknowledged.

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