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REPORT DOCUMENTATION PAGE   AD-A193 768

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 24122.1-MS		
6a. NAME OF PERFORMING ORGANIZATION University of Virgina	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office		
6c. ADDRESS (City, State, and ZIP Code) University of Virgina Charlottesville, VA 22904		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAL03-87-K-0057		
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS		

10. SOURCE OF FUNDING NUMBERS			
PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Structural Relationship Between Icosahedral and Frank-Kasper Phases of Al-Li-Cu

12. PERSONAL AUTHOR(S)
W. Dmoski and T. Egami Y Shen and S. J.Poon

13a. TYPE OF REPORT Reprint	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT 7

16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Abstract on reprint

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete.
UNCLASSIFIED

Structural relationship between icosahedral
and Frank–Kasper phases of Al–Li–Cu

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ABSTRACT

We report on an X-ray diffraction study of the structure of the icosahedral and Frank–Kasper phases of $Al_{5.5}Li_3Cu$. It is shown that the two phases have very similar local structure up to about 20 Å, while the long-range structure is quite distinct. A detailed analysis of the Frank–Kasper phase suggests that the reported atomic positions and site occupations of this compound are not accurate, and the local structure of this compound is actually closer to that of the quasicrystalline unit cells proposed for the icosahedral phase. The results are consistent with the decorated quasicrystalline lattice model.

Since the discovery of the phase exhibiting icosahedral point symmetry in rapidly quenched Al-Mn alloys (Shechtman, Blech, Gratias and Cahn 1984) the structural properties of icosahedral crystals have been extensively studied, both experimentally and theoretically. The diffraction patterns computed for the three-dimensional Penrose tiling (Levine and Steinhardt 1984) and so-called icosahedral glass (Shechtman and Blech 1985, Stephens and Goldman 1986) have been shown to reproduce the experimentally observed symmetry. However the exact microscopic structure and the atomic positions remain unknown. Recently interest has been focussed on the Al-Li-Cu system in which a stable compound, formerly designated as the T2 phase (Hardy and Silcock 1955) has been found to exhibit icosahedral symmetry (Sainfort, Dubost and Dubus 1985, Cassada, Shiflet and Poon 1986). In this system a Frank Kasper cubic phase of a similar composition can be formed. This phase (also called the R phase) was found (Cherkashin, Kripyakevich and Oleksiv 1964) to be isostructural with the $(Al, Zn)_{49}Mg_{32}$ phase (Bergman, Waugh and Pauling 1957).

In building a model of the icosahedral Al-Zn-Mg phase (Ramachandrarao and Sastry 1985), Henley and Elser (1986) considered the $(Al, Zn)_{49}Mg_{32}$ cubic structure as a starting point. In this structure 98 out of the 162 atoms in the unit cell have icosahedral coordination. However, according to Bergman *et al.* (1957) the local

icosahedra are distorted. Henley and Elser (1986) first moved atoms to ideal high-symmetry positions and then decomposed the cubic cell into prolate rhombohedra and rhombic dodecahedra, and related these to the icosahedral structure in a similar way as for α(Al Mn Si) (Elser and Henley 1985). Audier, Sainfort and Dubost (1986) considered a similar construction for the Al–Li–Cu system. They found that the Frank–Kasper cubic structure can be described in terms of triacontahedra which share rhomb faces along {100} planes and partialy overlap along ⟨111⟩ directions. By changing the number of overlapping-type connections between triacontahedra and their directions they start the construction of the icosahedral phase in a similar way as for i-(Al₄Mn) (Guyot and Audier 1985). Both approaches propose a close structural relationship between the i-phase and the corresponding cubic phase. In this Letter we describe the experimental results which confirm such a relationship for the Al Li Cu system. The reasons for choosing Al Li Cu for the study are that both single icosahedral and cubic phases of the same composition could be prepared, and that Li is a very weak X-ray scatterer as compared to Al and Cu, so that the compositional correlations are more readily assessed by analysing the X-ray diffraction intensities.

A sample of the i-phase of Al₆Li₃Cu was prepared by melt spinning. The Frank–Kasper cubic phase of the same composition was obtained by direct casting in a stainless-steel mould at room temperature. Both samples were annealed at 350 C for 12 h and then powdered. Diffraction intensities as a function of the scattering vector up to $12\,\text{Å}^{-1}$ were measured at the National Synchrotron Light Source, beam line X13-A, in transmission geometry. The incident beam was monochromatized using a Ge(220) crystal and the energy was 17·974 keV. The resolution was limited by the necessity for high counting rates and was $0.02\,\text{Å}^{-1}$ (f.w.h.m.). The maximum scattered intensity was about 2×10^{4} counts per second and data were collected using an intrinsic Ge solid-state detector with an energy resolution of 220 eV at 20 keV.

Because quasicrystals lack translational symmetry in three dimensions while preserving long-range bond orientational order, conventional methods of crystallographic data reduction cannot be applied and direct determination of the atomic structure is not possible. However, another approach, based on the pair-distribution function frequently used in the study of non-crystalline materials, has proved useful in the case of i-(Pd U Si) (Kofalt, Nanao, Egami, Wong and Poon 1986) and i-(Al Mn Si Cr) (Nanao, Dmowski, Egami, Richardson and Jorgensen 1987) alloys. After correcting for air scattering, absorption, multiple scattering (to second order), the scattering intensity normalized for one atom can be expressed as

$$I_{a}(Q) = \langle f(Q)_{i}^{2} \rangle - \langle f(Q) \rangle^{2} + \langle f(Q) \rangle^{2} S(Q) + F_{c}(Q). \tag{1}$$

where $S(Q)$ is the total structure factor, $\langle \ldots \rangle$ denotes a compositional average, and $F_{c}(Q)$ is the Compton-scattering intensity. After removing the Laue monotonic term and the Compton-scattering intensity, we obtain the structure factor and, by direct Fourier transformation of $S(Q)$, the pair-distribution function (PDF), $\rho(r)$, can be obtained:

$$\rho(r) = \rho_{0} + \frac{1}{2\pi^{2}r} \int [S(Q) - 1] \sin(Qr) Q \, dQ. \tag{2}$$

Figures 1 and 2 present the structure factors for the Frank Kasper and icosahedral phases respectively. The Frank Kasper phase can be indexed as a body-centred cubic lattice with a lattice constant of 13·95 Å. We may note that the presence of many small peaks in the pattern is characteristic of a structure with a large lattice constant and a

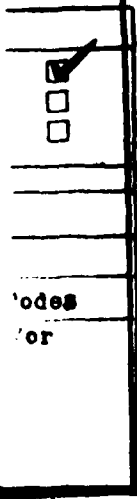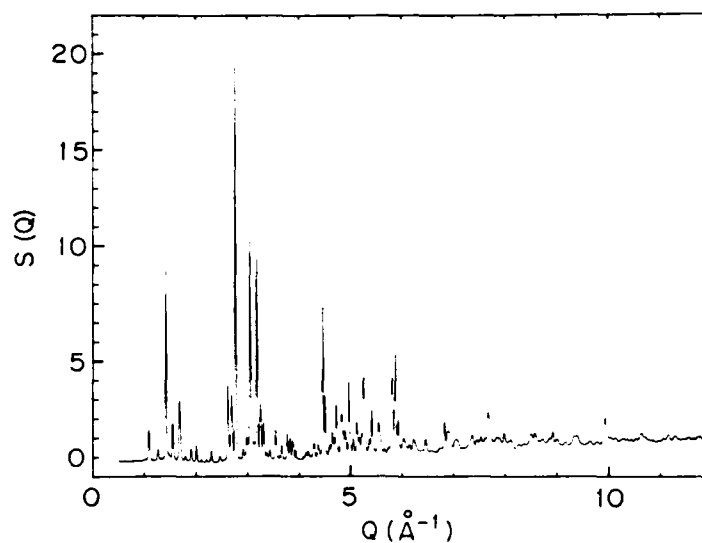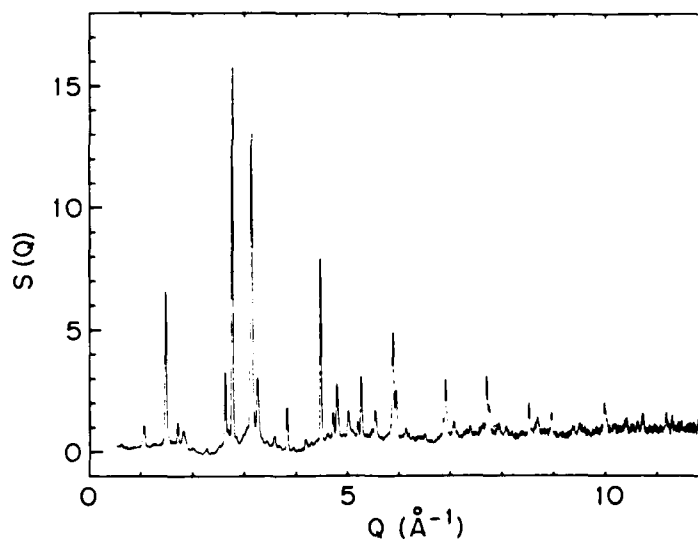Fig. 1

Structure factor for the Al₅.₅Li₃.₃Cu Frank Kasper phase.

Fig. 2

Structure factor for the Al₅.₅Li₃.₃Cu icosahedral phase.

large number of atoms in the unit cell. For the icosahedral phase we observe significant diffuse scattering, probably indicating some chemical disorder in occupancy between Cu and Al atoms. As in other icosahedral solids the structure factor diminishes rapidly with Q, indicating a wide distribution of the nearest-neighbour distances. Therefore the relatively low cut-off of Q does not decrease the accuracy of the PDF.

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The two structure factors presented in figs. 1 and 2 are obviously different. Nevertheless, very interestingly, the PDFs for the two phases look quite similar (fig. 3). More detailed inspection of fig. 3 shows some differences in the peak shapes and intensities, but basically up to 20 Å both PDFs are very similar to each other. Differences are clearly seen beyond 20 Å. The PDF describes the average distribution of interatomic distances weighted by atomic scattering factors. Although the information is one dimensional it is unique for a given structure. The fact that both PDFs are very similar up to 20 Å implies that similar 'structural units' are present in the Frank Kasper and icosahedral phases. In other words, the short-range atomic positional correlations are almost the same in these two phases whereas the long-range correlations are different.

It was suggested by Cherkashin *et al.* (1964) that the same atomic positions and site occupations used for $(Al, Zn)_{49}Mg_{32}$ may also be used for the Frank Kasper phase of Al_6Li_3Cu, if we substitute all Li and 12 Al atoms for Mg, and assume that Cu and Al randomly occupy most of the Al Zn sites. However our calculations based upon their atomic positions and site occupations are in strong disagreement with the observed intensities. The table presents a comparison between our calculations, I_{calc}, and experimental data, I_{obs}. We noted that much better agreement is achieved by the following alteration of the structure:

(i) The intensities of the (530) and (600) diffraction lines of I_{calc} are too strong compared to I_{obs}. This can be corrected by moving the atoms in the first and second shells such that they form regular, undistorted icosahedral coordination shells.

(ii) The intensity of the (110) line of I_{calc} is also too strong. This can be remedied by making the density more homogeneous, in particular by making the densities in the icosahedral cluster and in-between the clusters nearly equal.

Fig. 3
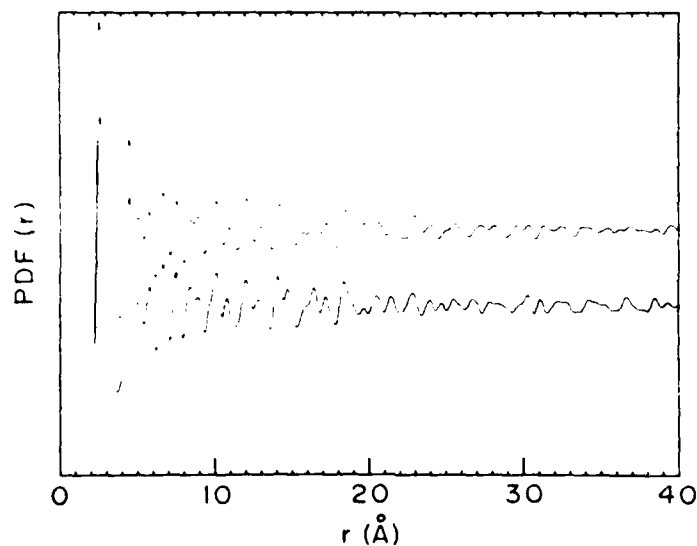
Pair-distribution functions for the Al_6Li_3Cu Frank-Kasper phase (top) and the icosahedral phase (bottom).

$Al_{5.5}Li_3Cu$ Frank-Kasper phase: experimental and calculated X-ray powder intensities, for several strong diffraction peaks, using positions and occupancies assigned by Cherkashin *et al.* (1964) (calculation 1) and after modification (calculation 2).

h	k	l	Experiment	Calc. 1	Calc. 2
1	1	0	< 1	40	2
2	1	1	14	81	6
3	1	0	68	30	66
2	3	1	28	67	22
5	3	0	21	63	21
4	3	3			
6	0	0	24	42	32
4	2	2			
5	3	2	100	100	100
6	1	1			
6	3	1	61	65	52
5	4	3	54	92	55
5	5	0			
7	1	0			

(iii) The intensity of the (310) line of I_{calc} on the other hand is too low. The *d*-spacing for this line (4·41 Å) corresponds to the second-neighbour separation. Thus it can be made stronger by avoiding Li atoms as nearest neighbours to each other, while in the original site occupation scheme Li atoms occupy well-defined shells, and are thus often nearest neighbours to each other. In general, dispersing Li atoms in the region between the icosahedral clusters and avoiding contact with each other produces a better result.

The calculated intensities for this modified structure are given in the table. As a consequence of these modifications structural units very similar to the rhombohedral unit cells for the quasicrystalline decoration model are found to be already present in the Frank-Kasper phase. This is consistent with our observation that the short-range correlations in icosahedral and Frank Kasper phases are nearly identical. Our results, along with our earlier paper on the diffraction intensities (Shen, Poon, Dmowski, Egami and Shiflet 1987), strongly support the basic ideas proposed by Henley and Elser (1986) and by Audier, Sainfort and Dubost (1986). However at present we cannot establish the exact atomic positions because the refinement of the cubic structure has not been carried out. Also a direct comparison of the measured PDF of the icosahedral phase with the PDF of the three-dimensional quasicrystalline model is left for future work. If we decorate all the vertices and edge centres of the quasicrystalline lattice by Al and Cu atoms, some of them are found to be too close to each other; thus vacancies have to be introduced to accommodate this situation. In a previous paper (Shen *et al.* 1987) only a simplified version of the Henley Audier model was used in which the vacant sites (about 18%) were randomly distributed. This assumption should be acceptable in comparing the diffraction intensities, since the vacancy correlations affect a wide range of Q space more or less evenly. However they will affect the short-range correlations in the PDF rather strongly, so that the simple model would not yield good agreement for the PDF. Satisfactory agreement is expected only when the positions of these vacancies are correctly specified.

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