Acta Cryst. (1986). B42, 336-339

Combining High-Resolution Electron Microscopy and Electron Diffraction to Determine Quasicrystal Structure

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(*Received* 1 *October* 1985; *accepted* 2 *January* 1986)

Abstract

Proposals are made to combine the structure information carried by high-resolution electron microscopic images and by electron diffraction patterns in quasicrystal structure determination. The method has been applied to samples of quasicrystals in rapidly quenched Al–Mn alloy. The projected structure model is given and the shortest bond lengths of Mn–Al and Al–Al are 2·82 and 2·96 Å, respectively.

1. Introduction

The discovery of quasicrystals in rapidly quenched alloys of Al–Mn, Al–Fe and Al–Cr systems (Shechtman, Blech, Gratias & Cahn, 1984) led to the task of developing different techniques for determining quasicrystal structures. Nowadays the grain size of quasicrystals is several micrometres. High-resolution electron microscopy (HREM) which is able to give images mirroring the projected structure of the object examined is a very useful technique in quasicrystal structure determination.

Different structural models have been proposed for the Al–Mn quasicrystal on the basis of the high-resolution electron microscopic images (Hiraga, Hirabayashi, Inoue & Masumoto 1985; Bursill & Peng, 1985; Liu, Li & Liu, 1986). The disadvantage of HREM is its limited resolution. At the present state of the art it is difficult to distinguish individual atoms in icosahedral quasicrystals from high-resolution images. However, the structure information obtained from electron diffraction (ED) patterns is much richer in the sense of the resolution although the phase of the diffracted waves is lost. It is easy to obtain some structural information of spatial frequency up to 1 $Å^{-1}$ from ED patterns. It has been shown that the combination of the HREM and ED information leads to a resolution enhancement in high-resolution electron microscopic image processing (Fan Hai-fu, Zhong Zi-yang, Zheng Chao-de & Li Fang-hua, 1985). In this paper a simple technique of combining the HREM and ED information to determine quasicrystal structures is proposed and applied to the quasicrystal in rapidly quenched Al-Mn alloy.

2. Principle

The Fourier transform of the potential distribution function $\varphi(r)$ of the object examined gives the diffracted wave function

$$Q(\mathbf{u}) = \int \varphi(r) \exp(2\pi i \mathbf{u}\mathbf{r})\, \mathrm{d}v_{\mathbf{r}}. \quad (1)$$

Generally, $\varphi(\mathbf{r})$ is a real function and the complex conjugate of $Q(\mathbf{u})$ is

$$Q^{i}(\mathbf{u}) = \int \varphi(\mathbf{r}) \exp(-2\pi i \mathbf{u}\mathbf{r})\, \mathrm{d}v_{\mathbf{r}}. \quad (2)$$

The diffracted wave intensity is

$$I_d(\mathbf{u}) = Q(\mathbf{u})Q^{i}(\mathbf{u}) = \mathscr{F}[\varphi(r) * \varphi(-r)]; \quad (3)$$

here $*$ denotes the convolution operation, and

$$\mathscr{F}^{-1}[I_d(\mathbf{u})] = \varphi(r) * \varphi(-r). \quad (4)$$

Formula (4) indicates that the inverse Fourier transform of the diffracted wave intensity equals the self convolution of $\varphi(\mathbf{r})$, which represents the assembly of atomic pairs in the object and is called the interatomic vector function. The interatomic vector function

$$P(\mathbf{r}) = \varphi(\mathbf{r}) * \varphi(-\mathbf{r}) \quad (5)$$

is equivalent to the Patterson function in X-ray and electron crystallography (Buerger, 1959; Vainshtein, 1956) and equivalent to the radial distribution function in diffraction analysis of amorphous materials (Klug & Alexander, 1974). Hence, some information about projected atomic configuration of resolution up to 1 Å might be obtained from the inverse Fourier transform of the intensity of an ED pattern.

It will be seen later that the optical Fourier transform (OFT) of ED patterns of icosahedral quasicrystals consists of sharp dots. An analysis of the OFT of ED patterns for quasicrystals should be similar to Patterson analysis for crystals (Buerger, 1959). However, quasicrystal structure determination based solely on ED information is far from straightforward and might lead to some ambiguity because only the intensity of the diffracted waves can be recorded while

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the phase is lost. Therefore, it is advisable to combine the high-resolution electron microscopic images and the Fourier transform of ED patterns to determine the quasicrystal structure. The Fourier transform of ED patterns can be obtained by computer or simply by optical methods as follows.

3. Experimental

Ion-thinning samples of a quasicrystal in rapidly quenched Al–14·3 at.% Mn alloy (Liu, Li & Liu, 1986) were observed in a JEM 200CX high-resolution electron microscope equipped with a top-entry goniometer. An evaporated gold thin foil was used to calibrate the ED camera length. A contracted ED pattern taken with the incident beam parallel to the fivefold axis and a one-dimensional grating of suitable spacing were used as the objects for taking the optical Fourier transform (OFT) of the ED pattern and the optical diffractogram of the grating at the same optical conditions in an LD-10 optical diffractogram. The spacing of the grating was measured in the same units as the ED pattern, namely in nm^{-1} (1 nm = 10 Å), so that the optical diffractogram of the grating, which consists of a series of equidistant spots, can be used to calibrate the scale in the OFT of the ED pattern and the magnification of the electron micrograph as well.

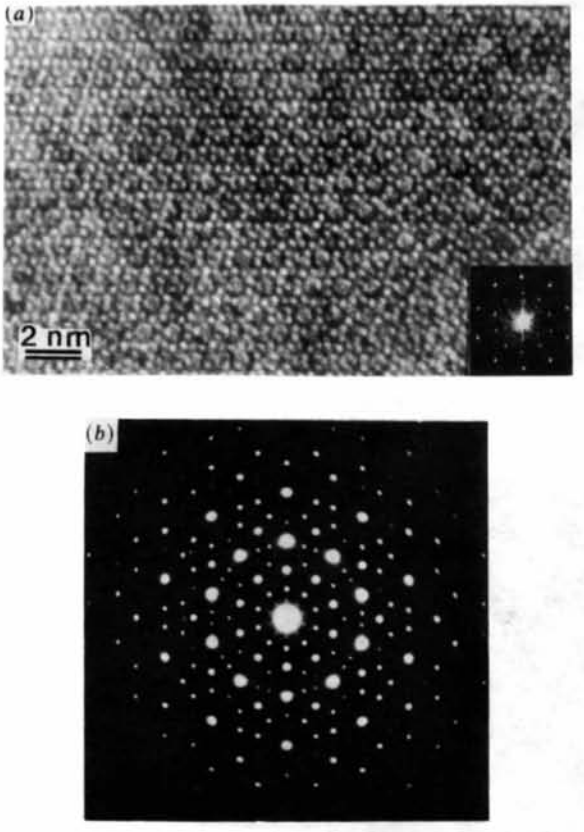

Fig. 1. (*a*) High-resolution electron microscopic image of a quasicrystal in rapidly quenched Al–14·3 at.% Mn alloy taken with the incident beam parallel to the fivefold axis; inset is the optical diffractogram. (*b*) Electron diffraction pattern corresponding to (*a*).

4. High-resolution image of Al–Mn quasicrystal and proposed model

Fig. 1(*a*) is an image taken with the incident beam parallel to the fivefold axis together with its optical diffractogram and Fig. 1(*b*) the corresponding ED pattern. The distance between two nearest white dots in the image is about 4 Å. A structure model has been proposed on the basis of the configuration of white dots assuming that the quasicrystal is constructed from fundamental icosahedra with an atom of Mn at the center and twelve atoms of Al at the corners (Fig. 2) (Hiraga, Hirabayashi, Inoue & Masumoto, 1985). Fig. 3 shows the projection of the proposed model along the fivefold axis. In Fig. 3(*a*) the elemental figure consisting of two pentagons with a 36° rotation between them represents the projection of a fundamental icosahedron. Large circles represent the projection of atoms of Mn together with Al and small circles only atoms of Al. Every six elemental figures form a larger figure, a pentagon of second order (Fig. 3*b*) which aggregates in sixes to form an even larger figure, a pentagon of third order (Fig. 3*c*).

Fig. 3(*d*) is an enlarged photograph of a region extracted from Fig. 1(*a*), which is superimposed with the model shown in Fig. 3(*c*). It can be seen that the image contrast is in good agreement with the proposed structure model. Atoms of Mn together with Al appear bright in the image, while atoms of Al and rhomb-shaped channels surrounded by atoms of Al appear dark. This can be explained by the pseudo-weak-phase-object approximation proposed by Li & Tang (1984, 1985).

Fig. 4(*b*) is also an enlarged photograph from a region of Fig. 1(*a*), which is superimposed with the model shown in Fig. 4(*a*) with the aim of clarifying the aggregation of fundamental icosahedra over a wider range. The arrangement of white dots is in good agreement with the model. Fig. 4 illustrates the aggregation of four pentagonal figures of second order with

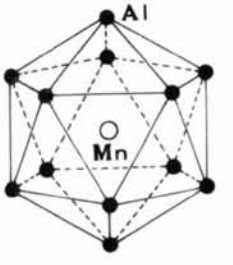

Fig. 2. Fundamental icosahedron with Mn atom at the center and twelve Al atoms at the corners.

a linking fundamental pentagon. A five-pointed-star-shaped channel could be located inside or outside a pentagon of third order depending on the azimuth of the linking pentagon or, rather, the linking icosahedron. It can be seen that the arrangement of white dots in the image and of elemental pentagonal figures in the projected model (Figs. 3*d* and 4*b*) is in good agreement with original Penrose tiling patterns (Penrose, 1979) located at the bottom left part of Figs. 3(*a*) and 4(*b*).

Table 1. *Lengths of interatomic vectors*

$t=(1+\sqrt{5})/2$.

Vector	r (Å)	r/r_{OC}
OA	1·56	$1/t^2$
OB	2·52	$1/t$
OC	4·08	1
OD	6·60	t
OE	10·68	t^2
OF	13·20	t^2+1/t
OG	14·76	t^2+1
OH	17·28	t^3

5. Analysis of the OFT of the ED pattern

The OFT of the ED pattern shown in Fig. 1(*b*) has the same symmetry as the ED pattern (Fig. 5). A schematic diagram showing a set of interatomic vectors corresponding to spots lying on the vertical line is on the right side of the OFT. The vector lengths are in the familiar golden ratio of $1:(1+\sqrt{5})/2$ (Table 1). The length of vector **OC** is 4·08 Å, which is close to the distance between two nearest white dots in the image. Assuming that vector **OC** corresponds to the projection of the nearest atomic pair of Mn–Mn located at centers of two edge-sharing icosahedra, it has been noticed that the assembly of interatomic vectors derived from Fig. 5 is in agreement with Fig. 3(*c*). Hence, the proposed model based on the image has been confirmed by the OFT of the ED pattern. The length of the longest interatomic vector which can be seen in the OFT of the ED pattern is about 35 Å. This indicates that the order range is close to

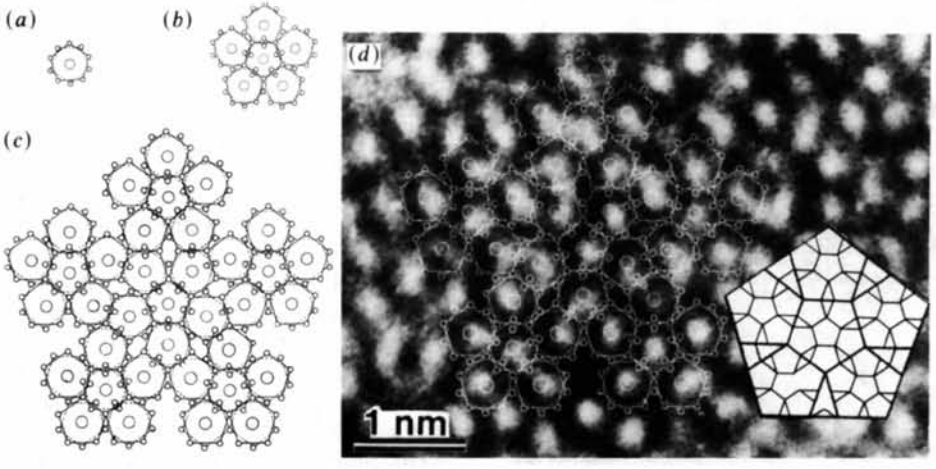

Fig. 3. (*a*) Projection of a fundamental icosahedron. (*b*) and (*c*) Projections of aggregations of fundamental icosahedra along the fivefold axis. (*d*) Enlarged photograph of a region of Fig. 1(*a*) superimposed with the model in (*c*).

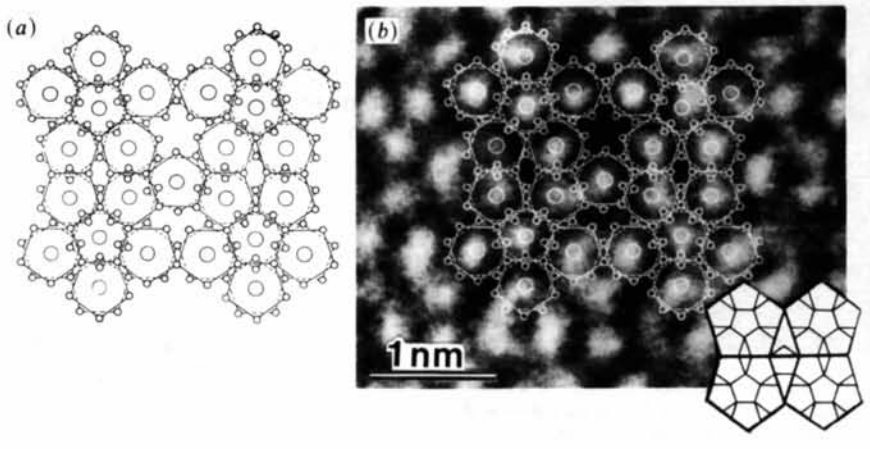

Fig. 4. (*a*) Projection of an aggregation of edge-sharing icosahedra. (*b*) Enlarged photograph from a region of Fig. 1(*a*) superimposed with the model shown in (*a*).

the size of the pentagonal figure of third order shown in Fig. 3(*c*).

Moreover, because vector **OB** corresponds to the projection of the atomic pair Mn–Al in the fundamental icosahedra, it is easy to determine the shortest bond lengths of Mn–Al and Al–Al in the fundamental icosahedron, which are 2·82 and 2·96 Å, respectively.

6. Discussion

Generally, it cannot be easily known whether atoms appear dark or bright without carrying out an image simulation. But in the present case the fact that each white dot represents a fundamental icosahedron in the proposed model can be explained by the pseudo-weak-phase-object approximation (Li & Tang, 1985). The thickness of the examined sample is above its critical value so that the projection of atoms of Mn superimposed with atoms of Al appears bright, while the projections of atoms of Al and channels of various shapes appear dark.

The advantage of a high-resolution image is in its intuitive recognition, while that of an ED pattern is in its structure information of higher resolution. The interatomic vector **OB** of length 2·52 Å which is beyond the resolution limit of the image reveals the existence of the fundamental icosahedron shown in Fig. 3(*a*) and gives the bound lengths Mn–Al and Al–Al close to those in the equilibrium phase. This indicates that the ED pattern does give some structure information which cannot be seen in the image. The interatomic vector **OC** of length 4·08 Å which is in the resolution limit of the image gives nothing new compared with the image. It can only give collateral evidence for the edge-sharing aggregation of fundamental icosahedra (Fig. 3*b*), which can be seen intuitively in the image. In order to keep the interatomic distances of Al–Al reasonable some corners of icosahedra would not be occupied.

Obviously, combining the assembly of interatomic vectors and the image is more beneficial in quasicrystal structure determination than using just one of them. This method would also be useful in crystal-structure determination when crystals are not large enough for X-ray diffraction analysis. The fact that under kinematical scattering conditions the Fourier transform of ED intensities is an assembly of interatomic vectors can also hold for thicker crystals if the peak height of spots in the OFT is not taken into consideration.

However, a complete determination of the structure should be based on the three-dimensional structure information for either crystals or quasicrystals. A more reliable result would be derived by combining the ED and the HREM information obtained with different orientations of the quasicrystal sample and also by image simulation. Here we would only like to emphasize the usefulness of the method itself.

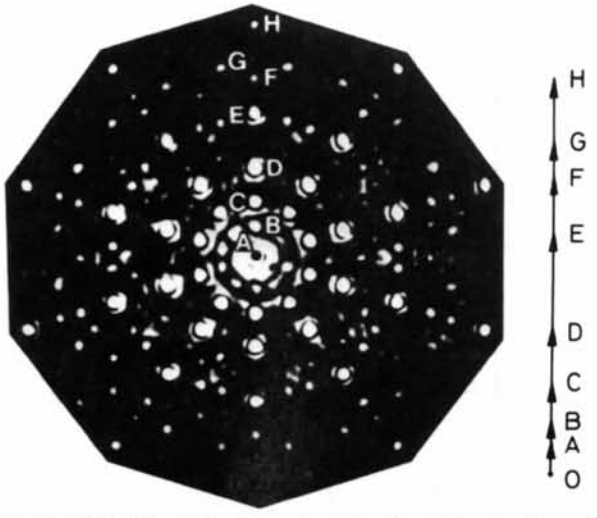

Fig. 5. OFT of the ED pattern shown in Fig. 1(*b*) and schematic diagram of interatomic vectors corresponding to spots lying on the centered vertical line of the OFT.

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