High-Resolution TEM Images of Zinc Phthalocyanine Polymorphs in Thin Films

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Abstract

The structure of a vacuum-deposited polycrystalline film of zinc phthalocyanine, $C_{32}H_{16}N_8Zn$, has been investigated by high-resolution electron microscopy. With the aid of a minimum-dose system, the molecular arrangements in crystals were observed and the existence of at least three polymorphs were confirmed in the film.

Introduction

It is well known that the crystal structures of phthalocyanine (abbreviated as Pc) and its derivatives of divalent first-transition metals are isomorphic and that they have at least two polymorphs, a metastable α form and a stable β form. The β form can be obtained as well grown single crystals to which X-ray structure analysis can be applied and some of them have been analysed in detail (Kirner, Dow & Scheidt, 1976; Scheidt & Dow, 1977; Brown, 1968; Mason, Williams, & Fielding, 1979). On the other hand, the α form exists only in the form of very fine powder or vacuum-deposited film and the structure has not been fully analysed. PtPc is exceptional because it exists normally as the stable α form in a single crystal. An X-ray analysis of the material has been done by Robertson & Woodward (1940) and corrected by Brown (1968) who has shown that there are two closely similar crystal structures both slightly differing from the result given by Robertson & Woodward (1940). The structure of the α form of other Pc derivatives has been assumed to be isomorphic with PtPc in the α form. However, this assumption is based only on the interplanar spacings of the fine crystals determined from a few diffuse lines in X-ray or electron diffraction patterns.

The recent remarkable development of high-resolution electron microscopy, both in the instrumental capability and in the observation technique, makes it possible to examine the structure of fine crystals through the direct observation of molecular images. This method is now widely recognized to be powerful, especially when the molecular structure is well known and only the packing or the arrangement of the molecules is the matter of concern. The application of high-resolution electron microscopy to organic materials has been limited because of the radiation damage caused by the electron beam. In order to observe an image of organic molecules, it was required to increase the resistivity of the molecule against the electron irradiation. Although the halogenation of molecules is the most effective method to enhance the resistivity, as reported and successfully applied by Uyeda, Kobayashi, Ohara, Watanabe, Taoka & Harada (1972) and Kobayashi & Reimer (1975), the method is not applicable to all organic molecules.

On the other hand, a new technique called the minimum-exposure method was proposed and performed by Williams & Fisher (1970) for the image recording of radiation-sensitive biological materials. Since being applied by Unwin & Henderson (1975) to crystalline biological specimens with a slight modification, this technique has proved to be promising for high-resolution observation of radiation-sensitive specimens.

In the present investigation, this method was adopted by developing an automated device to facilitate the whole performance and the structure of ZnPc thin films vacuum deposited on an amorphous carbon film has been revealed. The critical electron dose which is necessary to destroy a crystal of non-halogenated Pc derivative has been reported by Reimer (1965) to be 10–20 kC m^{-2} and the total electron dose needed on the sample in order to take each electron micrograph presented in this paper was only 2 kC m^{-2} or less. Therefore, the structure was investigated by the use of images which were free from serious distortion due to radiation damage.

Experimental

ZnPc was synthesized from pure zinc dust and phthalodinitrile through direct reaction and purified by

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repeated sublimation in a nitrogen gas flow at a temperature of 823 K. The needle-shaped crystals thus produced were identified as pure ZnPc by elemental analysis.

A thin carbon film was prepared on a freshly cleaved mica surface in a vacuum of $6 \cdot 7 \times 10^{-4}$ Pa through indirect deposition and the thickness was determined to be 30 Å by electron microscopy following the method developed by Adachi, Adachi, Katoh & Fukami (1968). The film was transferred onto a gold-coated microgrid and fixed with mesh cement to avoid incidental movement during the observation in the electron microscope.

The ZnPc crystal was vacuum deposited onto the thin carbon film at room temperature (298 K) in a vacuum of $6 \cdot 7 \times 10^{-5}$ Pa which remained at the same level during the evaporation of the material. The rate of deposition and the thickness of the film were monitored with a quartz-crystal microbalance to be $0 \cdot 5$ Å s^{-1} and 50 Å respectively. The high-resolution electron micrographs were obtained with a JEOL-100C electron microscope operated at 100 kV. The spherical aberration constant of the objective lens is $0 \cdot 7$ mm, which gives a theoretical point-to-point resolution of $2 \cdot 8$ Å at best. The observation was performed at the direct magnification of 220 000 and the images were recorded on Fuji-FG films with 2 s exposure. The minimum-exposure method was applied with the aid of the JEOL minimum-dose system (Fujiyoshi, Kobayashi, Ishizuka, Uyeda, Ishida & Harada, 1980).

Results and discussion

The molecular arrangements in the α form projected along the major crystal axes are depicted in Fig. 1 with those of the β form for comparison. They are quoted from the data reported by Brown (1968) for PtPc in the α form and by Scheidt & Dow (1977) for the β form of ZnPc. Figs. 1(a) and (d) are the b-axis projections of the α and β forms respectively and the projections along the a and c axes are shown in (b) and (e). As the α form belongs to the space group $C2/c$ or $C2/n$, half of the molecules shift alternately by a half period along the b axis. This finally necessitates taking dimensions which are twice as large along the a and c axes as those of the simple periodicities apparent in the projection in Fig. 1(a) and the intermolecular distance along the b axis in the projected image is half of the b-axis period in the crystal. The β form is monoclinic belonging to the space group $P2_1/a$. The unit-cell constants of the β form of ZnPc determined from X-ray diffraction are $a = 19 \cdot 27$, $b = 4 \cdot 854$, $c = 14 \cdot 55$ Å, $\beta = 120 \cdot 48°$ with two molecules in the unit cell. A planar molecule like phthalocyanine is apt to be piled up in parallel layers forming a molecular column in a crystal. The column axis is generally along the direction of the crystal b axis.

The intermolecular distance in such a column is about $3 \cdot 4$ Å as in other macrocyclic ring compounds. The difference in the angles between each molecule and the column axis results in the existence of polymorphs. Figs. 1(b), (c), (e) and (f) show such angles and molecular stackings in each polymorph.

High-resolution electron micrographs of ZnPc film show that the film is composed of many crystallites whose sizes are about 300 Å or less. The crystallites show various lattice fringes with different aspects as can be seen in Fig. 2. At the arrowed sites $A-E$ small crystallites can be observed with sufficient contrast. The contrast clearly indicates that each molecular image is not formed by a single molecule but by several molecules stacking in a molecular column. Very faint contrast at a crystal edge seems to be caused by the small number of molecules forming a column and disorder due to molecular vibration.

A raft-like image arrowed A has 13 Å spacing which corresponds to that of the (100) plane of the α form. In an a-axis projection and in all other projections along an axis perpendicular to the b axis of the α form, the molecules are superimposed on each other and the molecular images are inseparable. As a result the image including the b axis must show a lattice fringe like this image.

The electron micrograph shown in Fig. 3 also has 13 Å lattice spacings. In this crystal a stacking of molecules in a column can clearly be recognized along the b axis. The column images can be provisionally defined as in Fig. 3(b) according to a stacking of the molecules. A projection of the β form along the c axis is then represented as $...ABABA...$ as shown in Fig. 1(e) and also in the α form viewed along the a axis, although in the latter case the intermolecular distance in the column image is half of the b-axis period. In the crystal image in Fig. 3, the stacking sequence is not uniform.
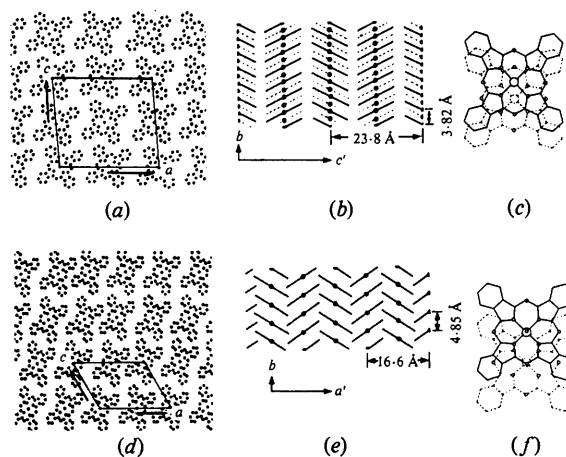

Fig. 1. Molecular arrangements in the α form (a)–(c) and the β form (d)–(f). (a), (d) Projection on (010) plane; (b), (e) projection on (100) and (001) planes; (c), (f) superposition of molecules related by translation along the b axis.

The major part of the crystal is represented as ...*AAAAA*... and partly as ...*ABA*... or ...*ACA*.... Such a stacking disorder, which is frequently observed in the present specimen, can be considered to be induced by the anisotropic intermolecular forces of Pc. The intermolecular force is stronger in the direction perpendicular to the molecular plane than in the direction parallel to the plane because the origin of the force is mostly from π-electron interactions. In any case, it is concluded that the crystal shown in Fig. 3 is a new polymorph because the image cannot be derived from the α or the β form.

The electron micrograph shown in Fig. 4 exhibits the same molecular arrangement as Fig. 1(a). The image shows periodicities of 13 and 12 Å in the directions of the *a* and *c* axes. The angle between the two axes is 93°, which agrees with the axial angle β of the α form of PtPc. When the lattice periods in both directions are doubled, the unit-cell dimensions coincide with those of the α polymorph of PtPc and also with those of CuPc epitaxially grown on KCl as reported by Ashida, Uyeda & Suito (1966). This polymorph was named here as the αI form. Murata, Fryer & Baird (1976) have reported some images of CuPc in the α form taken with their technique of minimum beam exposure. However, these are lattice images rather than molecular images and are not satisfactory for the discussion of the structure or molecular orientation in the crystal, although they refer to the orientation of molecules in an epitaxially grown crystal. Clark, Chapman & Ferrier (1979) have indicated on the basis of diffraction data that the result given by Murata *et al.* (1976) was not sufficient to discuss the molecular orientation because of the distortion of their image due to serious damage of the specimens by electron bombardment. The molecular images shown in Fig. 4 agree well in the molecular orientation with a Fourier image calculated from electron diffraction intensities by Clark *et al.* (1979).

In another crystal image shown in Fig. 5, molecules are stacked with equal lattice periodicities in two directions. The dimension differs slightly from the α form mentioned above. This crystal (αII form) has $a = c = 13$ Å and $\beta = 93°$ as lattice constants in two dimension. The existence of this polymorph has not been reported so far, probably because its coexistence with the αI form cannot be detected by means of any diffraction method because their lattice dimensions are close to each other and the crystallites are too small to allow the two forms to be separated.

The crystal image indicated by letter *C* in Fig. 2 is enlarged in Fig. 6. The structure of this crystal (αIII
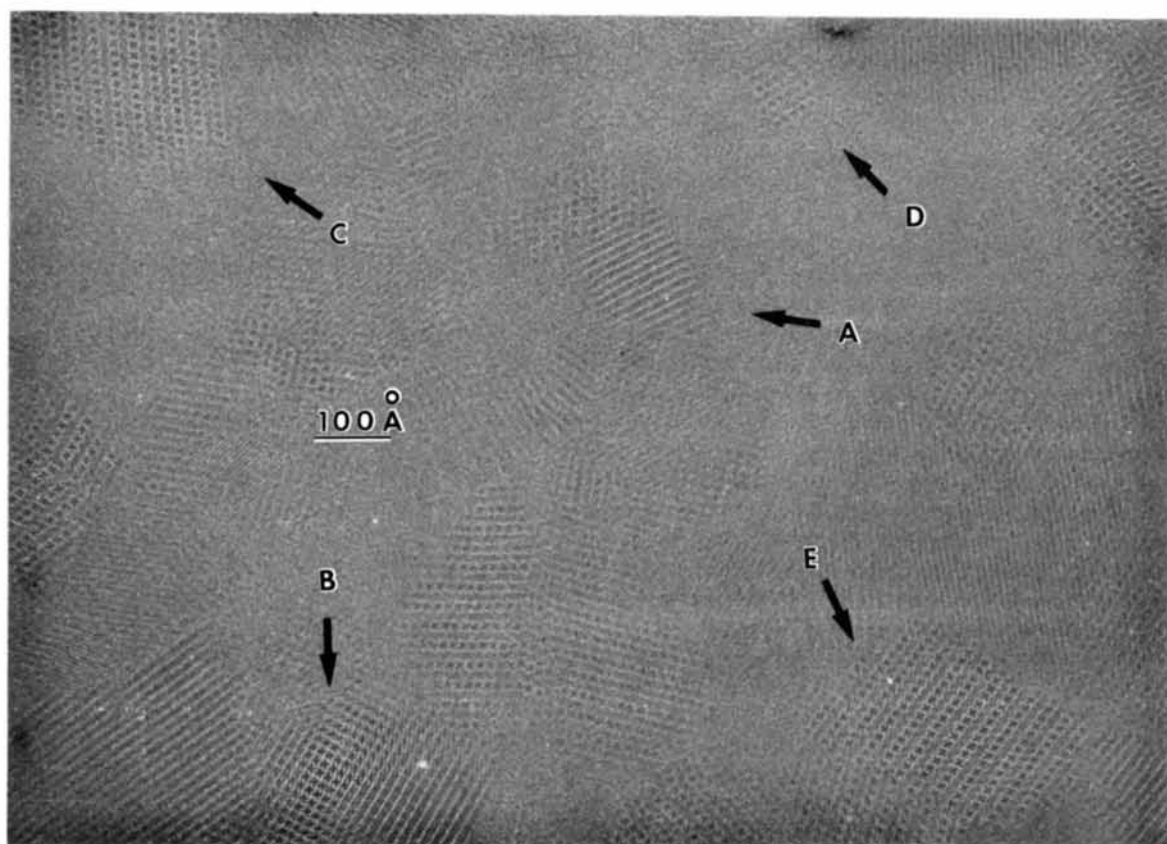
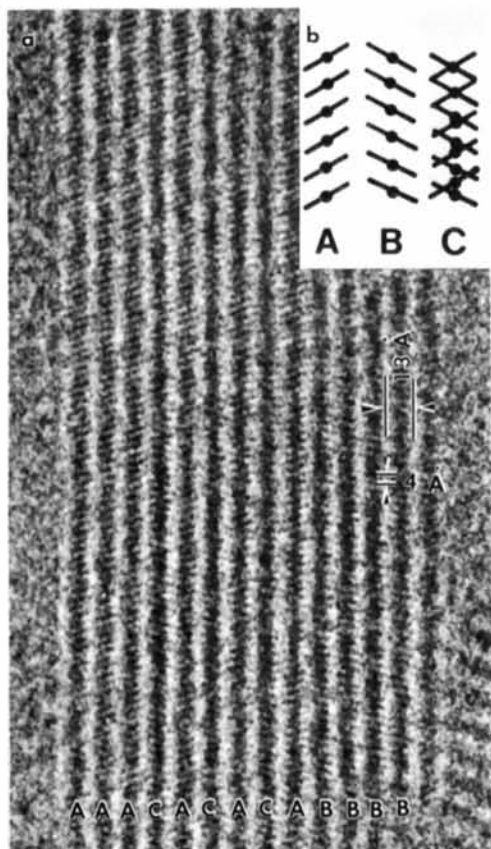

Fig. 2. Electron micrograph of a ZnPc thin film.

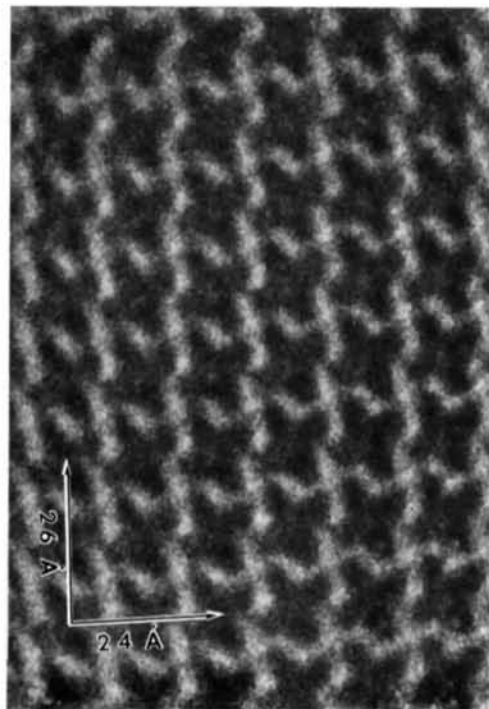Fig. 3. High-resolution image showing molecular stacking along the *b* axis.
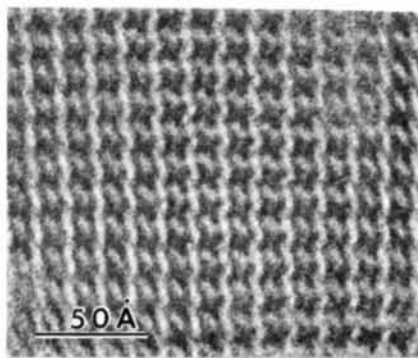

Fig. 4. Molecular images in the αI form.

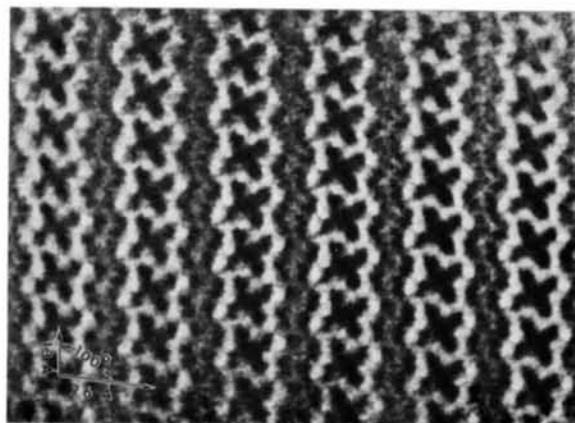form) differs from those in Figs. 1, 4 and 5. The crystal is composed of two kinds of molecular arrays arranged in different ways. In one kind of array, for instance, images of the Pc molecules are isolated, clearly revealing their shapes. In such an orientation the molecular plane is almost parallel to the substrate plane and the image is a projection of several molecules stacked along the projection axis to eclipse one another. On the other hand, the molecular images in the other kind of array are not clearly separated in the micrographs in Fig. 6. A superposition of two images displaced along the array in the image plane results in such images. The individual molecular orientation in each image is assumed to be as shown in Figs. 7(a),(b) with the molecules in the first arrays of the crystal image in Fig. 6. The crystal unit cell is composed of these two molecular layers (a) and (b) superimposed alternately along the *b* axis, that is, the projection axis of the images. The computer-simulated image based on this model is reproduced in Fig. 8 and shows a good agreement with the electron micrograph.

It is worth noting that the crystal image shown in Fig. 9 was occasionally found in the specimen. The images closely resemble the αIII form in appearance.

Fig. 5. Molecular images in the αII form.

Fig. 6. Molecular images in the αIII form. The electron micrograph is spatially averaged photographically.

Table 1. *Unit-cell constants for phthalocyanine polymorphs*

Phthalocyanine	a (Å)	b (Å)	c (Å)	β (°)	References
α-CuPc	25·92	3·79	23·92	90·4	Ashida *et al.* (1966)
α-PtPc	26·29	3·818	23·92	94·6	Brown (1968)
δ-CuPc	14·90	12·20	13·7	90·0	Saijo, Kobayashi & Uyeda (1977)
α I-ZnPc	26·0	–	24·0	93·0	Present work
αII-ZnPc	26·0	–	26·0	93·0	Present work
αIII-ZnPc	13·0	–	26·0	100·0	Present work

The axial angle was 97° whereas the angle of the αIII form is 100° and the molecular arrays II in the images apparently differ in profile from each other. However, any significant differences in the interplanar spacings could not be detected from measurements made on laser optical diffractograms of several electron micrographs. A small change in crystal orientation with respect to the illuminating beam direction should be taken into consideration in such a case. Especially

I   II   I   I   II   I

Fig. 7. Molecular arrangements in two different layers composing the αIII-form crystal. I and II indicate two molecular arrays in Fig. 6.

when a crystal is so thin as the present specimens, it is often observed that the small change in orientation causes an axial angle to distort while the shapes of the molecular images do not alter. Therefore, the conclusion that this crystal is also another new polymorph of ZnPc should be deferred until the structure is revealed with a resolution at atomic level.

The unit-cell constants of the new polymorphs are summarized in Table 1 with those of the other α forms reported.

Until now it has been said that vacuum-deposited films of Pc derivatives were composed of the α-form crystallites whose structure was isomorphic with that of PtPc reported by Robertson & Woodward (1940). The present study by high-resolution electron microscopy has revealed that such films are composed of many different polymorphs such as the αI, αII, and αIII forms. The coexistence of many crystal forms in a film suggests that there are some minima in intermolecular potential curves of Pc and consequently the structure of
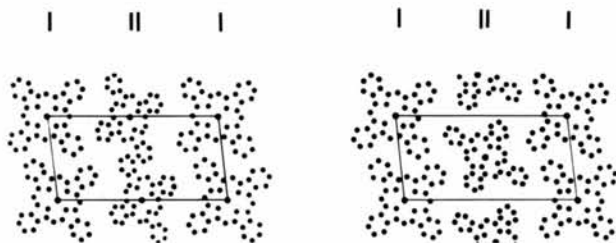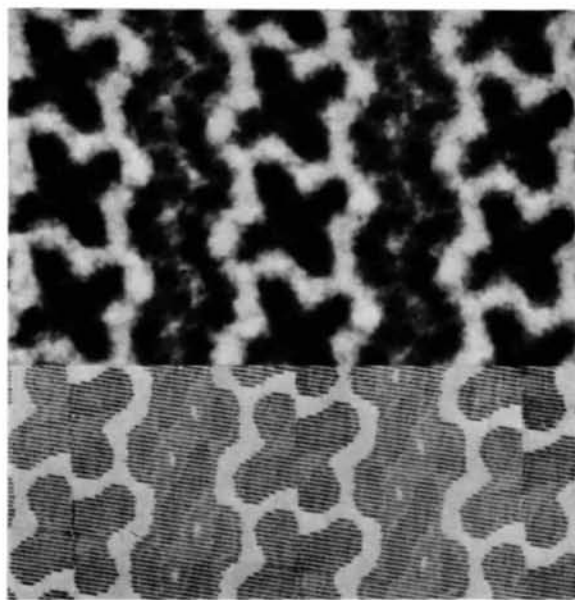

Fig. 8. The structure images of the αIII form at Scherzer focus and the corresponding computed image. The electron micrograph is spatially averaged photographically.
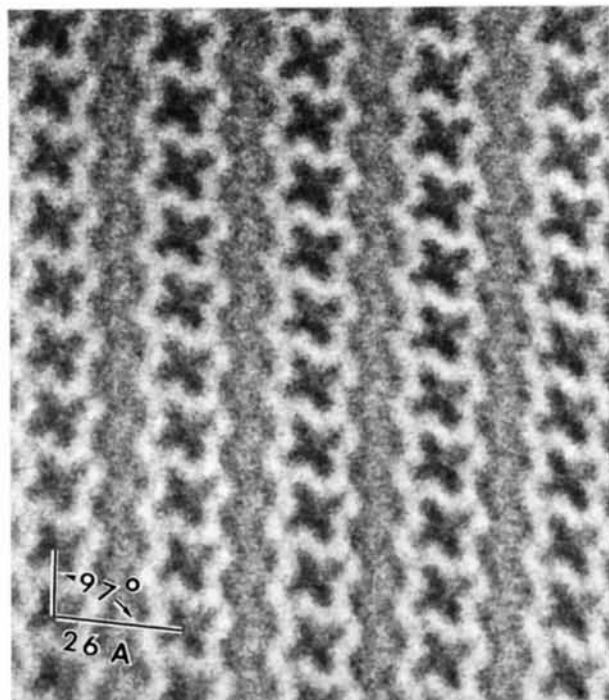

Fig. 9. Molecular images of ZnPc. The electron micrograph is spatially averaged photographically.

these crystals may vary easily with the conditions of crystal growth. The lattice energy and the crystal surface energy become of comparable size in such small crystals and therefore the interaction force acting between the crystal or molecules and the substrate is able to have an effect to some extent on the growth process.

References

ADACHI, K., ADACHI, M., KATOH, M. & FUKAMI, A. (1968). J. Electron Microsc. 17, 280.
ASHIDA, M., UYEDA, N. & SUITO, E. (1966). Bull. Chem. Soc. Jpn, 39, 2616–2624.
BROWN, C. J. (1968). J. Chem. Soc. A, 2488–2493, 2494–2498.
CLARK, W. R. K., CHAPMAN, J. N. & FERRIER, R. P. (1979). Nature (London), 277, 369–370.
FUJIYOSHI, Y., KOBAYASHI, T., ISHIZUKA, K., UYEDA, N., ISHIDA, Y. & HARADA, Y. (1980). Ultramicroscopy, 5, 459–468.
KIRNER, J. F., DOW, W. & SCHEIDT, W. R. (1976). Inorg. Chem. 15, 1685–1690.
KOBAYASHI, T. & REIMER, L. (1975). Bull. Inst. Chem. Res. Kyoto Univ. 53, 105–116.
MASON, R., WILLIAMS, G. A. & FIELDING, P. E. (1979). J. Chem. Soc. Dalton Trans. pp. 676–683.
MURATA, Y., FRYER, J. R. & BAIRD, T. (1976). J. Microsc. (Oxford), 108, 261–275.
REIMER, L. (1965). Lab. Invest. 14, 344–358.
ROBERTSON, J. M. & WOODWARD, I. (1940). J. Chem. Soc. A, 36–48.
SAIJO, H., KOBAYASHI, T. & UYEDA, N. (1977). J. Cryst. Growth, 40, 118–124.
SCHEIDT, W. R. & DOW, W. (1977). J. Am. Chem. Soc. 99, 1101–1104.
UNWIN, P. N. T. & HENDERSON, R. (1975). J. Mol. Biol. 94, 425–440.
UYEDA, N., KOBAYASHI, T., OHARA, M., WATANABE, M., TAOKA, T. & HARADA, Y. (1972). Proc. Fifth Eur. Conf. Electron Microsc., Manchester, p. 566.
WILLIAMS, R. C. & FISHER, H. W. (1970). J. Mol. Biol. 52, 121–123.

An X-ray Measurement of Charge Asphericity in Vanadium Metal

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Abstract

For b.c.c. vanadium metal the integrated intensities of 80 independent reflections were measured by using a spherically shaped single crystal 0·241 (3) mm in diameter with Ag $K\alpha$ radiation. It was confirmed that there are very small differences in integrated intensities between paired reflections, and these differences can be measured significantly beyond the experimental error. The ratios of the paired reflections are smaller than those obtained from platy crystals [Weiss & DeMarco (1965). Phys. Rev. A, 140, 1223–1225] but are in good agreement with those recalculated recently by means of the APW method [Wakoh & Kubo (1980). J. Phys. F, 10, 2707–2715].

Introduction

There is asphericity of the charge distribution around atoms in b.c.c. $3d$ metals and this causes a slight difference in the X-ray scattering factors for paired reflections having the same $\sin \theta/\lambda$, such as 442 and 600. Weiss & DeMarco (1965) attempted to detect the integrated intensity differences of the paired reflections using transmission with Mo $K\alpha$ radiation for a vanadium single-crystal plate 0·1 mm in thickness and perpendicular to [110]; they obtained the ratios listed in Table 1. The experimental ratios were much larger than the theoretical values calculated by employing the Green-function method (Wakoh & Yamashita, 1971). Diana & Mazzone (1975) repeated the experiment and obtained the same order of magnitude for the asphericity as that reported previously. A different type of experiment is desirable in order to obtain a clue to the disagreement between the experimental and