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Combination of Convergent-Beam Electron Diffraction and 1 MeV Structure Imaging in a Structure Determination of $\text{Na}_2\text{Ti}_9\text{O}_{19}$

BY YOSHIO BANDO*

Center for Solid State Science, Arizona State University, Tempe, AZ 85278, USA

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Abstract

The space group and atom configuration of monoclinic $\text{Na}_2\text{Ti}_9\text{O}_{19}$ have been studied by combining 1 MeV high-resolution electron microscope imaging with the convergent-beam electron diffraction (CBED) technique. The crystal has monoclinic symmetry with lattice parameters $a = 12.2$, $b = 3.78$, $c = 15.6$ Å and $\beta = 105^\circ$. The space group was determined uniquely to be centrosymmetric $C2/m$ by selecting the point group from the symmetry of the CBED pattern. On the basis of the 1 MeV structure-image observation reported previously and the space-group determination, the crystal structure of monoclinic $\text{Na}_2\text{Ti}_9\text{O}_{19}$ is proposed and atom coordinates are given.

The high-voltage high-resolution electron microscope working at NIRM, Japan, provides a very powerful method to determine a crystal structure on the basis of structure images taken along two or more principle directions, in which each cation site is resolved

(Horiuchi, Kikuchi & Goto, 1977; Bando, Watanabe, Sekikawa, Goto & Horiuchi, 1979; Bando, Watanabe & Sekikawa, 1979, 1980; Matsui, Kato, Kimizuka & Horiuchi, 1979). The possible space groups have been selected by extinction rules obtained from normal electron diffraction. However, the question still remains whether the crystal is non-centrosymmetric or centrosymmetric, since both space groups have the same Bragg conditions.

To distinguish between centrosymmetric and non-centrosymmetric space groups, the convergent-beam electron diffraction (CBED) method is very useful (Goodman, 1975; Buxton, Eades, Steeds & Rackham, 1976; Tanaka, Saito & Watanabe, 1980). A combination of structure imaging and CBED should then be very successful for determining unknown crystal structures. Bando, Sekikawa, Yamamura & Matsui (1981) have tried to combine 1 MeV high-resolution electron micrographs with CBED patterns to determine the crystal structure and space groups of $\text{Ca}_4\text{YFe}_5\text{O}_{13}$.

In a previous paper (Bando, Watanabe & Sekikawa, 1979), the crystal structure of monoclinic $\text{Na}_2\text{Ti}_9\text{O}_{19}$ was studied on the basis of 1 MeV high-resolution electron micrographs coupled with normal electron

* Present address: National Institute for Research in Inorganic Materials, 1-Namiki, Sakura-mura, Niihari-gun, Ibaraki 305, Japan.

diffraction, and the framework of the structure was determined. However, the true space group and atom coordinates are still uncertain.

The space group of the monoclinic crystal $\text{Na}_2\text{Ti}_9\text{O}_{19}$ has now been determined uniquely by selecting the point group from the symmetry of the CBED pattern. On the basis of both the space-group determination and the previous result of the 1 MeV structure image, a structural model of the monoclinic $\text{Na}_2\text{Ti}_9\text{O}_{19}$ crystal is proposed and atom coordinates are given.

The crystal was prepared by hydrothermal reaction (Watanabe, Tsutsumi, & Bando, 1979) and crushed in an agate mortar. The specimens were placed on a holey-carbon supporting grid. The CBED pattern was taken by a Philips 400 electron microscope, operating at an accelerating voltage of 120 kV. The probe diameter was almost 200 Å at the crystal.

Fig. 1 shows a 1 MeV structure image of monoclinic $\text{Na}_2\text{Ti}_9\text{O}_{19}$ taken along the b axis from a very thin region of the crystal (Bando, Watanabe & Sekikawa, 1979). The crystal has monoclinic symmetry with lattice parameters $a = 12.2$, $b = 3.78$, $c = 15.6$ Å and $\beta = 105^\circ$. The systematically absent reflections are hkl with $h + k = 2n + 1$. The possible groups for the crystal are therefore $C2$, Cm and $C2/m$. The image details can be viewed as sheets having dark and grey dots which alternate along the c axis. They are designated as B and D sheets. Sheet D consists of connected dark dots along the a axis in a dark zigzag shape, while sheet B consists of isolated grey dots. The dark and grey dots could be assigned as the sites of Ti atoms. The approximate separation of two adjacent Ti atoms within the D sheet is either 2 or 3 Å, which corresponds to the metal-to-metal distance between the edge-sharing TiO_6 octahedra located at the same level or at different levels, respectively. On the other hand, the Ti-Ti distance between the neighboring D sheets is about 4 Å, which corresponds to that between corner-sharing TiO_6 octahedra. On the basis of this direct observation of Ti atoms, a structural model has been inserted into the figure. It is clear that white dots correspond to the tunnels, two kinds of which are occupied by Na atoms.

It is obvious from Fig. 1 that a twofold axis along the b axis is present, because of the arrangement of dark, grey and white dots. This suggests that the two-dimensional space group must be $p2$. The possible space groups are therefore $C2$ and $C2/m$.

The $[010]$ zone axis which is used for imaging is also useful for inspecting the symmetry of the CBED pattern in monoclinic crystals. However, because of a relatively long c axis, the $[001]$ zone axis CBED pattern has been chosen to avoid the overlapping of each disk in the CBED pattern. The result appears in Fig. 2. As proposed by Buxton *et al.* (1976), the symmetry appearing in the CBED pattern can be described by 31 diffraction groups. Table 1 shows two

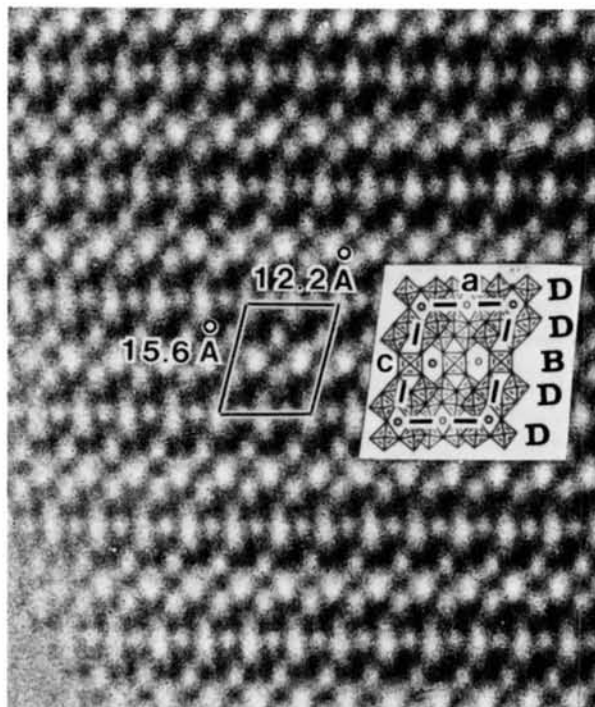


Fig. 1. 1 MeV high-resolution electron micrograph of the monoclinic $\text{Na}_2\text{Ti}_9\text{O}_{19}$ crystal, taken along the $[010]$ zone axis (as reported previously). The structure model is shown as an inset. The two types of sheets are indicated B and D . The structure consists of a succession of sheets of $--DDBDD--$ along the c axis at intervals of 15.6 Å. The bold squares indicate TiO_6 octahedra at $y = 0$, and the light ones TiO_6 octahedra at $y = \frac{1}{2}$. The open circles show Na atoms.

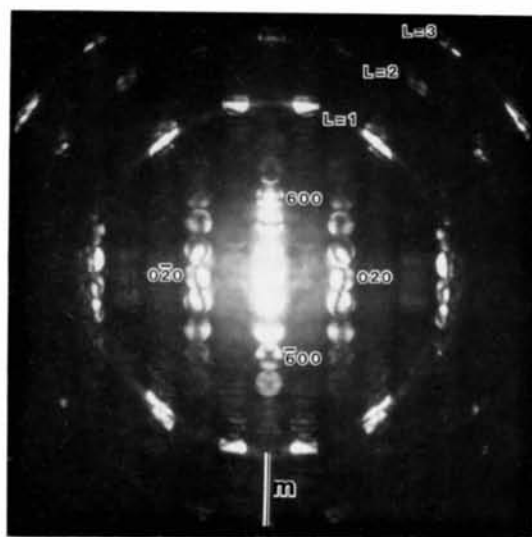


Fig. 2. Convergent-beam electron diffraction pattern taken along the $[001]$ zone axis. Upper-layer reflections are indicated as $L = 1, 2$ and 3 . The mirror line perpendicular to the b^* axis is shown.

Table 1. Symmetry of a [001] zone axis CBED pattern for space groups $C2$ and $C2/m$

Space group	Point group	Diffraction group	Whole-pattern symmetry
$C2$	2	m_R	1
$C2/m$	$2/m$	2_Rmm_R	m

point groups for the present space groups $C2$ and $C2/m$ and the corresponding diffraction groups for the [001] zone axis and the whole symmetry of the CBED pattern. Here, the symbols m_R and 2_R in the diffraction group refer to a horizontal twofold axis which is perpendicular to the incident-beam direction and an inversion center, respectively, while m stands for a mirror plane parallel to the incident-beam direction. The whole-pattern symmetries of CBED for the diffraction groups m_R and 2_Rmm_R are 1 and m , respectively. It is then clear that the true point group can be established if we examine the symmetry of the whole pattern. The whole pattern in Fig. 2 consists of a central bright-field disk and its surrounding disks in the zero-layer reflections, as well as upper-layer reflections such as first ($L = 1$), second ($L = 2$), and third ($L = 3$). It clearly demonstrates the presence of a mirror line perpendicular to the b^* axis. By inspection, for example, the fine structure appearing in the 020 reflection disk is identical to that of the 020 reflection disk, while the fine structure in the 600 reflection disk differs from that of the 600 reflection. This suggests that the present crystal belongs to the point group $2/m$. Therefore, the true space group must be $C2/m$.

It should be noted in Fig. 2 that the whole-pattern symmetry in the zero-layer reflections is the same as that of the upper-layer reflections. This indicates the influence of three-dimensional diffraction in the zero layer. This is expected in the present crystal because, owing to the long c axis, the interactions between reflections of the zero and upper layers are strong.

The crystal structure of monoclinic $\text{Na}_2\text{Ti}_9\text{O}_{19}$ projected onto the (010) plane is shown in Fig. 3, obtained from the previous model from the space-group determination. The structure consists of the framework of titanium dioxide bronze, $\text{Na}_x\text{Ti}_4\text{O}_8$ (Anderson & Wadsley, 1962), which is indicated as a double sheet DD . The bronze-type DD units are connected by bridging TiO_6 octahedra in a corner-sharing scheme, the rows of which are shown as B . The structure is thus built up of a succession of $--DDBDD--$ along the c axis.

The atomic coordinates are given in Table 2. The positions of the Ti and Na atoms were read from the structure image in Fig. 1. The positions of the O atoms were assigned from crystal-chemical considerations — *i.e.* the symmetry requirement, and reasonable metal-to-oxygen distances — because they do not show any contrast in the image. The Na atoms have two

Table 2. Atomic parameters

Space group $C2/m$: $(0,0,0; \frac{1}{2}, \frac{1}{2}, 0) +$.

Atom	Site	x	z
2Na(1)	2(a)	0	0
2Na(2)	4(i)	0.25	0.50
2Ti(1)	2(c)	0	$\frac{1}{2}$
4Ti(1)	4(i)	0.20	0.10
4Ti(2)	4(i)	0.10	0.30
4Ti(3)	4(i)	0.90	0.10
4Ti(4)	4(i)	0.75	0.30
2O(1)	2(d)	0	$\frac{1}{2}$
4O(2)	4(i)	0.15	0.00
4O(3)	4(i)	0.35	0.15
4O(4)	4(i)	0.25	0.25
4O(5)	4(i)	0.10	0.40
4O(6)	4(i)	0.90	0.25
4O(7)	4(i)	0.85	0.40
4O(8)	4(i)	0.60	0.25
4O(9)	4(i)	0.75	0.15
4O(10)	4(i)	0.05	0.15

crystallographically non-equivalent positions, which are shown as Na(1) and Na(2) in Table 2. The Na(1) located in the square-shaped hole occupies site 2(a), while the Na(2) in the hexagonal-shaped hole is in site 4(i). From the chemical composition of the present crystal, the two types of holes are fully occupied by Na atoms. Therefore the site occupancies for the 2(a) and 4(i) sites are 1 and 0.5, respectively.

The accuracy of the metal-atom positions is rather high compared to that of the O atom positions, because their positions were read directly from the image. The present coordinates will be used for future refinement by X-ray or neutron diffraction.

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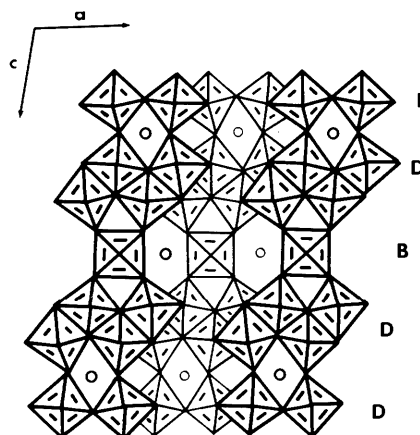


Fig. 3. A crystal structure model of monoclinic $\text{Na}_2\text{Ti}_9\text{O}_{19}$ projected onto the (010) plane. The bold and light squares show TiO_6 octahedra at $y = 0$ and $y = \frac{1}{2}$, respectively. The bold and light circles are Na atoms at $y = 0$ and $y = \frac{1}{2}$, respectively.

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Special-Point Ordering in General Crystal Structures

BY J. M. SANCHEZ,* D. GRATIAS† AND D. DE FONTAINE

Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720, USA

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Abstract

The classification of families of ordered structures, in terms of positions in reciprocal space where two or more symmetry elements of the pair potential intersect at a point, is extended to include general crystal structures. Only a relatively small number of space groups, 24 in all, are shown to be relevant to special-point ordering. The method is illustrated with the study of special-point families for a hexagonal crystal with two atoms per unit cell.

1. Introduction

General symmetry properties of pair potentials and of phenomenological free energies are, in many instances, sufficient to explain a wide range of phenomena related to order–disorder and/or magnetic phase transformations. The classical example of the power of such symmetry arguments is, undoubtedly, the well-known Landau theory of continuous phase transformations (Landau & Lifshitz, 1958). The concepts of symmetry,

and in particular that of ‘special points’ in reciprocal space – defined as points where two or more symmetry elements intersect – have been shown to be equally useful in the case of instabilities associated with other phase transitions (Khachatryan, 1973; de Fontaine, 1975). It follows from symmetry considerations that at such special points scalar functions, endowed with the symmetry of the reciprocal lattice, will have, invariably, a minimum, a maximum or a saddle point. Thus, special points would seem to play an important role in, for example, the search for the lowest-energy (ground state) ordered structures (Clapp & Moss, 1968). It turns out, however, that special points are quite insufficient for a complete description of ground states which, in general, are more conveniently treated in real space (Kanamori & Kakehashi, 1977; Kudo & Katsura, 1976; Richards & Cahn, 1971; Allen & Cahn, 1972; Sanchez & de Fontaine, 1981).

Among the most important applications of special points is the study of the onset of short-wavelength instabilities in alloys (de Fontaine, 1975). Such instabilities may take place below a first-order transition, frequently bearing no symmetry relation to either the high- or low-temperature (equilibrium) phases (de Fontaine, 1981). This particular metastable ordering mechanism, known as spinodal ordering, has been observed, for example, by Okamoto & Thomas (1971)

* Present address: Henry Krumb School of Mines, Columbia University, New York, NY 10027, USA.

† Permanent address: CECM/CNRS, 15 rue G. Urbain, 94400-Vitry, France.