*Acta Cryst.* (1979). A35, 429–430

# Determination of Crystal Point Group by a High-Resolution Electron Microscope Image

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(*Received* 3 *November* 1978; *accepted* 13 *December* 1978)

**Abstract**

Crystal symmetry is exposed in a high-resolution electron microscope image more clearly at the thick part than at the thin part of the crystal, through the dynamical scattering. The crystal point group can be determined by observing how the symmetry in the image changes with thickness. A proposed method is demonstrated with an example of a bismuth titanate, $Bi_7Ti_4NbO_{21}$.

One of the important applications of a 1 MV high-resolution electron microscope is direct imaging of atoms in crystals from more than two directions to determine the structure (Horiuchi, Kikuchi & Goto, 1977; Horiuchi, Muramatsu & Matsui, 1978; Bando, Watanabe, Sekikawa, Goto & Horiuchi, 1979). The technique can be applied even when crystals are too small to examine by X-ray or neutron diffraction. Another merit is that it does not matter even if they contain a number of lattice defects including twins. Atom positions are estimated from the contrast of structure images with the help of the space group. Possible space groups are readily known from the extinction of electron diffraction. One may expect to select the correct crystal point group from the image (Buxton, Eades, Steeds & Rackham, 1976). However, the unique selection is not necessarily straightforward, since crystals often appear in the structure image to be centrosymmetric even when they are really non-centrosymmetric. This is mainly because only the very thin part of the crystal fragment is observed.

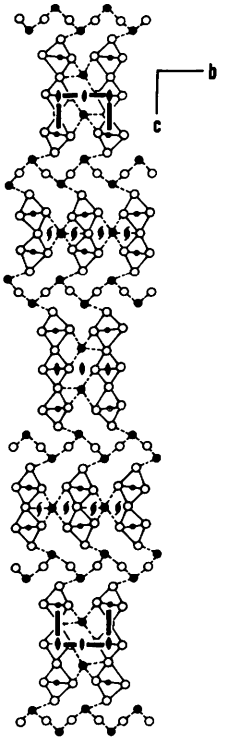


Fig. 1. Crystal structure of $Bi_7Ti_4NbO_{21}$, projected along [100]. The unit cell is orthorhombic, $a = 5{\cdot}45$, $b = 5{\cdot}42$ and $c = 58{\cdot}1$ Å. Large dots indicate Bi ions, small dots Ti or Nb ions and open circles O ions.

With increasing thickness the effect of many-beam dynamical scattering becomes prominent and the symmetry of the crystal is reflected more clearly in the image. This means that the correct point group can be read out in the image of a thick part rather than of a thin part of crystal, as the example below shows.

Fig. 1 is a schematic representation of the crystal structure of a mixed-layer bismuth titanate, $Bi_7Ti_4NbO_{21}$ (Horiuchi *et al.*, 1977). It has an orthorhombic system with lattice parameters $a = 5{\cdot}45$, $b = 5{\cdot}42$ and $c = 58{\cdot}1$ Å. Fig. 2 shows a 1 MV high-resolution image taken from a very thin part of the crystal. The incident beam is parallel to the [110] direction. There are two mirror planes normal to the $x$ and $y$ directions, where we take the axes as shown in Fig. 2 for convenience in the discussion below. Possible space groups obtained from the extinction of the electron diffraction are *Imcm* (centrosymmetric) and *I*2*cm* (non-centrosymmetric). Which of these is correct is unknown from the image in Fig. 2. In fact, the crystal is considered to be non-centrosymmetric because of the ferroelectricity, *i.e.* the octahedral cations must be slightly shifted in the direction normal to the sheet plane of Fig. 1.

Fig. 3 is an image of a thicker part of the crystal, photographed on the same film as Fig. 2. The resolution is somewhat poor compared to that in Fig. 2, mainly because of the chromatic aberration. It is clear that the mirror relation normal to the $x$ direction disappears while that normal to the $y$ direction still remains.

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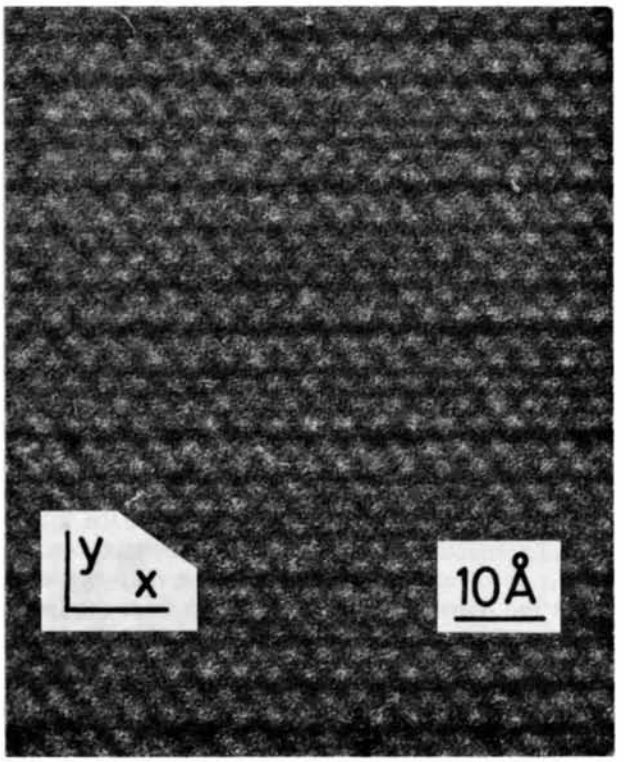


Fig. 2. 1 MV high-resolution electron microscope image of the very thin part of a $Bi_7Ti_4NbO_{21}$ crystal, taken with the incident beam parallel to [110]. The $x$ direction is normal to $(\bar{1}10)$ and $y$ to (001). The contrast shows the mirror relation normal to the $x$ as well as to the $y$ direction.

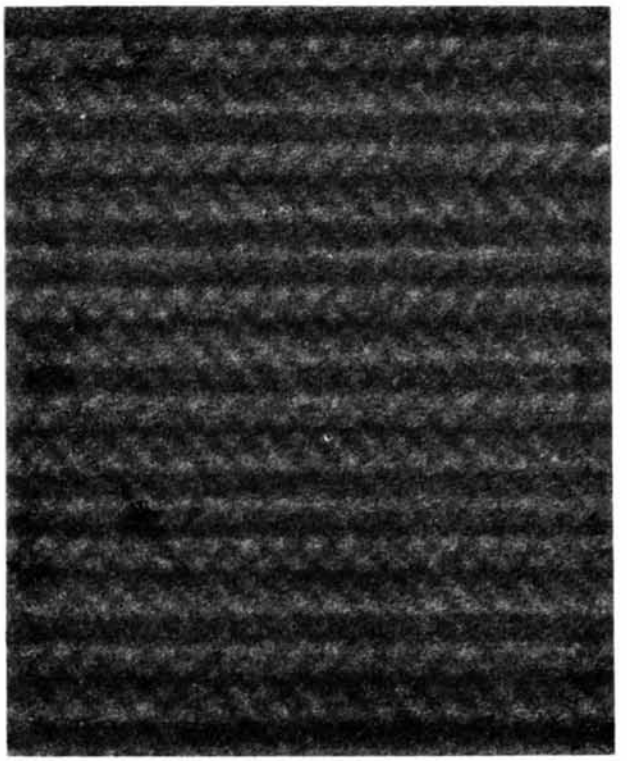

Fig. 3. 1 MV electron microscope image of a thick part of $Bi_7Ti_4NbO_{21}$ photographed on the same film as for Fig. 2. The mirror exists only normal to the $y$ direction. The crystal orientation and magnification are the same as those of Fig. 2.

If the crystal is non-centrosymmetric, the mirror may exist only normal to the $y$ direction since, using the reciprocal-lattice axes corresponding to $x$ and $y$,

$$F(h,k) = F(h,\bar{k}) \neq F(\bar{h},k) = F(\bar{h},\bar{k})$$

regardless of the crystal thickness, where $F$ means the dynamical structure factor. However, for the very thin part of crystal

$$F(h,k) = F(h,\bar{k}) \simeq F(\bar{h},k) = F(\bar{h},\bar{k}).$$

Another mirror should then appear apparently normal to the $x$ direction. This is why the present crystal seems centrosymmetric in the structure image in Fig. 2.

It must be emphasized that the above discussion assumes the exact orientation of the incident beam parallel to a zone axis of the crystal. When the crystal is tilted, the image symmetry is strongly modified especially in thick crystal regions. Detailed experimental analysis on the effect of crystal tilt will be reported elsewhere together with some numerical calculations. In any event, a clear diffraction pattern must be taken from as small a selected area as possible to check the crystal orientation. In this respect the higher voltage of an electron microscope is advantageous.

## References

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