APPENDIX B

Evaluation of the moments of the individual atom distributions in terms of the thermal-factor parameters

Let uvw be the reference Cartesian system for the anisotropic representation, $\varphi(u, v, w)$, for the atom displacements of an atom. Then,

$$\varphi_{(u,v,w)} = [1/(2\pi)^{3/2}\,\sigma_u\,\sigma_v\,\sigma_w] \exp(-u^2/2\sigma_u^2 - v^2/2\sigma_v^2 - w^2/2\sigma_w^2).$$

Let T_{xu}, T_{xv} and T_{xw} be the direction cosines of a direction x relative to u, v and w for atom A. Then, $x = uT_{xu} + vT_{xv} + wT_{xw}$ and

$$\overline{x_A^2} = \int (uT_{xu} + vT_{xv} + wT_{xw})^2\ \varphi(u, v, w)\,du\,dv\,dw$$
$$= \sigma_u^2\,T_{xu}^2 + \sigma_v^2\,T_{xv}^2 + \sigma_w^2\,T_{xw}^2.$$

These σ's are directly related to the anisotropic thermal factors given in (15) that are the refined parameters

$$\sigma_u^2 \times 2\pi^2 = \beta_u.$$

A fourth moment may be evaluated:

$$\overline{x_A^4} = 3(\sigma_u^4\,T_{xu}^4 + \sigma_v^4\,T_{xv}^4 + \sigma_w^4\,T_{xw}^4) + 6(\sigma_u^2\,\sigma_v^2\,T_{xu}^2\,T_{xv}^2 + \sigma_u^2\,\sigma_w^2\,T_{xu}^2\,T_{uw}^2 + \sigma_v^2\,\sigma_w^2\,T_{xv}^2\,T_{xw}^2).$$

In the same manner, the mixed moments may be evaluated:

$$\overline{x_A^2\,y_A^2} = 3(\sigma_u^4\,T_{xu}^2\,T_{yu}^2 + \sigma_v^4\,T_{xv}^2\,T_{yv}^2 + \sigma_w^4\,T_{xw}^2\,T_{yw}^2)$$
$$+ \sigma_u^2\,\sigma_v^2(T_{xu}^2\,T_{yv}^2 + T_{xv}^2\,T_{yu}^2 + 4T_{xu}\,T_{yv}\,T_{xv}\,T_{yu}) + \sigma_u^2\,\sigma_w^2(T_{xu}^2\,T_{yw}^2 + T_{xw}^2\,T_{yu}^2 + 4T_{xu}\,T_{yw}\,T_{yu}\,T_{xu})$$
$$+ \sigma_v^2\,\sigma_w^2(T_{xv}^2\,T_{yw}^2 + T_{xw}^2\,T_{yv}^2 + 4T_{xv}\,T_{yw}\,T_{xw}\,T_{yv}).$$

With these relationships, the variance given in (4) is related to the anisotropic thermal parameters being refined.

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Symmetry Determination of the Room-Temperature Form of $LnNbO_4$ (Ln = La,Nd) by Convergent-Beam Electron Diffraction

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Abstract

Three different space groups, $C2/c$, $C2$ and Cc, have been reported for the room-temperature form of the rare-earth orthoniobates, $LnNbO_4$ (Ln = La,Nd). They belong to different point groups: $2/m$, 2 and m, respectively. By means of convergent-beam electron diffraction, the point group has been determined to be $2/m$ in the present study. Therefore the true space group must be $C2/c$.

It has been reported that the rare-earth orthoniobates, $LnNbO_4$ (Ln = La,Nd), transform from the high-temperature tetragonal form with space group $I4_1/a$ to the room-temperature monoclinic form with space group $C2$ (Komkov, 1959; Stubican, 1964). Recently, however, Jeitschko, Sleight, McClellan & Weiher (1976) suggested that the point group of the room-temperature form is centrosymmetric, $2/m$, and Brixner, Whitney, Zumsteg & Jones (1977) reported that they transform from $I4_1/a$ to $C2/c$. On the other hand, Tsunekawa, Takei & Ishigame (1977) proposed from a

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Table 1. *Symmetries of CBED patterns expected for the three space groups C2/c, Cc and C2*

The diffraction groups described in column 3 are expected for the case of the [010] electron incidence.

Space group	Point group	Diffraction group	Bright field	Whole pattern	Dark field	$\pm G$
$C2/c$	$2/m$	21_R	2	2	2	21_R
Cc	m	1_R	2	1	2	1
$C2$	2	2	2	2	1	2

precise X-ray analysis using high-quality single crystals that the high-temperature form transforms into the intermediate form $C2/c$ at about 803 K and then to the room-temperature form Cc at about 768 K.

It is rather difficult to distinguish between $C2/c$ and Cc by the X-ray method, because they belong to the same Laue group and have the same conditions for possible Bragg reflections. However, since the three space groups $C2/c$, $C2$ and Cc fortunately belong to different point groups, $2/m$, 2 and m, respectively, the true space group can be selected by determining the point group. Convergent-beam electron diffraction (CBED) is most suitable for this purpose (Goodman, 1974; Buxton, Eades, Steeds & Rackham, 1976). All the point groups can be distinguished by observing the symmetries of CBED patterns. In the present note, the conclusive evidence obtained by the CBED method on the symmetry of the room-temperature form will be presented.

The specimens for CBED were prepared by chemical polishing of (010) crystals with hot phosphoric acid. Aluminum about 300 Å thick was deposited on them to prevent electrical charging. A JEM 100C electron microscope equipped with a condenser objective lens was used for taking CBED patterns. It was operated at 100 kV and the illuminated specimen area was about 100 Å in diameter. A square aperture was used as the second condenser lens aperture instead of a circular one in order to decrease the area cut off by the shadow edge of the aperture in the diffraction pattern (Tanaka, 1979).

Table 1 shows the point groups for the three space groups in question, corresponding diffraction groups for the present crystal setting and the symmetries of CBED patterns expected from the diffraction groups (Buxton *et al.*, 1976). It is clear from the table that if one examines the symmetries of the bright-field, dark-field and whole pattern of the CBED patterns, the point group can be identified.

Fig. 1(*a*) shows the zone-axis CBED pattern taken with the [010] electron incidence from a (010) $NdNbO_4$ specimen. The central square indicated by an arrow is called the bright-field pattern. The whole of the pattern which consists of the bright field and its surroundings is called the whole pattern. Figs. 1(*b*) and 1(*c*) show the CBED patterns taken with the electron incidences so tilted as to excite the 002 and $00\bar{2}$ Bragg reflections, respectively. The squares indicated by the arrows are called the 002 and $00\bar{2}$ dark-field patterns. The broad fringes and fine lines appearing in the patterns are produced by the interaction between the 0th Laue zone reflections and by the effect from the higher Laue zone reflections, respectively. The former gives the two-dimensional or projection information and the latter the three-dimensional. Both the fringes and lines in the bright field and those in the whole pattern have twofold symmetry, with the symmetry axis at the center of the bright field. The possibility of space group Cc is rejected, since the observed symmetry of the whole pattern is inconsistent with that given in the table. The dark field also shows twofold symmetry with respect to the exact Bragg position, the center of the dark field, and the space group $C2$ is excluded by referring to the table. Therefore, the true point-group symmetry must be $2/m$.

The symbols in column 7 of the table represent the symmetries existing between the $+G$ and $-G$ dark fields with respect to the center of the whole pattern. For example, the symmetry operation 21_R in column 7 is stated as follows: When the $+G$ dark field is rotated through π about the center of the whole pattern (operation 2), it coincides with the $-G$ dark field. And when each dark field is rotated through π about its own center, the exact Bragg position (operation 1_R), it coincides with itself. If the symmetry between $\pm G$ contains both symbols '2' and 'R', the corresponding point group is centrosymmetric (Buxton *et al.*, 1976). The symmetry 21_R expected from the point group $2/m$ is confirmed from the inspection of the 002 and $00\bar{2}$ dark fields in Figs. 1(*b*) and 1(*c*). This fact indicates directly that the room-temperature form of $NdNbO_4$ is centrosymmetric. In the case of $LaNbO_4$, the same results were also obtained.

In conclusion, the CBED method has been successfully applied to the crystal-symmetry identification of $LnNbO_4$. The point group of the room-temperature form is $2/m$, and then the space group must be $C2/c$ from Brixner's result.

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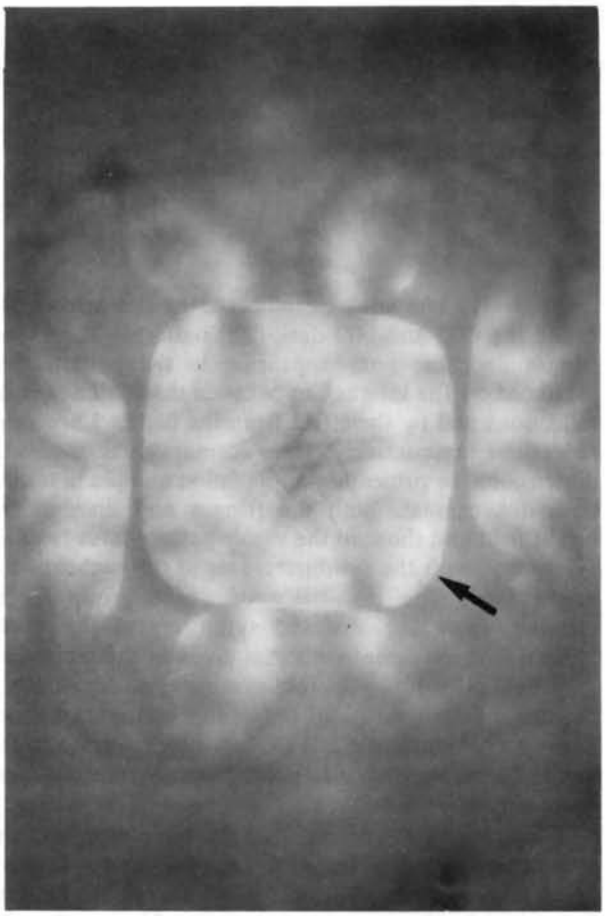
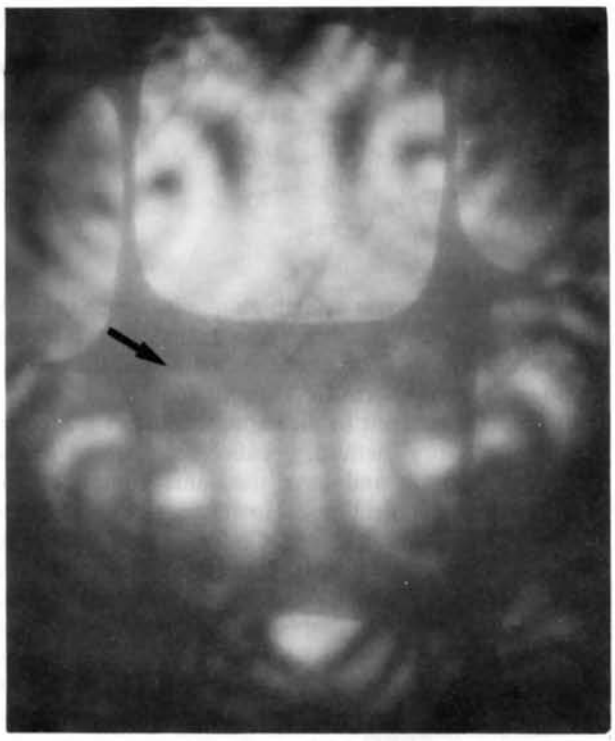
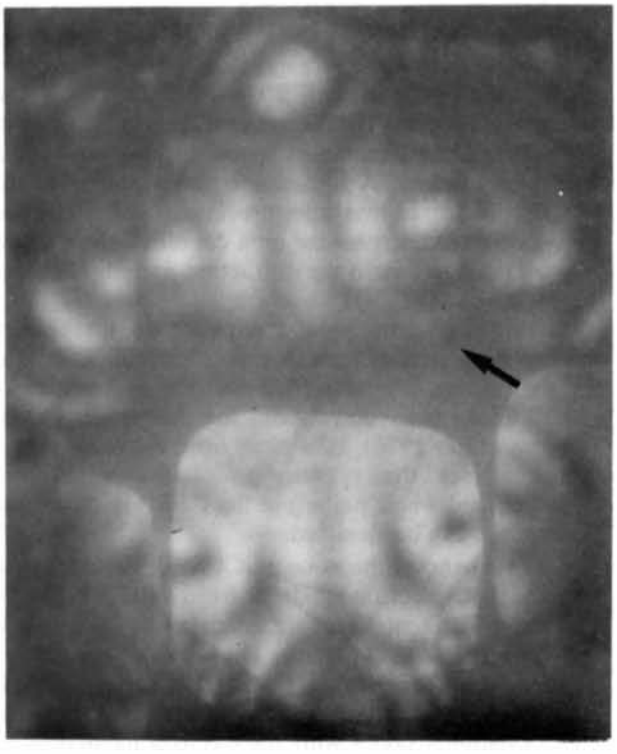


(*a*)



(*b*)



(*c*)

Fig. 1. Convergent-beam electron diffraction patterns. (*a*) Zone-axis pattern showing the whole pattern. The bright field is indicated by an arrow. (*b*) The 002 dark-field and (*c*) $00\bar{2}$ dark-field patterns are indicated by arrows.

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