and O(2*p*) interaction (Cruickshank, 1961) is indicated by asymmetric density distributions with respect to the S–O bond directions. The anion behaves like a rigid body and can be treated as a charged molecular fragment. Chemical assignments of charges such as S^{4+} and O^{2-} are not adequate and should not be used for refinement purposes. Conventional refinements of similar anions promise better agreement with observed densities if started with neutral atoms.

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Convergent-Beam Electron Diffraction Symmetry from a Disordered Structure (Ce, Ta) Ta_6O_{19}

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Abstract

The space group of (Ce,Ta)Ta_6O_{19} is shown by convergent-beam diffraction to be $P\bar{6}c2$ and not $P6_3/mcm$ as previously reported by X-ray diffraction. The X-ray structure, however, is essentially correct, the major change being the ordering of the Ce and Ta atoms in the special positions $\frac{1}{3}, \frac{2}{3}$ and $\frac{2}{3}, \frac{1}{3}$ in strings parallel to the *c* axis with Ce at $\frac{1}{3}, \frac{2}{3}$ and Ta at $\frac{2}{3}, \frac{1}{3}$. Occasional interchanging of these strings would explain the space group observed in the X-ray determination.

Introduction

This investigation of cerium tantalate by convergent-beam electron diffraction was undertaken with three aims in mind. These were to determine the space group of a structure which X-ray refinement had shown to possess a random distribution of some atoms, to further structural knowledge of cerium tantalate, and to extend experience in interpreting convergent-beam electron diffraction (CBED) patterns from unit cells with long axes. The work emphasizes the need to distinguish

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between instrumental and structural influences in the interpretation of CBED symmetries.

Application of the technique of CBED to the space-group determination of GaS and $Cu_3As_2S_3I$ will be reported by Goodman & Whitfield (1980).

Structure derived by X-rays

The structure of (Ce,Ta)Ta_6O_{19} was determined using X-rays by Gatehouse (1979) who found that it had the hexagonal space group $P6_3/mcm$ with $a = 6{\cdot}226$ and $c = 19{\cdot}976$ Å and two formula units per unit cell. The structure can be described as two identical sheets of Ta_6O_{19} pentagonal bipyramids lying perpendicular to the c axis. The sheets are a distance $c/2$ apart and are rotated with respect to each other about c by 180°. They sandwich two Ce and two Ta atoms distributed randomly over the special positions 4(d) ($\frac{1}{3},\frac{2}{3},0$; $\frac{2}{3},\frac{1}{3},0$; $\frac{1}{3},\frac{2}{3},\frac{1}{2}$; $\frac{2}{3},\frac{1}{3},\frac{1}{2}$). The random distribution of the Ce and Ta atoms over the 4(d) sites may be criticized on chemical grounds, but there seems no reason to doubt the validity of the remainder of the structure, as the systematic absences observed by X-rays are also seen in electron diffraction (ED) patterns, and the intensities of reflexions in ED patterns of very thin crystals follow those of X-ray patterns. Consequently, structural interpretation of the CBED patterns has been made in terms of this pentagonal-bipyramidal sheet structure of composition Ta_6O_{19}. The question then remaining relates to the distribution of the two Ce atoms and the two Ta atoms over the '4(d) sites'.

Microscopically (using regions of about 200 Å across), CBED patterns are trigonal, rather than hexagonal as required by the X-ray space group. Examination of several crystals by the transmission X-ray Laue method, on the other hand, consistently gave hexagonal symmetry. This difference is discussed in detail below.

Experimental details

The electron diffraction was performed at 100 keV using both ion-thinned and crushed crystals cooled during examination to less than 150 K in a modified Siemens Elmiskop I (Dowell & Goodman, 1976). The crystal thickness was mostly 1000 to 2000 Å and the probe diameter during CBED less than 200 Å at the crystal. The crushed preparations gave many plates with extended ($hk0$) faces and ion-thinned crystals were prepared with (0001) faces, as the tabular habit of the flux-grown crystals favoured these faces.

Interpretation

The interpretation of the CBED pattern symmetries follows those of Goodman (1975) who has summarized the subject; subsequent relevant papers include that of Buxton, Eades, Steeds & Rackham (1976).

To facilitate understanding of this paper, a brief statement of the relevant relations between symmetries in the CBED patterns, and those in the crystal producing them, is given here. We assume the surface normals of the crystal sheet make angles of less than about 30° to the incident electron beam. To a first approximation the surface influence on symmetry can then be neglected.

(1) Mirror lines in the whole pattern: These arise when either a mirror plane or a glide plane lie parallel to the incident electron cone axis. A perfect mirror line implies the presence of a mirror plane or a glide plane with its glide vector perpendicular to the electron beam. A less perfect mirror line results when the glide vector is parallel to the beam.

(2) Mirror lines perpendicular to the scattering vector in individual disks: These will arise (passing through the exact Bragg position) when the whole crystal has either one central or many regularly spaced twofold rotor or screw axes perpendicular to the incident beam.

(3) Centrosymmetric zero beam: This will arise when the whole crystal has either one central mirror plane, or many regularly spaced mirror planes perpendicular to the incident electron beam. In a thick crystal a small shift of the mirror plane from the midpoint of the crystal will have little effect on the zero-beam symmetry.

(4) Centre-of-symmetry test: The observation of equality of an hkl reflexion in one pattern with the $\bar{h}\bar{k}\bar{l}$ reflexion taken in a second, reciprocal pattern as defined in Fig. 1 implies one centre of symmetry in the whole crystal.

(5) Hexagonal space groups of form $P\bar{6}$: These show trigonal diffraction symmetry in CBED.

Results

Point ED patterns from crushed crystals shown in Figs. 2(a) and 3(a) confirm the unit-cell dimensions and the $hh\bar{2}h0l$, $l \neq 2n$ extinction condition found by Gatehouse

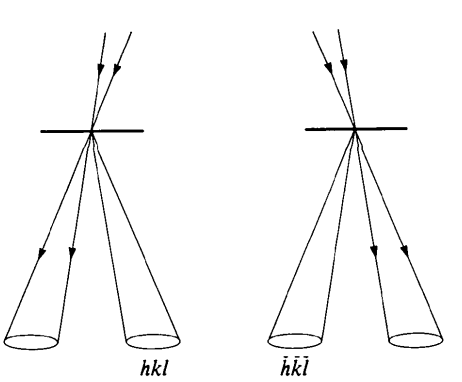

Fig. 1. The relative settings of the two CBED patterns required for a centre-of-symmetry test. An example of this test using cerium tantalate is shown in Fig. 5.

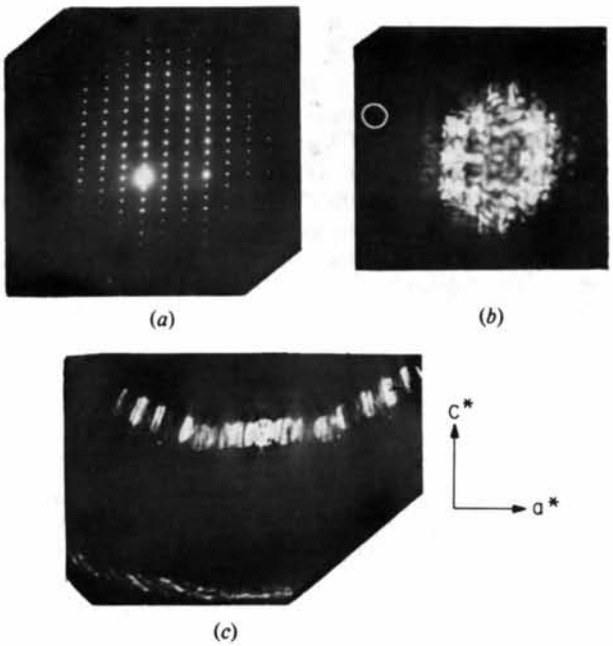

Fig. 2. (*a*) Point pattern taken within 2° of the *a*-axis zone showing the extinction condition $h\bar{h}0l$, $l \neq 2n$. (*b*) CB pattern taken with the crystal rotated 0·25° about *c* from the *a*-axis zone. The lack of perfection of the mirror line is evident. The geometrical distortion is known to be instrumental. The aperture size used for all CB patterns is indicated by the circle. (*c*) CB pattern taken with the crystal rotated approximately 5° about $[1\bar{1}20]$ away from the *a*-axis zone. Lack of a mirror line perpendicular to $[1\bar{1}20]$ is clearly evident in the 100 and 200 reflexion pairs.

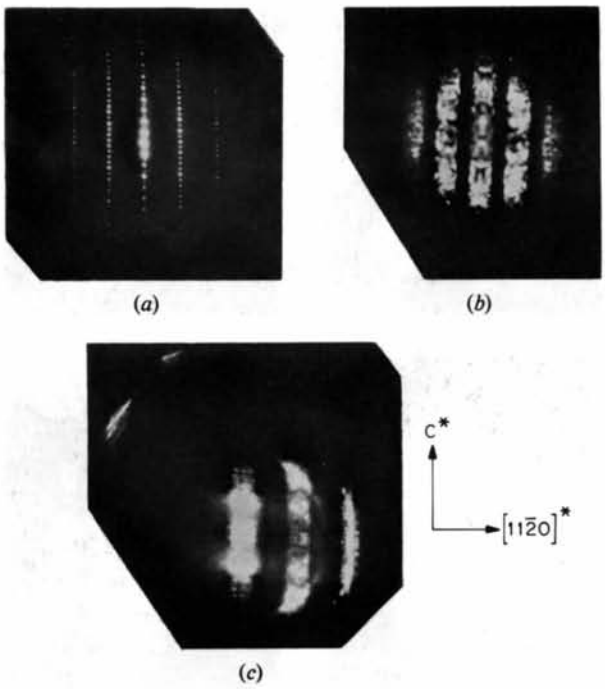

Fig. 3. (*a*) Point pattern taken looking nearly perpendicular to the *ac* plane. The space-group forbidden reflexions 000*l*, *l* odd, have significant intensity in this type of pattern. (*b*) CB pattern, close to the orientation of the point-pattern crystal, rotated away from the zone axis about the *a* axis. The perfection of the mirror line in the *c*-axis direction is dependent on both the symmetry and the setting accuracy of the aperture, due to the heavy overlapping of the reflexions. (*c*) CB pattern, rotated approximately 15° about the *c* axis, instead of the *a* axis as in (*b*), indicating a mirror or glide plane perpendicular to *c*. Instrumental distortion is evident here.

(1979). The trigonal CBED pattern, Fig. 4, from ion-thinned crystals demonstrates that the expected three mirror planes of $P6_3/mcm$, containing *c*, are absent; the 0000-beam symmetry indicates mirror planes perpendicular to *c* [see condition (3) above]. However, a critical examination of patterns taken at orientations more sensitive to the existence of this mirror plane or planes [Figs. 2(*b*) and 3(*c*)] shows that deviations from perfect mirror symmetry exist. In patterns (not reproduced here) taken at varying tilts of a few degrees away from the 0000 zone-axis orientation of Fig. 4, disks of index $h\bar{h}00$ and their 60° related disks showed perfect mirror lines [see condition (2) above]. Disks of the set $hh\bar{2}h0$ showed much less perfect lines. All these results were confirmed by observations on many crystals at varying orientations.

For centre-of-symmetry tests [condition (4) above], some 15 pairs of reciprocally related patterns were obtained from fragments resulting from crushing a crystal. In only one case (Fig. 5) the experiment showed equality between the reciprocally related *hkl* and $\bar{h}\bar{k}\bar{l}$ reflexions; all other results showed lesser degrees of equality.

Finally, no diffraction evidence for disorder, such as diffuse spots or streaks, could be observed, either by X-ray or electron diffraction.

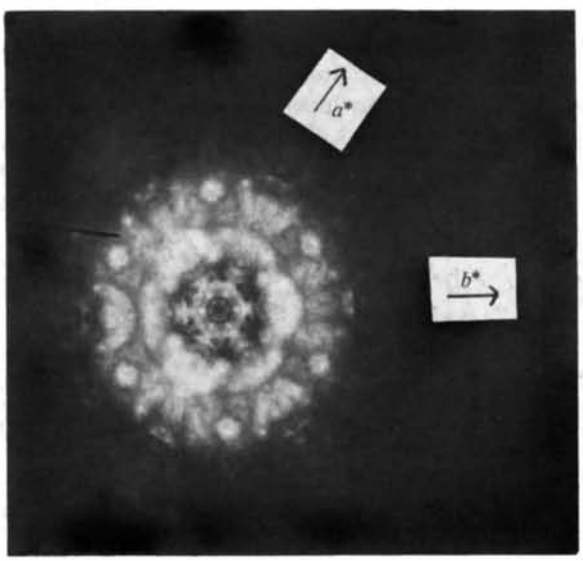

Fig. 4. CB pattern taken (at 100 keV) down the [0001] zone axis with a circular aperture the size of which was sufficient for each order to just overlap.

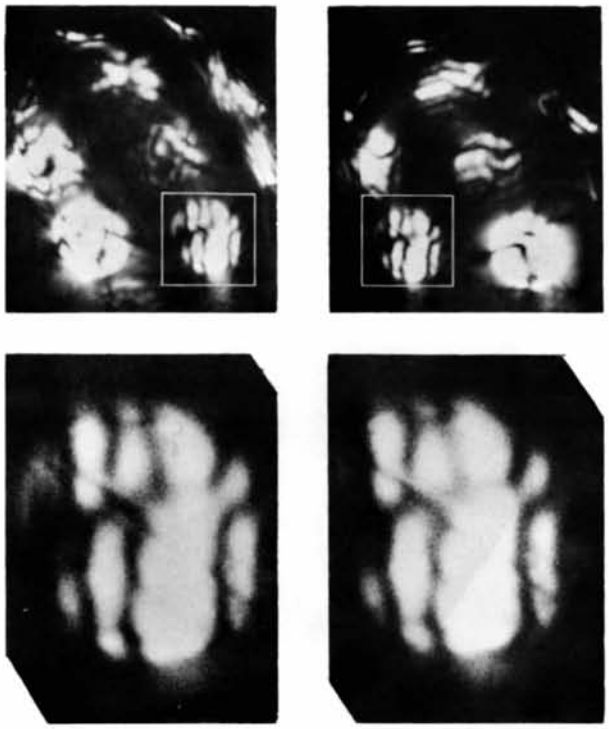

Fig. 5. An example of the two patterns for the centre-of-symmetry test, in which the relevant reflexions to be compared are outlined and shown enlarged below.

Conclusions

The space group $P6_3/mcm$ is clearly not admissible. The extinction conditions are also compatible with space groups $P3c1$, $P\bar{3}c1$ and $P\bar{6}c2$. The first has no twofold operators and the second has twofold operators parallel to the cell edges; both are at variance with the observations. Space group $P\bar{6}c2$ fits the observations, providing the imperfection of the basal mirror plane can be explained. Ordering of those Ce and Ta atoms that were random in $P6_3/mcm$, so that two Ce atoms are in 2(*e*) and two Ta atoms are in 2(*c*), results in strings of Ta and Ce atoms parallel to the *c* axis. Occasional faults causing Ta and Ce strings to be interchanged would be sufficient to obscure from X-ray examination the noncentrosymmetric space group $P\bar{6}c2$ and lead to refinement in $P6_3/mcm$. Such faults would also lead to the deviations from perfect mirror symmetry of the basal mirror plane, shown in Figs. 2(*b*) and 3(*c*) and described under *Results*. The observations are not consistent with any other form of Ce, Ta ordering or of twinning.

The above conclusions do not depend on, but are consistent with, the variable results of the centre-of-symmetry tests. It is clear that a greater understanding is necessary of the reliability and sensitivity with which symmetry operators may be determined. In particular, the use of lenses with low spherical aberration will assist in more reliable centre-of-symmetry determinations.

With the space-group allocation, $P\bar{6}c2$, chemical objections to the previous structure are removed.

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