

The Average Structure of K_2MoO_4 in the Incommensurate Phase at 633 K

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Abstract. Average structure in the incommensurate phase, $Ccmm$, $a = 10.933(3)$, $b = 6.312(2)$, $c = 7.944(2)$ Å, $V = 548.2$ Å³, $Z = 4$, $\mu(Mo K\alpha) = 37.7$ cm⁻¹, $T = 633$ K. Data were collected with a four-circle diffractometer from a multiply twinned spherical crystal. The structure was solved with a Simplex powder program. The final weighted R factor based on intensities was 6.3% for 71 independent reflections. An overall isotropic thermal parameter was used. The modulation consists of a periodic shift of K^+ ions in the z direction with a correlated flipping over of the MoO_4^{2-} ions.

Introduction. Several compounds of the structural family A_2BO_4 have, between the room-temperature phase and the high-temperature α form, a phase which is either a commensurate or an incommensurate superstructure of the hexagonal α form (Tuinstra & van den Berg, 1983) common to many of the A_2BO_4 compounds including K_2SO_4 (van den Berg & Tuinstra, 1978). In order to prove the relationship among the phases, an attempt was made to solve the structure of K_2MoO_4 in its intermediate phase, which is incommensurate and which is stable between 593 and 733 K (Warczewski, 1979).

For a complete structure analysis of an incommensurate structure, the intensities of all reflections, including the satellite reflections, are required. However, all our attempts to grow single crystals of the incommensurate phase failed. As a consequence the number of observable independent data was restricted.

For this reason we have limited our goal to the analysis of the average structure which needs only a few adjustable parameters. This implies, however, that we have necessarily to operate with (multiply-) split atomic positions, in order to simulate in a first approximation a possibly more continuous distribution of atomic positions.

Experimental. The samples were obtained following the procedure described by Kools, Koster & Rieck (1970).

A preliminary study was performed, using the X-ray powder high-temperature Guinier–Lenné camera. Powder patterns taken just above the phase transition at

593 K showed indications of orthorhombic rather than hexagonal symmetry (Tuinstra & van den Berg, 1983). For the structure analysis powder patterns were taken at 633 K. With an optical densitometer peak intensities of 28 diffraction lines were measured, corresponding to main reflections of the (pseudo-) hexagonal reciprocal lattice. A structure refinement was performed using the same procedure as in the case of $\alpha-K_2SO_4$ (van den Berg & Tuinstra, 1978). The analysis provided us with starting parameters for the subsequently undertaken 'single-crystal' analysis.

From the crude powder sample aggregates were taken which looked like single crystals. These samples actually turned out to be multiply-twinned crystals: all of the constituent crystallites have the c axis in common, while they are nearly equally distributed among three orientations rotated around the c axis through multiples of 60° with respect to one another. Since the deviation from the hexagonal metric of the lattice is very small indeed, the diffraction pattern of such an aggregate can hardly be distinguished from a true single crystal except for the satellite reflections. The intensities of these satellite reflections did not obey the hexagonal symmetry; they were the key to the proof that the actual symmetry of the structure is orthorhombic. The volume fractions of the different orientations present in an aggregate could be determined by means of these intensities. Measurements on several aggregates always gave percentages between 30 and 40% for each of the three orientations. One of these multiple twins was mounted on a four-circle diffractometer (Hilger & Watts). During data collection the sample was kept at 633 K with a small crystal oven (see Tuinstra & Fraase Storm, 1978). Integrated intensities were measured for 143 main reflections. The sample was nearly spherical, with a diameter of 0.2 mm.

Within the range of values of θ used, the corresponding variation in an absorption correction would amount to only a few per cent; therefore, no absorption correction was applied. The small error introduced in this way may slightly raise the resulting temperature factor B . The usual Lorentz–polarization corrections were applied.

Since the reflections of the hexagonal lattice emerge continuously from the reflections of the hexagonal high-temperature form, the incommensurate phase

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should contain two formula units per pseudo-hexagonal cell.

The actual symmetry of the incommensurate phase is orthorhombic, so the *C*-centered unit cell contains four formula units. The cell dimensions at 633 K are given in the *Abstract*. As the sample is a composite crystal, each of the measured reflection intensities must be regarded as being the sum of the intensities of three contributing reflections. Only in the case of 001 reflections might the intensities be affected by coherence of domains in the *c* direction. Indeed the 002 and 004 reflections gave intensities about twice as large as was to be expected from the powder diagrams. The 002, 004 and 006 reflections were for this reason omitted from the data.

The systematic extinctions allow the space groups *Cc2m*, *Ccm2* and *Ccmm*. Using the intensities obtained with the four-circle diffractometer a Fourier synthesis was carried out in the centrosymmetric space group. The *F*'s were given the signs which resulted from the preliminary powder diffraction analysis in which the K^+ and Mo^{6+} ions obtained the following positions: K(1) at 0,0,0; K(2) at 0.33,0,0.25 and Mo at 0.33,0,0.75. The positions of the O atoms did not affect the signs assigned to the F_o 's. In the resulting electron density maps the O positions are clearly visible. The electron density of two of the O atoms and the Mo atom is concentrated at $y=0$ with no appreciable extension in the *b* direction. The modulation displacements of these atoms have apparently no components perpendicular to the plane $y=0$. Since this is in accordance with a mirror plane at $y=0$, it makes the space group *Cc2m* less probable.

Therefore we refined the structure in the two space groups *Ccmm* and *Ccm2*.

Since the number of measured reflection intensities is relatively small we decided to limit the number of adjustable parameters by assuming the MoO_4^{2-} ion to form a regular tetrahedron. This is justified by the very close-to-regular form of the MoO_4^{2-} ion in the low-temperature monoclinic phase (Gatehouse & Leverett, 1969). This leaves two parameters to be adjusted for the O positions: the distance $r = MoO$ and an angle φ which defines the orientation of the anion around the direction of the *b* axis. In the Fourier maps the electron density of K(1) was spherically centered around 0,0,0. The positions of K(2) and Mo showed no deviation from the pseudo-trigonal axes. We therefore kept K(1) at 0,0,0; K(2) at $\frac{1}{3}, 0, z_{K(2)}$ and Mo at $\frac{1}{3}, 0, z_{Mo}$. Together with an overall isotropic thermal *B* factor the number of parameters is six.

After applying the Lorentz-polarization correction the intensities were used in a Simplex structure refinement program (Bassi, 1968). The program minimizes a residual *R* defined by $R = 100 \sum w(\Delta I)^2 / \sum wI_o^2$, where $\Delta I = I_o - I_c$ and $w = (1 + I_o)^{-1/2}$. The weighted *R* factor is defined as $R_2 = [\sum w(\Delta I)^2 / \sum wI_o^2]^{1/2}$. The atomic form factors for K^+ , Mo^+ and O^- were those

given by Moore (1963). Since the Simplex program is essentially a powder program, it is designed to cope with overlapping reflection intensities, such as occur here because of the twinning. The intensities used in the program were averages over (pseudo-) equivalent reflections. The number of independent reflections was 71.*

The resulting residual *R* was considerably lower in space group *Ccmm* (0.40) than in *Ccm2* (0.57). The final value for the Mo-O distance *r* was 1.59 Å in *Ccm2*, which is at least 0.1 Å shorter than the values reported in the literature for that distance in the molybdate ion. The value of 1.7 Å found in the space group *Ccmm* is short but quite acceptable as no bond-length correction for the libration of the anion was applied. Finally, in space group *Ccm2* the agreement between I_c and I_o of some reflections was unacceptably poor in a few cases; this did not occur in *Ccmm*.

Discussion. From the above-mentioned arguments we conclude that the space group of the average structure of K_2MoO_4 in the incommensurate phase is *Ccmm*. The atomic positions are given in Table 1. The value of the overall thermal parameter $B = 15.2 \text{ \AA}^2$.

The atoms K(1) and Mo occupy single positions; they seem barely to contribute to the modulation. The other atoms, K(2) and the O atoms, occupy split positions in the average structure. They are apparently involved in the modulation which consists of a periodic shift of K(2) in the *z* direction with an amplitude of about 0.75 Å together with a flipping over of the tetrahedra formed by the O atoms. Fig. 1 shows the average structure projected along the *b* axis. Of the two circles indicating separate positions of a 'split atom', one is drawn in full, the other is dashed. Keeping in mind normal ionic radii, some combinations of atomic positions are obviously impossible. If, moreover, the anion is treated as a rigid tetrahedral unit, only two distinct combinations of possible atomic positions for K(2) and the O atoms emerge. These two combinations are depicted in Fig. 1: Either the fully drawn combination or the combination of dashed circles is compatible with normal ionic radii. The combinations

* A list of measured and calculated intensities has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38367 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters*

| | <i>x</i> | <i>y</i> | <i>z</i> |
|------|---------------|-----------|-----------|
| K(1) | 0 | 0 | 0 |
| K(2) | $\frac{1}{3}$ | 0 | 0.320 (3) |
| Mo | $\frac{1}{3}$ | 0 | 0.760 (4) |
| O(1) | 0.179 (1) | 0 | 0.791 (4) |
| O(2) | 0.406 (2) | 0 | 0.950 (4) |
| O(3) | 0.374 (1) | 0.221 (1) | 0.650 (4) |

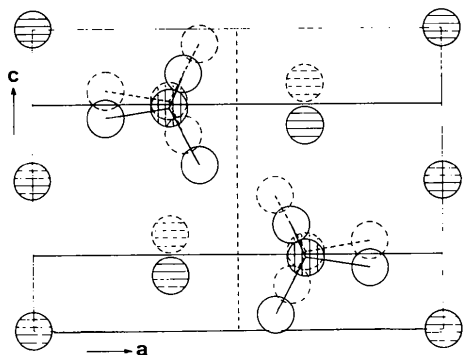


Fig. 1. Projection along the *b* axis of the average structure of incommensurate K₂MoO₄. The full circles show one specimen of a split-atom set, while the dashed circles show the other. K⁺ ions are hatched horizontally, Mo atoms vertically; the O atoms are shown by the open circles. The radii of the circles are chosen to show the 50% probability spheres.

are of course related by the *c* mirror plane of the average structure. This proves that a strong correlation must exist between the position of K(2) and the orientation of the MoO₄²⁻ ions above and below it (in the *z* direction) and *vice versa*. It should be pointed out here that moving from one orientation of the anion to the other can be performed by a rotation through only 60° around an axis roughly parallel to *b*.

The resulting overall isotropic temperature factor *B* is rather high. This can partly be attributed to the

relatively high temperature and the fact that two phase-transition temperatures are nearby. The high value of *B*, however, might well be an indication that the simple split-atom model is too crude. The latter is compatible only with a block-wave modulation. If the actual modulation waves for K(2) and O have a more continuous form, in addition to the split-atom positions intermediate positions would also be present, which in the split-atom model would lead to an increase of *B*.

It should be noted that the anionic tetrahedra have an orientation with respect to the *z* axis which quite closely resembles that of the low-temperature monoclinic phase.

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Reinvestigation of the Structure of Tetracadmium Sodium Orthovanadate, Cd₄Na(VO₄)₃

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Abstract. *M_r* = 817.407, orthorhombic, *Pnma*, *a* = 9.8189 (3), *b* = 7.0298 (2), *c* = 5.3610 (1) Å at 294 K, *V* = 370.04 (3) Å³, *Z* = 4(Cd_{4/3}Na_{1/3}VO₄), *D_m* = 4.71 (26), *D_x* = 4.890 g cm⁻³, λ(Mo *Kα*) = 0.71073 Å, μ = 99.387 cm⁻¹, *T* = 294 K. Final *R* = 0.0185 for 1289 unique reflections. Crystal growth from melt in oxygen atmosphere. Least-squares structural refinement and normal-probability-plot analyses confirm results of physical tests that structure is centrosymmetric, in contrast to previous report that space

group is *Pn2₁a*. One Cd atom per formula occupies an octahedron with ⟨Cd–O⟩ = 2.307 Å, one V atom a tetrahedron with ⟨V–O⟩ = 1.718 Å, remaining one-third Cd and one-third Na atom a distorted tetrahedron with ⟨Cd/Na–O⟩ = 2.374 Å. CdO₆ octahedra form infinite edge-sharing chains linked by corner sharing VO₄ and Cd/NaO₄ tetrahedra.

Introduction. The crystal structure of Cd₄Na(VO₄)₃ was reported by Ben Amara, Vlasse, Olazcuaga & Le