Acta Cryst. (1973). B**29**, 586

Modulated Structures of Some Alkali Molybdates and Tungstates

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(*Received* 16 *October* 1972; *accepted* 7 *November* 1972)

Some of the high-temperature phases of K_2MoO_4, K_2WO_4 and Rb_2WO_4 are shown to have modulated structures. The modulation wave vector **k** is rationally independent of the basic vectors of the unit cell. The diffraction patterns have symmetry $6/mmm$. The **k** vector points in the direction of the a^* axis; $\mathbf{k}=\kappa\mathbf{a}^*$. For K_2MoO_4 the value of κ changes continuously from 0·297 at 360°C to 0·290 at 430°C. The values for K_2WO_4 and Rb_2WO_4 are 0·250 at 395°C and 0·363 at 435°C respectively. A model for the modulation is proposed. In this model the modulation is assumed to be a periodic change in the orientations of the anion tetrahedra.

Introduction

Displacive modulation of structures of pure stoichiometric compounds has been reported for γ-Na_2CO_3 (Brouns, Visser & de Wolff 1964; Dubbeldam & de Wolff 1969) and $NaNO_2$ (Hoshino & Motegi, 1967). The modulation is observed through the presence of satellite reflexions in the X-ray diffraction patterns. Modulated structures of this type differ from superstructures in that the modulation wave vector is rationally independent from the basic vectors of the unit cell. In both examples mentioned the fractional components of this vector change continously with temperature.

As we will show in the present paper some more compounds can be added to this group, namely some molybdates and tungstates of potassium and rubidium.

Van den Akker, Koster & Rieck (1970) recently reported non-indexable lines in certain high temperature phases of K_2MoO_4, K_2WO_4 and Rb_2WO_4. The present investigation of K_2MoO_4 shows that this phase has a modulated structure. For K_2WO_4 and Rb_2WO_4 Dr A. S. Koster was kind enough to put the powder patterns, used in the above mentioned paper, at our disposal. The same type of modulation was found to apply to these diffraction patterns as to those for K_2MoO_4.

For the examples of the modulated structures mentioned above, as well as for the cases reported here, the phase transitions and the range in which the modulation is present are indicated in Fig. 1.

Experimental

Samples of K_2MoO_4 were obtained in the manner described by Kools, Koster & Rieck (1970). From the powdered samples, pellets of about 0·1 mm thickness were pressed. These pellets served as specimens in a Guinier–Lenné camera. From the original samples crystalline aggregates were selected, which seemed to be of the right size for single-crystal work. Inserted in a capillary tube and mounted in a precession camera these aggregates, however, proved to consist of numerous crystallites of the monoclinic low temperature phase (Gatehouse & Leverett, 1969), having the c axis in common. The a^* axes of these crystallites are equally distributed among three directions making angles of 120° with respect to one another. The $hk0$ diffraction pattern consequently showed a hexagonal appearance. On being heated beyond 320°C the crystalline aggregate transformed into a single crystal of the intermediate temperature phase. With a precession camera the reflexions in the reciprocal planes $hk0$, $hk1$, $hk2$, $h0l$, $h1l$, $h2l$ and hhl were recorded at 360°C using polaroid films. The sample heating was achieved by using a thin Ni–Cr filament wound around the capillary tube which contained the crystallite and a thermocouple junction. The temperature was controlled electronically to within 5°C.

Indexing

K_2MoO_4

We were able to account for all observed reflexions from K_2MoO_4 at 366°C using a hexagonal reciprocal lattice in which several lattice points are surrounded by a hexagon of six satellites. These hexagons are oriented perpendicularly to the c^* axis, the satellites occurring in the directions of the adjacent main lattice points. The indexing was fully confirmed in the single crystal patterns, two of which are shown in Fig. 2(a) and (b). The indexing of our powder pattern is shown in Table 1. The satellite reflexions are described by two extra integer indices m and n defining the corresponding reciprocal lattice vector:

$$\mathbf{R}=\mathbf{H}(hkl)+\mathbf{k}(mn)=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+\kappa(m\mathbf{a}^*+n\mathbf{b}^*)\,,$$

where

$$(m,n)=\pm(1,0),\pm(1,\bar{1})\text{ or }\pm(0,1)\,.$$

No higher order satellites were observed. The number κ is non-integer. Its value was found to change continuously with temperature from 0·297 (±0·001) at about

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360 °C to 0·290 (±0·001) at about 430 °C, that is about 10 °C below the higher transition point. These results were obtained after a least-squares refinement using both the main lattice reflexions and the satellite reflexions; the numbers in parentheses are standard deviations.

Table 1. *Observed spacings and indexing of the modulated structure of* K_2MoO_4 *at* 366 °C (Cu *Kα*)

d (Å)	*I*	*h*	*k*	*l*	*m*	*n*	$2\theta_{calc}-2\theta_{obs}$
7·29	*vvw*	0	0	1	1	0	−0·01
5·47	*m*	1	0	0	–	–	+0·01
4·86	*vvw*	1	0	1	$\bar{1}$	1	+0·09
4·507	*vs*	1	0	1	–	–	+0·02
3·974	*m*	0	0	2	–	–	+0·01
3·538	*w*	1	0	2	$\bar{1}$	0	+0·01
3·336	*w*	1	0	2	$\bar{1}$	1	0·00
3·213	*s*	1	0	2	–	–	0·00
3·156	*vs*	1	1	0	–	–	+0·01
3·016	*w*	1	0	2	0	1	−0·02
2·891	*w*	1	0	2	1	0	0·00
2·734	*w*	2	0	0	–	–	0·00
2·586	*vw*	2	0	1	–	–	+0·03
2·509	*vw*	1	0	3	$\bar{1}$	0	+0·03
		2	0	2	$\bar{1}$	0	+0·18
2·471	*m*	1	1	2	–	–	−0·01
2·383	*m*	1	0	3	–	–	−0·01
2·355	*w*	2	0	2	$\bar{1}$	1	+0·01
2·252	*m*	2	0	2	–	–	0·00
2·131	*w*	2	0	2	0	1	0·00
2·067	*vw*	2	1	0	–	–	+0·02
2·039	*vvw*	2	0	2	1	0	−0·07
2·000	*m*	2	1	1	–	–	+0·01
1·9864	*w*	0	0	4	–	–	+0·01
1·9628	*vvw*	3	0	1	$\bar{1}$	0	+0·07
1·9263	*vvw*	1	0	4	$\bar{1}$	0	+0·05
1·9023	*w*	2	0	3	–	–	+0·01
1·8897	*vw*	1	0	4	$\bar{1}$	1	0·00
1·8538	*vvw*	2	1	2	$\bar{1}$	1	−0·03
1·8325	*m*	2	1	2	–	–	−0·02
1·8219	*m*	3	0	0	–	–	−0·01
1·7961	*vw*	1	0	4	1	0	−0·02
		2	1	2	1	$\bar{1}$	+0·04
1·7152	*vvw*	2	1	2	0	1	+0·03
1·6903	*vvw*	3	0	1	0	1	−0·02
		2	1	2	1	0	+0·02
		2	0	4	$\bar{1}$	0	+0·05
1·6805	*w*	1	1	4	–	–	−0·01
1·6562	*w*	3	0	2	–	–	0·00
1·6426	*vw*	2	0	4	$\bar{1}$	1	−0·02
1·6284	*w*	2	1	3	–	–	−0·02
1·5783	*m*	2	2	0	–	–	+0·01
1·5620	*vw*	2	0	4	0	1	+0·03
1·5260	*vw*	1	0	5	–	–	+0·01
1·4897	*w*	3	1	1	–	–	+0·02
1·4664	*w*	2	2	2	–	–	−0·01
1·4419	*vvw*	2	1	4	$\bar{1}$	1	−0·02
1·4160	*w*	3	1	2	–	–	−0·03

The Laue symmetry of the whole diffraction pattern is 6/*mmm*. In the Guinier–Lenné powder photographs, with the temperature increasing continuously through the 440 °C transition, the positions of the main lattice reflexions change almost continuously (there appears to be a small jump in the length of the *c* axis). No discontinuity at all is visible in the intensities of these lines. In particular the extinction rule: *hhl* absent for *l* odd, applies both to the main pattern below 440 °C and to the pattern above this transition point. This was corroborated by the precession photographs taken at 360 °C and some additional photographs taken at 480 °C. On the single crystal patterns satellites are observed around the following reflexions:

001, 101, 201, 301, 211, 102, 202, 212, 003, 103, 104, 204, 214, 005, 115, 106 and 206.

Not all of these are present in Table 1, because some were too weak to be observed in the powder diagrams.

K_2WO_4 and Rb_2WO_4

The powder patterns in the intermediate phases of these compounds were explained in a similar fashion as the one of K_2MoO_4. The phase transitions have already been reported (van den Akker, Koster & Rieck 1970).

The average structures display the same extinction rule as for K_2MoO_4. The values of κ are: 0·250 for K_2WO_4 (at 395 °C) and 0·363 for Rb_2WO_4 (st 435 °C). The indexings for K_2WO_4 and Rb_2WO_4 are given in the Tables 2 and 3 respectively.

Table 2. *Observed spacings and indexing of the modulated structure of* K_2WO_4 *at* 395 °C*

d (Å)	*I*	*h*	*k*	*l*	*m*	*n*	*Δ2θ*
7·52	*w*	0	0	1	0	1	+0·03
6·07	*w* (broad)	1	0	0	$\bar{1}$	1	−0·08
5·512	*vs*	1	0	0	–	–	+0·02
4·843	*w*	1	0	1	$\bar{1}$	1	−0·02
4·543	*vvs*	1	0	1	–	–	+0·06
3·993	*vs*	0	0	2	–	–	+0·03
3·507	*w*	1	0	2	$\bar{1}$	0	+0·02
3·338	*m*	1	0	2	$\bar{1}$	1	−0·01
3·233	*vs*	1	0	2	–	–	+0·03
3·179	*vs*	1	1	0	–	–	+0·02
3·068	*m*	1	0	2	0	1	0·00
2·959	*w*	1	0	2	1	0	+0·03
2·926	*w*	1	1	1	$\bar{1}$	1	0·00
2·753	*s*	2	0	0	–	–	+0·02
2·657	*w*	1	1	1	0	1	0·00
2·600	*s*	2	0	1	–	–	−0·01
2·486	*s*	1	1	2	–	–	+0·01
2·394	*s*	1	0	3	–	–	−0·01
2·352	*w*	2	0	2	$\bar{1}$	1	−0·03
2·264	*s*	2	0	2	–	–	−0·01
2·163	*w*	2	0	2	0	1	−0·02
2·143	*w*	1	1	3	$\bar{1}$	0	+0·01
2·086	*vw*	2	0	2	1	0	+0·02
2·079	*m*	2	1	0	–	–	−0·02
2·012	*vs*	2	1	1	–	–	−0·02
1·995	*m*	0	0	4	–	–	+0·02
1·983	*w*	2	1	2	$\bar{1}$	0	+0·05
1·949	*vw*	2	1	2	0	$\bar{1}$	−0·02
1·923	*vw*	1	0	4	$\bar{1}$	0	−0·03
1·912	*m*	2	0	3	–	–	0·00

* The values of *d* and the intensities were provided by Dr A. S. Koster. In the column *Δ2θ*, the values refer to differences between 2θ values calculated using $a=6·354$, $c=7·977$ Å and $\kappa=0·250$, and 2θ values calculated from the d_{obs} list with $\lambda=1·54$ Å.

Table 3. *Observed spacings and indexing of the modulated structure of* Rb_2WO_4 *at* 435 °C*

d (Å)	*I*	*h*	*k*	*l*	*m*	*n*	*Δ2θ*
5·681	*m*	1	0	0	–	–	0·01
4·687	*s*	1	0	1	–	–	0·01
4·154	*m*	0	0	2	–	–	0·03
3·758	*w*	1	0	2	$\bar{1}$	0	−0·01
3·492	*w*	1	0	2	$\bar{1}$	1	−0·01
3·352	*s*	1	0	2	–	–	0·02
3·280	*vs*	1	1	0	–	–	0·02
3·100	*f*	1	0	2	0	1	0·06
2·951	*f*	1	0	2	1	0	0·11
2·839	*w*	2	0	0	–	–	0·00
2·687	*w*	2	0	1	–	–	0·01
2·659	*vf*	2	0	2	$\bar{1}$	0	−0·02
2·573	*m*	1	1	2	–	–	0·02
2·488	*m*	1	0	3	–	–	0·03
2·468	*f*	2	0	2	$\bar{1}$	1	−0·04
2·343	*s*	2	0	2	–	–	0·00
2·188	*vf*	2	0	2	0	1	0·00
2·147	*vf*	2	1	0	–	–	0·02
2·118	*vf*	2	1	2	$\bar{1}$	0	0·02
2·076	*m*	2	0	2	1	0	−0·06
1·9796	*f*	2	0	3	–	–	−0·03
1·9071	*m*	2	1	2	–	–	0·03
1·8917	*m*	3	0	0	–	–	−0·02
1·7528	*m*	1	1	4	–	–	0·00
1·6953	*w*	2	1	3	–	–	0·00
1·6392	*m*	2	2	0	–	–	0·01
1·5923	*f*	1	0	5	–	–	−0·01
1·5466	*f*	3	1	1	–	–	−0·02

* See footnote to Table 2. Here $a=6{\cdot}556$, $c=8{\cdot}296$ Å and $\kappa=0{\cdot}363$.

Discussion

K_2MoO_4

Because of the Laue symmetry and the systematic absences the space group can be $P\bar{6}2c$, $P6_3mc$ or $P6_3/mmc$. This applies to both the average modulated structure and the hexagonal structure above 440 °C. At 366 °C the unit-cell parameters are: $a=6{\cdot}31$ and $c=7{\cdot}94$ Å. The corresponding cell is occupied by two K_2MoO_4 groups. The structure is a derivative of the 'basic structure', which Eysel (1971) showed to be underlying many structures of A_2BX_4 compounds, including K_2MoO_4, Rb_2WO_4 and K_2WO_4. In this structure four K^+ ions are located at $0,0,0$; $0,0,\frac{1}{2}$; $\frac{1}{3},\frac{2}{3}, z_k$; $\frac{2}{3},\frac{1}{3},\frac{1}{2}+z_k$. The two Mo atoms occupy positions $\frac{1}{3},\frac{2}{3},z_m$ and $\frac{2}{3},\frac{1}{3},\frac{1}{2}+z_m$ (see also Fischmeister, 1962).

In this basic structure the space groups $P\bar{6}2c$ and $P6_3/mmc$ would generate two superposed MoO_4 tetrahedra around each anion position. The mean value of the parameters z_{m1} and z_{m2} of the corresponding two Mo atoms is 0·25 (or 0·75). Of the two interpenetrating MoO_4 tetrahedra, one is upside down with respect to the other (assuming the *c* axis to be vertical). Such a structure could well represent the average modulated structure.

On the other hand, the space group $P6_3mc$ does not require more than one MoO_4 group at each of the anion positions of the basic structure. Taking into account the sizes of the ions, only one structural type is feasible. This structure type was recently proposed by Eysel & Hahn (1970) (the high K_2SO_4 type) for a series of high-temperature modifications of compounds A_2BX_4, including K_2MoO_4, Rb_2WO_4 and K_2WO_4 (see Eysel, 1971). In this structure, which of course corresponds to Eysel's 'basic structure', all tetrahedra are pointing in the same sense along the **c** direction. With this structure, in which z_m and z_k are still to be chosen properly, we tried to account for the striking absence of some reflexions (104, 204 and 214) in the pattern of K_2MoO_4 (see also Fig. 2). We found that this is impossible, unless very unrealistic interatomic distances are assumed.

If we assume that the anion positions in the average structure are occupied by two MoO_4 groups (of weight $\frac{1}{2}$), the above mentioned absences can be easily accounted for. Such a structure, which does not lead to

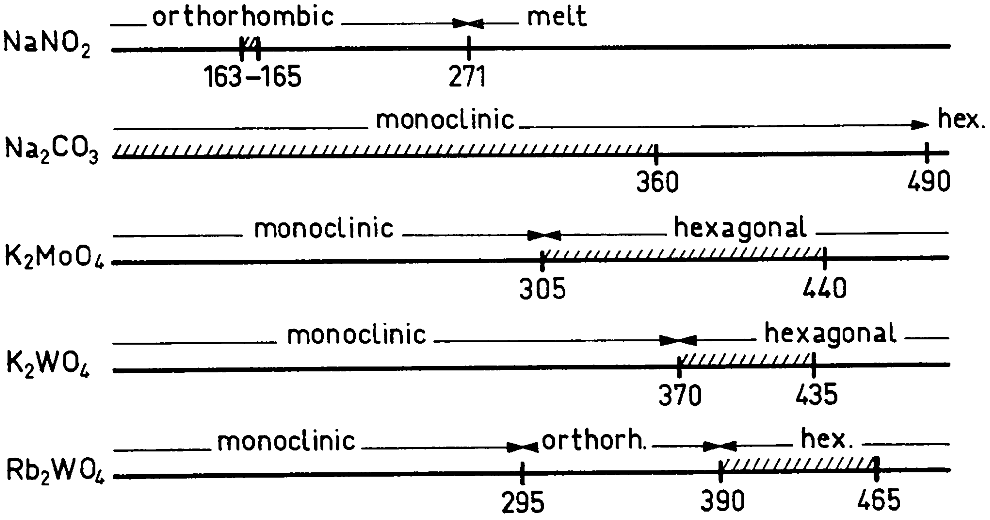
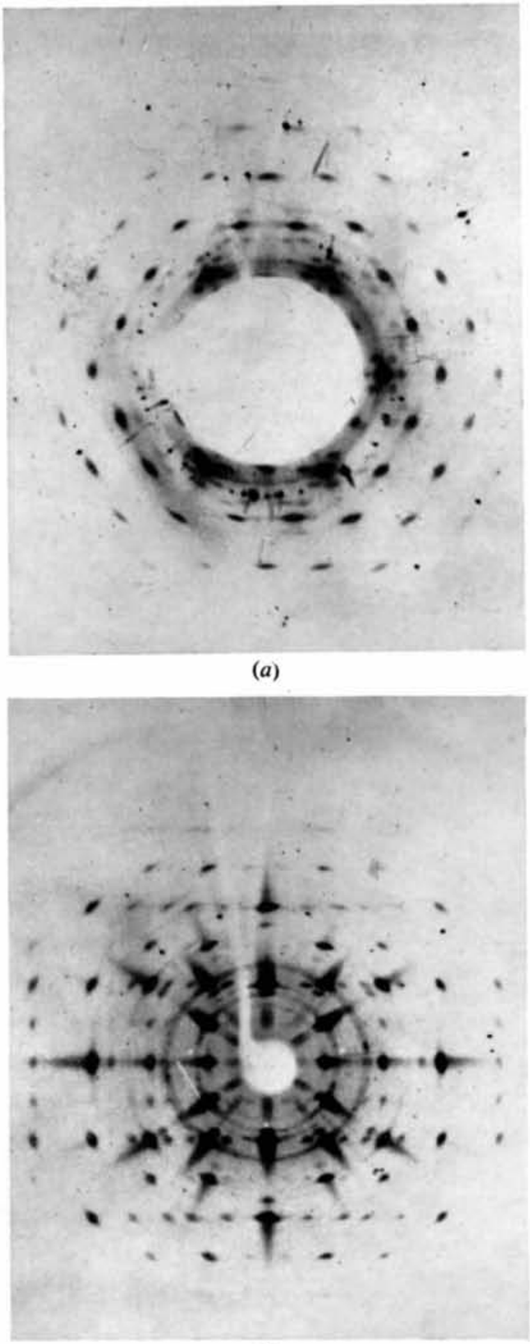


Fig. 1. In the hatched regions modulated structures have been observed. The numbers underneath each line indicate the temperature in °C.



(*a*)

(*b*)

Fig. 2. Precession photographs of K_2MoO_4. (*a*) The plane *hk*2 in reciprocal space. The a^* axis is horizontal. (*b*) The *h*0*k* plane. Satellites are particularly observable at $l=2$ and $l=4$. The c^* axis is vertical. (The sharp irregular spots are reflexions due to the heating filament.)

unacceptable interatomic distances, fits naturally the space groups $P\bar{6}2c$ and $P6_3/mmc$ already discussed. It makes the space group $P6_3mc$ rather unlikely though not impossible.

The modulation in this case thus could well be a long-range order in the orientations of the MoO_4 tetrahedra oriented approximately with their peaks upward over one half of the modulation period and downward over the other half of the period. Above the transition point at 440°C, the tetrahedra will presumably be distributed at random among the possible orientations.

It seems possible that this distribution stems to some extent from rotational freedom of the anion (see also Bredig, 1943). However, this cannot be decided from our data.

The model proposed here agrees well with predictions of Fischmeister (1962) based on steric calculations carried out for the high temperature modifications of a series of sulphates. The structure of these sulphates also belongs to the basic structure type. Using steric as well as thermodynamic evidence, Fischmeister proposed three possible structure types:

(i) two possible orientations of the anion tetrahedra, pointing either upward or downward along the **c** direction, are randomly distributed among the anion positions,

(ii) domains are present in which the orientation of all tetrahedra is the same,

(iii) a superstructure is present.

In all of these cases at least two anions with weight $\frac{1}{2}$ must be superposed in order to get the average structure. Our model of the modulated structure can be described as a special case of (ii) or a generalization of (iii).

Since the average modulated structure has been shown to be essentially identical to the hexagonal high temperature form, the latter is not likely to possess Eysel's high K_2SO_4 structure either. We believe that it represents Fischmeister's type (i).

K_2WO_4, Rb_2WO_4

The above interpretation applies equally well to these compounds. In the case of K_2WO_4 a superstructure with $\kappa=\frac{1}{4}$ seems to be possible. Some reflexions with $l=4$, which were absent in K_2MoO_4 are present here with very weak intensities.

We thank Professor P. M. de Wolff for his valuable advice and criticism, Mr G. M. Fraase Storm for his skillful technical assistance and Dr A. S. Koster for putting the diffraction patterns of Rb_2WO_4 and K_2WO_4 at our disposal.

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Acta Cryst. (1973). **B29**, 589

Least-squares Refinement and the Weighted Difference Synthesis

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(*Received* 2 *November* 1972; *accepted* 10 *November* 1972)

The weights to be assigned in least-squares refinements of crystal structures are discussed in terms of a weighted difference synthesis in which electron density differences close to atomic centres are regarded as more important than those in other regions. Least-squares refinement with suitably modified weights is shown to produce more acceptable atomic parameters in certain cases than those obtained with experimental weights.

Relation between least-squares refinement and difference synthesis

Suppose that we wish to refine the parameters describing a crystal structure by the method of least squares and that we have at our disposal a set of experimental F_o values of uniform quality and free from systematic error. It is easily shown that minimization of

$$Q=\sum_h w(\mathbf{h})[F_o(\mathbf{h})-F_c(\mathbf{h})]^2 \qquad (1)$$