stration apparatus to an irradiation of the model by the 'plane of light' D (produced by the lamp A inside the box B and the vertical slit C). The other orientations of the crystallites perpendicular to the incident beam can be obtained starting from this arbitrarily chosen orientation by (*a*) a rotation about the c^* axis, (*b*) a rotation of the whole set of orientations so obtained about an axis perpendicular to the c^* axis, i.e. parallel to the direction of the incident electron beam.

The first rotation leaves the 'disk' (0002) in its original position and moves the other disks *outside* the 'plane of reflexion'; it is therefore immaterial and need not be realized.† The second rotation can be achieved by means of the motor M, which causes the model to rotate about the axis N, parallel to the electron beam. If now we use for lamp A a sodium or mercury gas-discharge lamp,‡ we obtain the stroboscopic effect shown in Fig. 2, which is a photograph of the actual pattern visible in a darkened room. The demonstration illustrates in a rather striking way the difference in direction of the individual diffraction striae, namely, perpendicular, parallel and oblique to the diffraction circles, as it has to be on the basis of the actual shape transform in reciprocal space.

The resemblance with the electron-diffraction photograph, however, cannot be expected to be more than 'qualitative', as diffraction by needles in an *oblique* position with regard to the incident beam, although not giving rise to (0002) reflexions on account of the small value of the glancing angle θ, might give reflexions such as $(10\bar{1}0)$, for example. These reflexions would show shapes corresponding to a different 'cross-section' of the 'plane of reflexion' with the disk-shaped shape transforms. Actually, the $(10\bar{1}0)$ diffraction ring shows, apart from striae perpendicular to the circumference of the ring, also more 'roundish' (disk-shaped) spots.

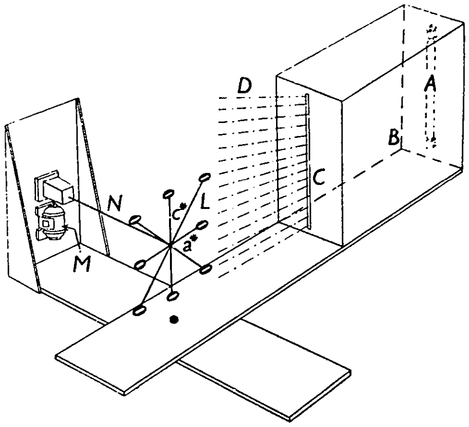

Fig. 3. Demonstration apparatus with reciprocal-lattice model of ZnO. A, sodium gas-discharge lamp; B, metal box; C, slit; L, reciprocal-lattice model; M, motor; N, axis of rotation parallel to direction of incident electron beam.

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† This rotation would, however, bring the $(11\bar{2}0)$ domain, discussed in Rees & Spink's paper, into the 'plane of reflexion' and show the 'radial' direction of the corresponding interference striae. As this would require an extension of the model in the direction of the b^* axis, which would make it more 'voluminous', we have left this out, as the same effect could be shown more easily for the $(10\bar{1}0)$ reflexion.

‡ I am indebted to Dr F. J. Lebbink for this suggestion.

References

Burgers, W. G. & Amstel, J. J. A. Ploos van (1936). *Z. Krystallogr.* A, **95**, 54.
Hillier, J. & Baker, R. F. (1946). *J. Appl. Phys.* **17**, 12.
Rees, A. L. G. & Spink, J. A. (1950). *Acta Cryst.* **3**, 316.
Trillat, J. J. (1939). *J. Phys. Radium*, **10**, 465.

Acta Cryst. (1951). **4**, 503

Pseudo-Cubic Alkaline-Earth Tungstates and Molybdates of the R_3MX_6 Type*

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The formation of R_3WO_6-type alkaline-earth tungstates containing one or more alkaline-earth metals is described. They have structures approaching, and in some examples attaining, cubic symmetry (space group $Fm3m$–O_h^5). A structure, suggested by analogy with $(NH_4)_3FeF_6$, is tested and found to be correct in representing this arrangement.

The deformations from true cubic symmetry exhibited by the compounds are briefly discussed, and examples are given of the temperature dependence of this deformation.

Molybdates of the same type may be formed.

Introduction

Many tungstates of the type RWO_4, where R is an alkaline earth or other divalent element, are well-established chemical compounds. The crystal structures of these alkaline-earth compounds belong to two main classes. Calcium, strontium and barium tungstates are tetragonal, with space group $I4_1/a$–C_{4h}^6, whilst magnesium tungstate is a member of a class, including

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cadmium and zinc tungstates, with a monoclinic crystal structure and space group $P2/c\text{–}C_{2h}^4$.

Calcium tungstate or scheelite is one of the best known of fluorescent minerals, and the other tungstates mentioned are notable for their luminescent properties. Both calcium tungstate and magnesium tungstate, for example, prepared as powders, have been widely used in discharge-lamp applications. During investigations of the luminescent properties of the synthetic tungstates, the effect of additions of alkaline earth oxide above the stoichiometric requirements for the normal tungstate was studied, and new phases were disclosed in X-ray examinations of such preparations. It was found that tungstates of higher alkaline-earth-oxide content than corresponds with the molecular formula RWO_4 were being formed, but that the crystal structures of such tungstates were closely related to one another whatever the nature of the alkaline-earth element being used (Rooksby & Steward, 1946).

Although these compounds, unlike the normal tungstates, were non-fluorescent in the absence of impurities, McKeag & Ranby (1939) found that luminescent properties could be developed by the use of uranium and bismuth as impurity activators. A luminescent magnesium calcium tungstate having the crystal structure characteristic of this new class was developed in 1939, and later other tungstates of similar structure were described.

Occurrence of tungstates of similar constitution has also been observed on tungsten-base thermionic oxide cathodes. An oxide film formed on the surface of the base metal, either during preparation or processing of the cathode, reacts with the alkaline-earth-oxide coating. X-ray studies prove, however, that the compound formed is not $(Ba,Sr)WO_4$, but possesses a crystal structure identifying it with the new class containing a greater concentration of alkaline-earth oxide (Rooksby & Steward, 1951). Compounds of similar crystal structure are found when the base metal is molybdenum instead of tungsten.

A brief description of appropriate methods of preparation of the new tungstates in polycrystalline form is included here, but the main purpose of the paper is to report the results of crystal-structure studies. The crystal-structure work has been carried out wholly by means of X-ray powder photographs, as no single crystals have been grown.

Preparation of the new tungstates and molybdates

As raw materials, high-purity alkaline-earth carbonates and tungstic oxide or molybdic oxide were used. Mixtures of varying compositions were ground together in an agate mortar and fired in platinum crucibles at temperatures of 1000° C. or higher, in air. The resulting materials were reground and refired until examination by the conventional X-ray powder method showed that reaction was complete and that a homogeneous product had been obtained.

The preparation of Ba_2CaWO_6 may be briefly outlined to indicate procedure. 0·7895 g. $BaCO_3$ were mixed with 0·2002 g. $CaCO_3$ and 0·4638 g. WO_3. The mixture was thoroughly ground in an agate mortar and fired in a platinum crucible at 1200° C. for 1 hr. A powder photograph of the product showed that a high proportion of the required tungstate had been formed. The reaction was not complete, however, and further firing at 1400° C. was necessary to form a homogeneous single phase.

With some mixtures difficulty may be experienced in preparing the required tungstate because of a tendency to formation of a 'preferred' compound of different composition. For example, when preparing $MgSr_2WO_6$, initial firings may result in $MgSr_2WO_6$, Sr_3WO_6 and uncombined MgO, but successive regrinding and refiring treatments lead finally to a homogeneous product of $MgSr_2WO_6$. Rapid cooling (or quenching) from the high temperature of formation may be desirable in some instances to avoid decomposition during the cooling cycle. There is evidence that many compounds in the class are metastable at intermediate temperatures with respect to tungstates of the more usual RWO_4 type.

With the preparation of molybdates, the ease with which molybdic oxide sublimes introduces a difficulty. The addition of excess oxide to allow for sublimation is not permissible, since this encourages the formation of the $RMoO_4$ compound. Here, therefore, the lowest temperature at which reaction will take place has to be determined, and excess molybdic oxide added at a later stage as necessary.

From the various experiments it was established beyond doubt that the new compounds contained alkaline-earth oxide and tungstic oxide (or molybdic oxide) in the stoichiometric ratio 3:1. They were, in fact, of the R_3MX_6 type.

A wide variety of tungstates of this composition was prepared, including many containing two or more alkaline earth metals.

Crystal structure

X-ray powder photographs showed that the crystal structures of the new compounds approached cubic symmetry, and in Fig. 1 photographs are shown of several such compounds. It will be seen that different compositions display varying degrees and kinds of deformation from the ideal cubic lattice. Such deformations are manifest in the characteristic appearance of line splitting and of groups of lines where single reflexions for a normal cubic structure would occur.

It was observed, however, that in some instances, when the alkaline-earth positions in the structure were occupied by two kinds of atoms of appreciably different ionic size, the packing of ions allowed the lattice to assume an undeformed face-centred cubic arrangement. The compound Ba_2CaWO_6 is an example of this type (Fig. 1).

More recently, an analogy with compounds such as

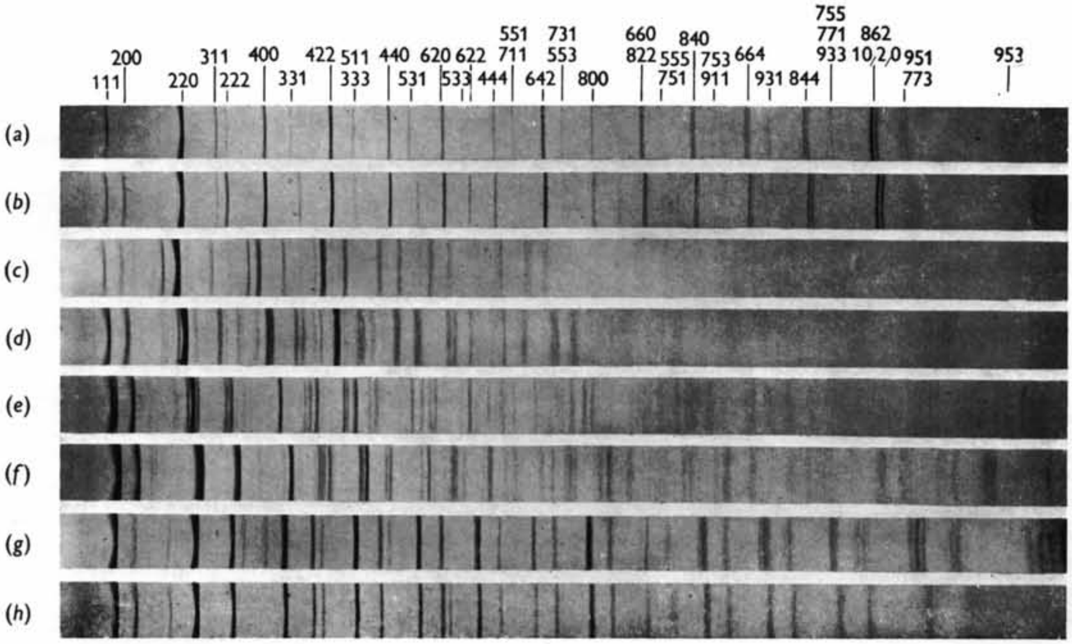

Fig. 1. X-ray powder photographs of R_3MX_6-type tungstates and molybdates (Cu $K\alpha$ radiation; 19 cm. diameter camera). (*a*) Ba_2CaWO_6; (*b*) Ba_2CaMoO_6; (*c*) Ba_3WO_6; (*d*) Sr_3WO_6; (*e*) Ca_3WO_6; (*f*) $MgCa_2WO_6$; (*g*) Sr_2MgWO_6; (*h*) $MgSrCaWO_6$.

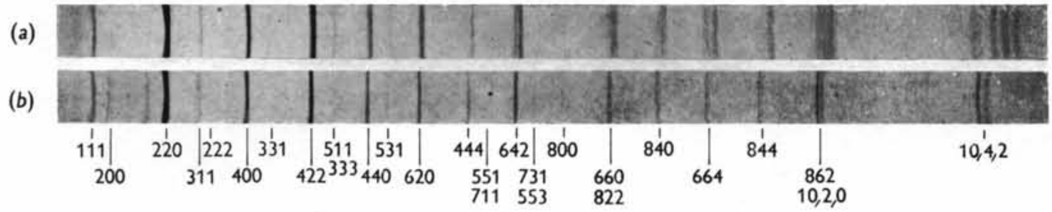

Fig. 2. X-ray powder photographs of Ba_2SrWO_6 at (*a*) room temperature, (*b*) approx. 500° C. (Cu $K\alpha$ radiation; 19 cm. diameter camera.)

$(NH_4)_3FeF_6$ has become evident. If the tungstates have this structure (Wyckoff, 1931), the arrangement would be that shown in Fig. 3, and the co-ordinates would be the following special cases of the space group $Fm3m\text{–}O_h^5$:

R: $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4}; \frac{1}{4}, \frac{1}{4}, \frac{3}{4};$
$\frac{1}{4}, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{1}{4}, \frac{1}{4}.$

R: $0, 0, \frac{1}{2}; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$

W (or Mo): $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}.$

O: u, 0, 0; etc. (24 equivalent points).

Specific-gravity measurements for Ba_2CaWO_6 and Ca_3WO_6 confirmed the presence of four molecules in the unit cell, the actual results being:

	Molecules per unit cell	Specific gravity	
		Calc.	Obs.
Ba_2CaWO_6	3·8	6·68	6·36
Ca_3WO_6	3·9	5·16	5·07

Indexing of reflexions for a tungstate such as Ba_2CaWO_6 confirms the absence of reflexions for which the sum of any two indices is odd. This is consistent with, though of course not peculiar to, the space group $Fm3m\text{–}O_h^5$.

To test the possibility that the structures are of the $(NH_4)_3FeF_6$ form, intensities were calculated for the three principal reflexions for Ba_3WO_6, Sr_3WO_6 and Ca_3WO_6. As seen from Fig. 1, these particular compounds exhibit appreciable deformation from cubic symmetry. An approximation to the ideal cubic arrangement can be made, however, and if the $(NH_4)_3FeF_6$ structure applies, alkaline-earth metal atoms would 'replace' ammonium groups, tungsten atoms would 'replace' iron atoms, and oxygen atoms would take up the octahedral positions around tungsten atoms (Fig. 3).

The oxygen parameters were assessed from considerations of ionic radii and structure-cell dimensions (see below). An approximate value of $u = 0{\cdot}20$ was used for all three compounds.

From Fig. 1 (*c*, *d* and *e*) it will be seen that the relative intensities of the 111, 200 and 220 reflexions for Ba_3WO_6, Sr_3WO_6 and Ca_3WO_6 change considerably from one tungstate to the other. These reflexions would therefore act as a first test of the general 'fit' of the structure.

Table 1 lists the calculated and observed intensities for the three reflexions in each case. Observed intensities are very approximate and include an attempt to integrate qualitatively the intensities for the doublets and triplets of reflexions 'split' on account of the lower symmetries actually involved.

The measure of agreement will be seen to be quite satisfactory in view of the approximations in oxygen parameters, etc., made at this stage.

Having established general agreement between the $(NH_4)_3FeF_6$ structure and the idealized form of the tungstates, a more complete check was made for Ba_2CaWO_6. Here the structure was of true cubic symmetry, no structural deformations, revealed by line splitting in the X-ray photographs even at high angles, being detectable.

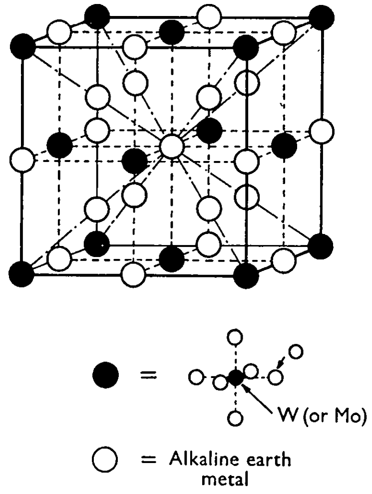

Fig. 3. Atomic arrangement in cubic R_3MX_6-type structures, where R denotes alkaline-earth metal, M denotes tungsten or molybdenum, X denotes oxygen.

The structure shown in Fig. 3 involves two different sets of positions for what will now be the alkaline-earth atoms. For the Ba_2CaWO_6 compound, it appears that barium atoms would occupy the positions:

$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4}; \frac{1}{4}, \frac{1}{4}, \frac{3}{4};$
$\frac{1}{4}, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{1}{4}, \frac{1}{4}.$

The calcium atoms would then occupy the positions:

$0, 0, \frac{1}{2}; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (Fig. 3).

From a consideration of ionic radii and the unit-cell dimension, the oxygen parameter in the structure of Ba_2CaWO_6 was estimated to be approximately $u = 0{\cdot}23$.

Using the above arrangements, intensities have been calculated for all the reflexions recorded with Cu $K\alpha$ radiation and a cylindrical (19 cm.) powder camera. The indexed photograph is shown in Fig. 1.

The usual corrections for multiplicity, Lorentz and polarization factors were applied, and the resulting values for intensities are given in Table 2, together with the observed values. The visual estimates are approxi-

Table 1. *Calculated and observed intensities for barium, calcium and strontium tungstates of* R_3WO_6 *type*

	Ba_3WO_6		Sr_3WO_6		Ca_3WO_6	
	I_c	I_o	I_c	I_o	I_c	I_o
111	9	*w*	20	*m*	35	*s*
200	6	*vw*	12	*wm*	20	*m*
220	201	*vvs*	105	*vvs*	48	*vs*

mate and were made semi-quantitatively using, for some reflexions, the multiple-film technique. From the close agreement between calculated and observed intensities, it is evident that the structure is a correct one.

Table 2. *Calculated and observed intensities for* Ba_2CaWO_6

hkl	I_c	I_o
111	2·4	2·2
200	0·01	0·1
220	10·0	10·0
311	1·1	0·9
222	0·3	0·4
400	2·9	3·0
331	0·4	0·4
422	3·9	3·7
511; 333	0·4	0·4
440	1·6	1·5
531	0·4	0·4
620	1·7	1·5
533	0·1	0·1
622	0·1	0·1
444	0·6	0·6
551; 711	0·2	0·3
642	2·0	2·2
731; 553	0·4	0·3
800	0·3	0·3
660; 822	1·2	1·2
555; 751	0·2	0·2
840	1·1	0·8
753; 911	0·2	0·3
664	1·0	0·7
931	0·2	0·3
844	1·3	1·1
755; 771; 933	0·4	0·4
862; 10,2,0	4·1	3·7
951; 773	0·6	0·6
953	0·7	0·7

In this structure tungsten atoms exhibit 6-co-ordination with oxygen, and the structure involves, on account of the high symmetry, a 'doubling' of all valencies compared with $(NH_4)_3FeF_6$. In the corresponding molybdates, molybdenum atoms replace tungsten atoms in an octahedral co-ordination with oxygen atoms.

Structure-cell dimensions

In the foregoing section, reference has been made to the structure-cell dimensions of the R_3WO_6 compounds, and to the varying deformations from true cubic symmetry which these compounds exhibit. Table 3 lists the structure-cell dimensions of a number of the tungstates and a molybdate, assuming where necessary an approximation to a cubic form. A broad qualitative assessment of the varying magnitudes of deformation is included in the table. It should be noted that where large deformations from a cubic structure are manifest in the X-ray patterns, the values tabulated are inevitably very approximate.

The ions Mo^{6+} and W^{6+} have almost identical radii and their interchangeability in the structure is demonstrated by the close similarity between the X-ray data for Ba_2CaWO_6 and Ba_2CaMoO_6. The powder photographs of these are included in Fig. 1 (*a* and *b*), and the cell dimensions are given in Table 3. The difference in structure factors between molybdenum and tungsten would, however, be expected to result in some changes in relative intensities of certain powder lines. Such alterations are apparent when X-ray patterns of Ba_2CaWO_6 and Ba_2CaMoO_6 are compared: note, for example, in passing from the powder pattern of Ba_2CaWO_6 to that of Ba_2CaMoO_6 the increase of intensity of 200 relative to 111, or 222 relative to 113.

Table 3. *Cell dimensions*

R_3MX_6	Structure-cell dimension assuming, where necessary, a cubic approximation (A.)	Extent of deformation from cubic symmetry*
Ba_3WO_6	$8{\cdot}6_2$	*C*
Ba_2SrWO_6	$8{\cdot}5_7$	*M*
Ba_2CaWO_6	8·390	*N*
$Ba_{1{\cdot}5}Ca_{1{\cdot}5}WO_6$	$8{\cdot}3_3$	*M*
Sr_3WO_6	$8{\cdot}2_9$	*C*
$BaSrCaWO_6$	$8{\cdot}2_9$	*M*
$BaSrMgWO_6$	$8{\cdot}2_9$	*M*
Sr_2CaWO_6	$8{\cdot}2_0$	*C*
Ca_2SrWO_6	$8{\cdot}1_4$	*C*
Ba_2MgWO_6	8·099	*S*
Ca_3WO_6	$8{\cdot}0_2$	*C*
Sr_2MgWO_6	$7{\cdot}9_1$	*M*
$MgSrCaWO_6$	$7{\cdot}8_3$	*M*
$MgCa_2WO_6$	$7{\cdot}7_5$	*C*
Ba_2CaMoO_6	8·355	*N*

* *C* = considerable; *M* = moderate; *S* = slight; *N* = none detectable.

High-temperature studies

The structural deformations referred to in the preceding sections must, of course, originate with the particular packing of ions permissible in any given instance. For this reason, it was felt that at temperatures either above or below room temperature, these deformed structures might well be able, by lattice expansion or contraction, to adopt the higher symmetry state.

Proof of this was obtained with, for example, Ba_2SrWO_6 whose structure is noticeably 'distorted' at room temperature. On raising the temperature to approximately 500° C. the structure assumes the ideal cubic form, the rearrangement resulting from a lattice expansion from $8{\cdot}5_7$ A. at room temperature to $8{\cdot}6_1$ A. at 500° C. Photographs taken at room temperature and at 500° C. for this material are shown in Fig. 2.

$MgCa_2WO_6$, which exhibited a considerably greater departure from cubic symmetry at room temperature than Ba_2SrWO_6 (see Figs. 1 (*f*) and 2 (*a*)), was examined at temperatures up to approximately 900° C. A considerable reduction in deformation of the structure was observed, and there was every indication that at a higher temperature this compound would also reach cubic symmetry.

Character of the structural deformations

The departures from the ideal cubic structure that occur for the majority of these tungstates and molybdates have not been analysed in detail. Some general observations, however, may be made.

It is significant that some compounds analogous to $(NH_4)_3FeF_6$, though closely related to it in crystal structure, are not cubic. In Na_3AlF_6 there is a framework of AlF_6 octahedra similar to that of the FeF_6 groups in $(NH)_3FeF_6$, but the octahedra are slightly rotated or displaced out of the highest symmetry orientation (Náray-Szabó & Sasvari, 1938). The true structure therefore becomes monoclinic and falls into space group $P2_1/m$.

It appears probable that similar displacements from symmetrical orientation, this time of the WO_6 octahedra, are responsible for the departures from the cubic system observed in R_3WO_6-type tungstates. Indeed, the form that the multiplicity of X-ray powder lines takes for, say, Ca_3WO_6 so closely resembles that in powder photographs of Na_3AlF_6 that the atomic arrangements may be in fact almost identical.

Nevertheless, it is improbable that all the structural deformations take exactly the same form. It is more likely that several different structure types occur, and in this connexion the relationship between members of the perovskite family may be recalled. Náray-Szabó (1943), in discussion of the perovskite group, has used the term 'sister-structures' to describe a family of structures that bear a very close likeness to one another and yet are not strictly isomorphous. The tungstates and molybdates appear to comprise another group of compounds for which the term 'sister-structures' is appropriate to emphasize the family resemblance. This group may also be regarded as embracing a number of fluorides of which $(NH)_3FeF_6$ is the prototype.

References

McKeag, A. H. & Ranby, P. W. (1939). British Patent No. 526,675.

Náray-Szabó, St.v. (1943). *Naturwissenschaften*, **31**, 466.

Náray-Szabó, St.v. & Sasvari, K. (1938). *Z. Krystallogr.* **99**, 27.

Rooksby, H. P. & Steward, E. G. (1946). *Nature, Lond.*, **157**, 548.

Rooksby, H. P. & Steward, E. G. (1951). *J. Appl. Phys.* **22**, 358.

Wyckoff, R. W. G. (1931). *The Structure of Crystals*, 2nd ed. New York: Reinhold.

Acta Cryst. (1951). **4**, 507

Diffuse Scattering by an Ordering Alloy*

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At an early stage of the ordering reaction process in CoPt crystals, thin platelets of the ordered phase form on {110} planes of the disordered matrix phase. These platelets are coherent with the matrix. Since {110} planes of the two phases are not identical, when each is in an unstrained condition, they mutually strain each other, causing characteristic diffuse X-ray diffraction effects and the marked changes in physical properties previously reported.

Introduction

A report has recently been published concerning an experimental investigation of the order–disorder phenomena in cobalt–platinum alloys whose compositions lie near 50 atomic % (Newkirk, Geisler, Martin & Smoluchowski, 1950, 1951). In that report the nature of the ordering reaction was described, but only brief reference was made to a part of the investigation in which the state of a partially ordered crystal of CoPt produced diffuse X-ray diffraction effects. It is intended in the present paper to enlarge upon that part of the study, describing new techniques employed and discussing the analysis of the observed diffraction effects in detail.

The phase diagram (Fig. 1) shows that above 825° C., CoPt alloys form an unbroken series of solid solutions having a random face-centered cubic lattice. Below 825° C. alloys close to CoPt in composition become ordered, forming a tetragonal unit cell analogous to the ordered CuAu cell. Parameter measurements are reported elsewhere (Newkirk *et al.* 1950, 1951).

The disordered state of CoPt may be retained by quenching from above 825° C., and the progress of the ordering reaction may be followed by aging at lower temperatures. The time required to approach closely

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* This work represents part of a Doctoral Dissertation submitted by the first-named author to the Department of Metallurgical Engineering, Carnegie Institute of Technology, in June 1950.

† Now studying under Fulbright grant at Cavendish Laboratory, Cambridge, England.