SOVIET PHYSICS – CRYSTALLOGRAPHY VOL. 6, NO. 4 JAN.-FEB., 1962

THE CRYSTALLINE STRUCTURE OF RHOMBOHEDRAL MoS_2

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Translated from Kristallografiya, Vol. 6, No. 4,
pp. 536-540, July-August, 1961
Original article submitted October 31, 1960

According to the data of American authors, in rhombohedral (synthetic) MoS_2 the Mo atom should be in the octahedron. In this paper it is shown that this structure is erroneous and a model is proposed of a structure with the Mo atom situated in a trigonal prism. This model corresponds much more closely to the experimental intensities than the model of the American authors.

An analogy has been made between laminar structures of the type MoS_2 and GaS (GaSe, InSe). For the rhombohedral modification of InSe a structure is proposed which is similar to the structure of rhombohedral MoS_2.

In textbooks on crystal chemistry molybdenite usually occurs, together with cadmium iodide and chloride, as a classical example of laminar structures. It is emphasized that in contrast to the octahedral coordination, characteristic of CdI_2 and $CdCl_2$, in molybenite there is coordination in the form of a trigonal prism [1].

This coordination is connected with features in the structure of the electron shell of the Mo atom. Pauling shows [2] that in MoS_2 the tetravalent Mo atom with one unshared pair of 4d-electrons has not two but four d-orbits for the formation of bonds. As a result of valence electrons from a configuration d^4sp (and, not d^2sp^3) which, in accordance with theoretical calculations [3], leads to coordination in the form of a trigonal prism.

It is known [4] that the basis of structures of the type CdI_2 and $CdCl_2$ is some packing of halogen atoms and the Cd atoms are placed in layers in the octahedral voids of the packing. These structures are conveniently considered as being made up of packets of XCdX. Each such packet can be ascribed, as when describing the densest spherical packings, a certain letter, i.e., A, B, or C, depending on the position of the packet.

In contrast to CdI_2 and $CdCl_2$, in the structure of MoS_2 the sulfur atoms do not form the densest packing but are arranged according to the law BBCCBB.

However, if we consider the mutual orientation of three-layer packets then they are placed according to the law of double-layer hexagonal packing, i.e., the same as in one of the modifications of CdI_2

$$\underbrace{BcB}_{B'}\quad\underbrace{CbC}_{C'}\quad\underbrace{BcB}_{B'}\ldots$$

In 1957 the results of Bell and Herfert [5] were published for an x-ray study of synthetic molybdenum disulfide. The authors showed that the structure of synthetic MoS_2 differs from that of the natural mineral. The constants a of both modifications were the same and the constant c of the new modification is related to the constant of the old modification as 3 to 2 (a = 3.16 A; c = 18.45 A). The x-ray patterns only had reflections with $h-k+l=3n$, which points to the rhombohedral symmetry of the new structure.

Both structures are characterized by the same interatomic distances. Their difference is that, according to the authors [5], in the new structure one layer of sulfur atoms in the packet (for example the top) is turned relative to the other (bottom) through 60° (structure with a center of symmetry, simple face-centered $D_{3d}^5-R\bar{3}m$).

The authors did not pay attention to the fact that this harmless rotation through 60° leads to a very important result – after rotation the Mo atom is not in the center of the prism but in the center of the octahedron (Fig. 1).

Therefore, according to the data of Bell and Herfert in synthetic molybdenum disulfide, in contrast to the natural material, the Mo atom is at the center of the octahedron and not in the center of the prism. This result is rather suprising since for almost 40 years molybdenite has been considered a classical representative of structures with prismatic coordination.

In connection with this problem naturally arises of how reliable is the structure of the rhombohedral modification of MoS_2, proposed by Bell and Herfert, whether a structure can be plotted which would have rhombohedral symmetry and in which the coordination would be maintained about the Mo atom in the form of a trigonal prism. These authors did not consider this possibility and, using the connection between hexagonal and rhombohedral packings established by Belov [4], a structure can readily be obtained with three packets in the unit cell and with the Mo atoms at the centers of trigonal prisms.

In fact if in hexagonal molybdenite with a constant c = 12.30 A we have two packets placed according to the law of double-layer packing, then in a rhombohedral modification with a constant which is $1\frac{1}{2}$ times greater than the constant of the hexagonal phase, these piles should be placed according to the law of three-layer cubic packing

$$A'B'C' \qquad A'B'C' \ldots$$

Revealing the content of the packets, we obtain a detailed formula for the structure in the form

$$\overset{|}{\underset{|}{\mathrm{aB}}} \quad \underbrace{\mathrm{AcA}} \quad \underbrace{\mathrm{CbC}} \quad \overset{|}{\underbrace{\mathrm{BaB}}_{|}} \quad \underbrace{\mathrm{AcA}} \ldots \qquad (1)$$

It can readily be seen that this structure does not have a center of symmetry and consequently belongs to the group C_{3v}^5 – R3m.

The model proposed by Bell and Herfert is written similarly in the form

$$\overset{|}{\underset{|}{\mathrm{aC}}} \quad \underbrace{\mathrm{AcB}} \quad \underbrace{\mathrm{CbA}} \quad \overset{|}{\underbrace{\mathrm{BaC}}_{|}} \ \mathrm{A} \ldots \qquad (2)$$

This structure belongs to the well-known type of $CdCl_2$ (the group D_{3d}^5 – $R\bar{3}m$).

When checking this formula the authors of [5] only compared the theoretical and experimental intensities of the $000l$ reflections.

The structures of (1) and (2) differ very little from one another and the check showed that the theoretical intensities of the $000l$ reflections in both cases are the same (this applies to any reflections with l = 3n and, in particular, to hki0 reflections).

This can be seen from the fact that in both cases the Mo and S atoms are placed on ternary (simple and screw) axes and have the following coordinates:

1) C_{3v}^5 — $R3m$	2) D_{3d}^5 — $R\bar{3}m$
3 Mo — 3 (*a*) — 000	3Mo — 3 (*a*) — 000
3S — 3 (*a*) — 00 $^1/_4$	6S — 6 (*e*) $\pm$ 00 $^1/_4$
3S — 3 (*a*) — 00 $^5/_{12}$	

The structural amplitudes then have the form

$$1)\ A = 3f_{\mathrm{Mo}} + 3f_{\mathrm{S}}\left(\cos 2\pi\frac{l}{4} + \cos 2\pi\frac{5l}{12}\right),$$

$$2)\ A = 3f_{\mathrm{Mo}} + 6f_{\mathrm{S}}\cos 2\pi\, l/4,$$

$$B = 3f_{\mathrm{S}}\left(\sin 2\pi\frac{l}{4} + \sin 2\pi\frac{5l}{12}\right).$$

To solve the problem of which of the above-described variants best satisfies the experimental results it was therefore necessary to calculate the intensities of the reflections with $l \neq 3n$. These calculations were performed for reflections whose experimental intensities were given in the paper by Bell and Herfert [5] (reflections of the type $10\bar{1}l$ and $20\bar{2}l$).

The results of the calculations are given in the table.

They indicate that preference should be given to the model without a center of symmetry, i.e., with the molybdenum atom at the centers of trigonal prisms. This model is obtained from the hexagonal model by rotating whole packets through 60° but not one of the layers of the same packet.

It is obvious that the interatomic distances in both modifications of MoS_2 should be the same. For this instead of "ideal" parameters $^1/_4$ and $^5/_{12}$ (0.416) it is necessary to take 0.252 and 0.414.

Therefore, in the rhombohedral modification of MoS_2, as in the hexagonal modification, the Mo atom is at the center of a trigonal prism, and not in the octahedron, as follows from the work of Bell and Herfert.

In the structural type of molybdenite we can also arbitrarily include the laminar structures of CaS, GaSe and InSe [6-9]. Here, as in the case of molybdenite, the sulfur or selenium atoms are placed according to the law

$$\mathrm{BBCC} \ldots,$$

and the atoms of Ga or In are in pairs on straight lines passing through the centers of the trigonal prisms. The difference is that instead of one Mo atom in the trigonal prisms there are pairs of atoms (Fig. 2). The four-layer piles of the type SeInInSe are placed, as in molybdenite, according to the law of double-layer packing, forming the structure

$$\mathrm{BccB} \qquad \mathrm{CbbC} \ldots$$

The space group is the same as in the case of molybdenite – holohedral hexagonal.

Earlier the author noted that a characteristic feature of these structures is their closeness to structures of the wurtzite type [9]. This followed from the fact that in InSe the In atom is in a tetrahedron formed by three Se atoms and one In atom (Fig. 2), the interatomic distances

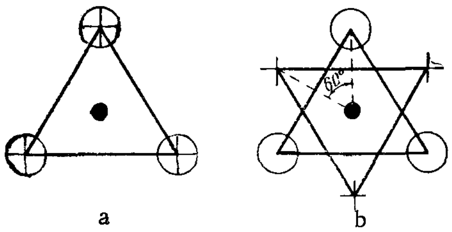

Fig. 1. Mo coordination: a) in a hexagonal and b) in a rhombohedral modification of MoS_2 according to the data of Bell and Herfert [5]: ● – Mo; O – S in the bottom layer of the packet; + – S in the top layer of the packet.

Theoretical and Experimental Intensities of Reflections with $l \neq 3n$ of the Rhombohedral Modification of MoS_2

hkil	*d*	I_{exp} from [5]	I_{theor} of model (1)	I_{theor} of model (2) from [5]
011*	2.72	19(?)	64	21
102	2.64	14	14	0
014	2.36	18	25	55
105	2.20	20	26	10
017	1.90	9	15	5
108	1.77	5	7	17
01.10	1.53	18	2	0
00.12			10	10
10.11	1.43	1	1	2
201*	1.37	2(?)	3	1
022*	1.32	2(?)	1	0
204	1.30	2	2	4

*In Table II of [5] apparently erroneous reflections are given of 100, 200, and 203, having intensities equal to 19, 2, and 2, respectively, these reflections contradict the rhombohedral condition of extinctions and should not be present on the x-ray patterns. Because of this we changed the indices of these reflections to 011, 201, and 022; the experimental intensities of the given reflections are therefore open to doubt.

of In-Se (2.50 A) being close to the sum of the covalent tetrahedral radii of In and Se (2.58 A). This picture is also observed in the case of GaS and GaSe.

On the basis of this it was concluded that the nature of the chemical reaction between different types of atoms in the studied compounds is similar to the nature of reaction in structures of the ZnS type with a purely tetrahedral coordination. However, it is clear that the analogy with structures of the ZnS type is somewhat extended since here we have laminar structures with very perfect cleavage which are presumably closer to molybdenite than to the ZnS type.

In this case the analogy with molybdenite is also justified by the fact that for compounds of GeSe and InSe, apart from the described hexagonal modifications, rhombohedral modifications are also known [7, 10], as in the case of MoS_2 the constants $\underline{a}$ of the latter being equal to the corresponding constants of the hexagonal modifications and the constants $\underline{c}$ being $1\frac{1}{2}$ times greater, i.e., they are related to the constants $\underline{c}$ of the hexagonal phases as 3 to 2.

For the rhombohedral modification of GaSe in [7] a structure was proposed, consisting of three packets with pairs of Ga atoms situated in trigonal prisms, i.e., AbbA, BccB, CaaC.... As regards In selenide, the authors of [10] state that they were not yet able to establish a law of arrangement of packets in this compound. (Its hexagonal modification was established by electron diffraction studies of thin films [9].)

Returning to the case of rhombohedral MoS_2 it is possible to propose for the rhombohedral modifications of GaSe and InSe two variants of the structure – with the pairs of Ga or In atoms situated in trigonal prisms (simple face-centered C_{3v}^5) and with them situated in octahedra (simple face-centered D_{3d}^5).

In the case of GaSe in [7] the second variant was not considered, and in this case its probability is much greater than in the case of MoS_2, since in the structures of GaSe and InSe we have pairs of atoms and therefore, on rotation of any layer of the pile the coordination of each of these atoms does not change.

It is obvious that these two variants differ very little from one another and, as in the case of MoS_2, the theoretical intensities of the reflections with $l = 3n$ for both variants are the same, and consequently, for a check or

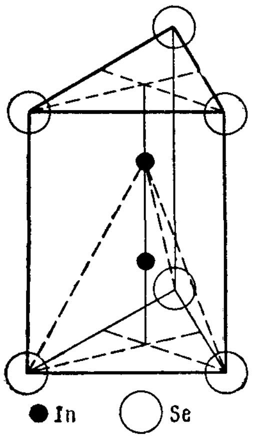

Fig. 2. Packet of indium selenide structure InSe according to [9].

to distinguish the first variant from the second it is essential to take a reflection with $l \neq 3n$.

In the paper by Schubert and co-workers [7] experimental intensities are given for reflections of the rhombohedral modification of GaSe, and we therefore calculated the theoretical intensities for these two variants of the rhombohedral structure of this compound.

In these variants the atoms are placed in the following way:

1) $C_{3v}^{5} — R3m$

$3\,\mathrm{Ga} — 3(a) — 00,\ 0.05$

$3\,\mathrm{Ga} — 3(a) — 00,\ —0.05$

$3\,\mathrm{Se} — 3(a) — 00,\ {}^{1}/_{3} + 0.1$

$3\,\mathrm{Se} — 3(a) — 00,\ {}^{1}/_{3} — 0.1$

2) $D_{3d}^{5} — R\bar{3}m —$

$6\,\mathrm{Ga} — 6(c) — 00,\ 0.05$

$6\,\mathrm{Se} — 6(c) — 00,\ {}^{1}/_{3} — 0.1 = 00,\ 0.233$

The parameters z were chosen on the basis that the interatomic distances in the rhombohedral modification should be the same as in the hexagonal. The results of the calculations point to the correctness of the model chosen by Schubert. This structure can be proposed with considerable reliability for the rhombohedral modification of the selenide In-InSe.

It is well known that in the case of laminar structure there is often the formation of two or more modifications, or polytypical forms, differing only in the different position of the piles of the same structure and composition (SiC, CdI_2, ZnS, etc.).

The case MoS_2, GaSe and InSe is still another example of the same kind of polymorphism: instead of the packets being arranged with prismatic coordination according to the law of hexagonal double-layer packing in rhombohedral modifications the same packets are arranged according to the law of cubic packing.

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