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TRANSITION-METAL CHALCOGENIDES WITH LAYER STRUCTURES AND FEATURES OF THE FILLING OF THEIR BRILLOUIN ZONES

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1. INTRODUCTION

MOST of the transition metals of groups IV-VIII (Cr, V, Ti, Zr, Hf, Nb, Ta, Mo, W, Re, Th, U) form compounds with sulfur, selenium, and tellurium having the composition MX_2 (dichalcogenides), where M is one of the metals and X is a chalcogen.

Certain compounds of this type, namely the disulfides and diselenides of the metals W, Mo, Nb, and Ta, as well as Mo ditelluride, have recently attracted the attention of many researchers in physics and materials science. All these compounds have layer structures close to ideal and good antifriction properties, while some of them have good thermoelectric properties, show superconductivity at relatively high temperatures, and possibly possess a non-phonon mechanism of transition to the superconducting state. Among these compounds only MoS_2 (molybdenite), and in small amounts WS_2 , occur in the Earth's crust, and have been known for a long time. The rest of the compounds have been synthesized mainly in the last decade, and are being studied very intensively.

In spite of the fact that the structure and properties of these compounds have not at all been studied fully, some of them have found application as elements of sliding electrical contacts and thermoelectric sources, as they have made a quite considerable technical impact.

There are several reviews on the structure,^[1-3] electrical and optical properties,^[4] antifriction properties^[5-7] and chemical and galvanomagnetic^[8] properties of these compounds. However, none of these reviews includes all of the studied properties of the dichalcogenides, and most of them were written rather long ago, and they do not contain the results from 1965-1970.

2. CRYSTAL STRUCTURE

Table I gives the structures of the valence shells of W, Mo, Nb, Ta, S, and Se, the ionic radii of the quadruply-ionized metals and the doubly-ionized chalcogens, and also the covalent radii of the latter.^[9-12]

Table I

^{41}Nb $4d^45s$ $4^+, 0.67\text{\AA}$	^{42}Mo $4d^55s$ $4^+, 0.68\text{\AA}$	^{16}S $3s^23p^4$ $2^-, 1.82\text{\AA}; K, 1.04\text{\AA}$
^{73}Ta $5d^36s^2$ $4^+, 0.67\text{\AA}$	^{74}W $5d^46s^2$ $4^+, 0.68\text{\AA}$	^{34}Se $4s^24p^4$ $2^-, 1.93\text{\AA}; K, 1.17\text{\AA}$

However, these electronic configurations are disputable. Thus, a number of researchers consider Mo to have the configuration $4d^45s5p$.^[13-15]

Also, Hultgren^[16] and Kimball^[17] have started with ideas of the directed-valence theory^[18] and have applied group theory to predict a coordination number of six for the electronic configurations d^4sp and d^5s of the metal atom. When bonding is covalent, they predicted either an octahedral or a trigonal-prismatic coordination by the metalloid atoms. Such a coordination is not predicted for the configurations d^4s , d^3s^2 , and d^5s^2 . Nevertheless, all of the currently known disulfides and diselenides of W, Mo, Nb, and Ta have structures composed of layers made of trigonal prisms or octahedra with the metal atoms lying at their centers (Fig. 1). Here the chalcogen atoms lying in two adjacent layers that are not separated by metal atoms are arranged according to the principle of closest packing of spheres. One of these structures (natural molybdenite MoS_2) was solved for the first time in^[19,20]. In the MoS_2 crystal, each Mo atom is surrounded by six sulfur atoms at the vertices of a trigonal prism. The prisms in adjacent layers having Mo atoms at their centers are in antiparallel orientations, and they are arranged so that Mo atoms lie above and below sulfur atoms (Fig. 2). In this structure every third layer repeats the first, and the unit cell consists of two Mo atoms and four S atoms. This structure belongs to the hexagonal system.

We can imagine two other physically non-equivalent ways of arranging adjacent layers in which the unit cell involves two layers: their orientation can be antiparallel, with the prisms having metal atoms at their centers arranged so that the same atoms always lie

FIG. 1. Subcells of layer structures having octahedral (a) and trigonal-prismatic (b) coordination by the chalcogen atoms.

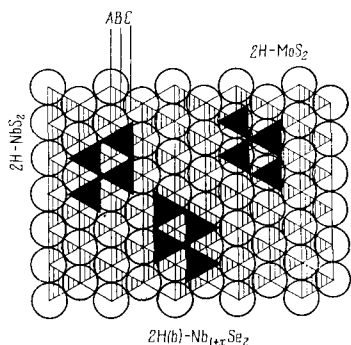
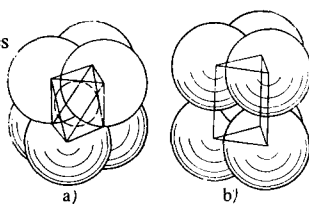


FIG. 2. Different variants of structures having a repeat period of two layers. View on the (0001) plane. Circles are chalcogen atoms. The cross-hatched or black triangles are faces of prisms having metal atoms at their centers.

Table II

Sequence of layers	Space group	Structure type
<i>AbABaB</i>	$D_{6h}^4 - P6_3/mmc$	2H-MoS ₂
<i>AbACbC</i>	$D_{6h}^3 - P6_3/mc$	2H-NbS ₂
<i>AbACaC</i>	$D_{3h}^2 - P6_3/m2$	2H(b)-Nb _{1+x} Se ₂
<i>AbC</i>	$D_{3d}^5 - P3m1$	Cd(OH) ₂
<i>AbABcBCaC</i>	$C_{3v}^2 - R3m$	3R-MoS ₂
<i>AbABcBAbAcA</i>	$P6m2$	4H-NbSe ₂
<i>AbABcBAcAcBcC</i>	$P3m1$	4H(c)-TaSe ₂
<i>AcB.AcABcABcB</i>	$D_{6h}^4 - P6_3/mc$	4H(b)-TaSe ₂
<i>AbCAcABcABaBCaBCbC</i>	$C_{3v}^2 - R3m$	6H-TaS ₂
<i>AbACbCBcBAcACaCBaB</i>	$D_{6h}^4 - P6_3/mc$	6H-Ta _{1+x} S ₂
<i>AcBCbABaC</i>	$D_{3d}^5 - R3m$	CdCl ₂

above and below the metal; or the orientation of the prisms can be parallel (see Fig. 2). If we denote the possible positions of the centers of chalcogens by A, B, and C and the centers of the metal atoms by a, b, and c, then these structures can be symbolized as shown in Table II.

Models of the structure have been constructed theoretically in^[21-24] in which the unit cell consists of up to six layers. Here account was taken of the possible existence of both trigonal-prismatic and octahedral coordination. In^[21,22], they did not take account of the principle of homogeneity of the structure. As structure analysis of some of the dichalcogenides (Nb and Ta) has shown, such structures actually exist. Table II gives a list of the alternation of layers in these structures, and Fig. 3 shows cross-sections of the unit cells in the 11 $\bar{2}$ 0 plane. Within the layers of these structures, which amount to two-dimensional molecules, the bonds are strong and they approach valence bonds in their nature. The layers are bonded to one another by weak van der Waals forces that decline rapidly with distance. Therefore, the layers slide past one another very

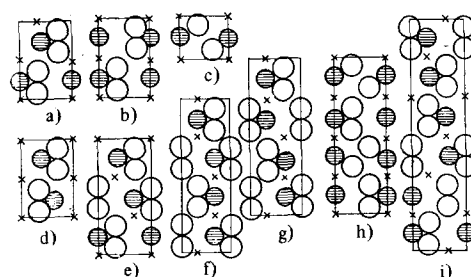


FIG. 3. Cross-sections in the 11 $\bar{2}$ 0 plane of elementary layer structures of different types: 2H(b)-NbSe₂ (a); 2H-NbS₂ (b); CdI₂ (c); 2H-MoS₂ (d); 3R-MoS₂ (e); 4H-NbSe₂ (f); 4H(c)-TaSe₂ (g); 4H(b)-TaSe₂ (h); and 6H-TaS₂ (i).

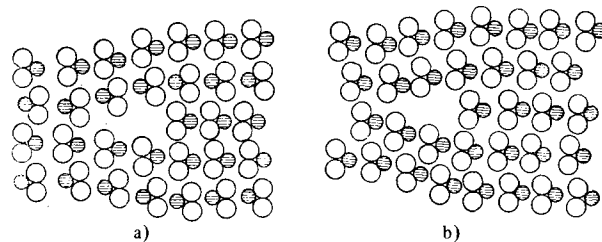


FIG. 4. Layer-stacking errors caused by an edge dislocation in a structure having antiparallel orientation of the trigonal prisms in adjacent layers (a), and in a structure having parallel orientation of prisms (b).

easily. For the same reason, structures that differ only in their layer sequences have almost the same internal energy. This gives rise to stacking defects of the layers during crystallization of the compounds whenever this is favorable from the standpoint of kinetics of crystal growth. Existence of these defects makes the lines diffuse that have $h - k \neq 3n$ (with respect to the hexagonal axes). Owing to the high concentration of defects and their small width, this diffuseness is always quite substantial (up to several degrees). During growth of crystals having antiparallel packing of consecutive layers, the stacking defects are introduced by dislocations having a Burgers vector equal to the thickness of the layer (Fig. 4a). Such errors cannot be eliminated without complete recrystallization of the structure. Consequently, the stacking errors and hence also the line broadening are not eliminated by annealing. In structures having a parallel orientation of layers, the stacking errors can be eliminated either by migration (in Cd(OH)₂-type structures) or splitting (in 3R-MoS₂-type structures) of dislocations (Fig. 4b). This occurs when specimens are held at temperatures of the order of 800–1000°C.^[25]

A particular dichalcogenide can occur is several modifications. If the numbers of layers per unit cell are the same, the lattice periods are also almost identical. Then the x-ray diffraction patterns from different modifications differ only in the intensity relations of the diffraction lines. The intensity relations calculated for different models of a structure in^[22-28] and other studies usually differ from the experimentally-observed values by no more than 10–15%.

The composition of the compounds of Mo, W, Nb, and Ta can differ somewhat from the stoichiometric

Table III

Compound	<i>c</i> , Å	<i>a</i> , Å	<i>c</i> / <i>na</i> , Å°	X-X, Å	M-X, Å	Reference
2H-MoS ₂	12.295	3.1604	1.945	3.47	2.41	69
3R-MoS ₂	18.41	3.166	1.936	3.50	2.41	24
2H-WSe ₂	12.362	3.154	1.960			71
3R-WSe ₂	18.501	3.162	1.950			41
2H-NbS ₂	11.891	3.310	1.796		2.47	32
3R-NbS ₂	17.901	3.310	1.783			32
1H-TaS ₂	5.86	3.346	1.751			25
2H-TaS ₂	12.10	3.315	1.826			25
3R-TaS ₂	17.90	3.32	1.797			25
6H-TaS ₂	35.85	3.335	1.792			25
2H-MoSe ₂	12.931	3.288	1.962	3.75	2.49	72
3R-MoSe ₂	19.392	3.292	1.963			71
2H-WSe ₂	12.976	32.86	1.974			44
2H-NbSe ₂	12.55	3.450	1.822	3.52	2.60	21
2H(b)-Nb _{1-x} Se ₂	12.58	3.454	1.821			60
4H-NbSe ₂	25.24	3.440	1.835	3.55	2.60	21
3R-NbSe ₂	18.88	3.450	1.824	3.54	2.59	21
1H-TaSe ₂	6.272	3.477	1.804			68
2H-TaSe ₂	12.696	3.436	1.847			58
3R-TaSe ₂	19.177	3.435	1.861			58
4H(a)-TaSe ₂	25.399	3.436	1.848			68
4H(b)-TaSe ₂	25.143	3.457	1.818			68
4H(c)-TaSe ₂	25.32	3.450	1.835			27
6H-TaSe ₂	37.83	3.456	1.832			58
2H(b)-Ta _{1-x} Se ₂	12.62	3.442	1.833			60

MX₂ in the direction of increased metal content. The excess metal atoms lie between the layers in octahedral holes, as indicated by the crosses in Fig. 3. This increases the period along the *c* axis while the *a*-axis period remains almost invariant.

We note that similar layer structures are obtained also with octahedral coordination by the chalcogen atoms (Cd(OH)₂ and CdCl₂-type structures). This amounts to closest packing of these atoms.^[29] In a number of cases (e.g., TaS₂), calculation of the intensities of the diffraction lines for this model of the structure gives the same results as for the model with trigonal-prismatic coordination.^[30] However, the ratio *c*/*a* must be a multiple of 1.633 for the octahedral model, rather than 1.816,^[22] as is the case for trigonal coordination, and as is observed experimentally. While the first systematic studies of the synthetic dichalcogenides of W, Mo, Nb, and Ta date back to the middle fifties, the number of these studies is rather extensive.

Table III summarizes the crystal-chemical characteristics of most of the studied disulfides and diselenides of W, Mo, Nb, and Ta.

The synthetic MoS₂ obtained in^[31] had a structure different from the structure 2H-MoS₂ characteristic of natural molybdenite. The authors of^[31] erroneously assigned this structure to the space group R $\bar{3}m$ (the CdCl₂ type) with octahedral coordination by the sulfur atoms.

However, it was shown in^[27,32] that the intensity relations of the diffraction lines for this MoS₂ do not correspond to the space group R $\bar{3}m$, but to the group R3m, in which the sulfur atoms lie at the corners of trigonal prisms.

Later, MoS₂ with this structure was found also in natural deposits of molybdenite.^[33,34] Molybdenum disulfide is a compound of variable composition with a narrow homogeneity range, which has not been studied in detail.^[35,36]

Compounds Mo_xRe_{1-x}S₂^[37] are known that have the R3m structure. The fraction of molybdenum atoms re-

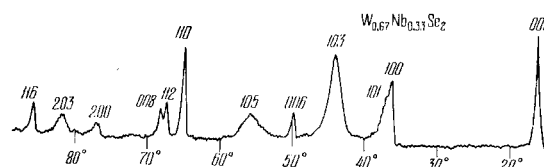


FIG. 5. X-ray diffraction pattern of the compound W_{0.67}Nb_{0.33}Se₂.

placed by rhenium in these compounds was as much as 15 atom percent.

We have established¹⁾ that in MoS₂ (as well as in WS₂) one can replace up to 50 atom percent of the Mo (or W) atoms by Nb or Ta atoms without changing the structure type. However, this produces a large number of stacking defects, and causes the corresponding reflections on the X-ray diffraction patterns to be highly diffuse.

Just like MoS₂, WS₂ is found in the Earth's crust, although it is considerably rarer.^[34] WS₂ has also been prepared synthetically.^[38-43] WS₂ is isostructural with MoS₂, and is known both in a modification of the type of 2H-MoS₂ and of type 3R-MoS₂.^[41,42,70] WS₂ also has a narrow homogeneity range on the side of metal excess.^[43]

Tungsten diselenide is known only in a modification of the 2H-MoS₂ type,^[39] WSe₂ is a compound of practically strict stoichiometric composition.^[44,45] One can replace up to 45 atom percent of the W atoms in WSe₂ with niobium or tantalum atoms without changing the type of crystal structure.^[46,47] However, a large number of layer-stacking errors are produced in the quasibinary alloys, just as in WS₂. This makes the corresponding lines in the x-ray diffraction patterns very diffuse (Fig. 5).

Molybdenum diselenide was first obtained in a modification isostructural with 2H-MoS₂.^[48]

MoSe₂ is known in a modification of the 3R-MoS₂ type,^[49] which was obtained from 2H-MoSe₂ by heating the latter to 1500°C under 40 kbar pressure.

As with WSe₂, no homogeneity interval was found for this compound.^[50]

In MoSe₂, one can also replace up to 40–45% of the Mo atoms with Nb or Ta atoms without changing the crystal-structure type. As in the previous cases, a considerable number of layer-stacking errors are produced here in the crystals of the quasibinary alloys.

The quasibinary system WSe₂-MoSe₂ is a system or unrestricted solubility, and in this system also part of the W and Mo atoms can be replaced with Nb or Ta atoms without changing the structure type.^[51]

The sulfides of niobium were first described in^[52]. A systematic study of the niobium disulfides on a modern level has been made in^[52,53]. Niobium disulfide can crystallize in a two-layer structure having an anti-parallel orientation of trigonal prisms that differs from 2H-MoS₂ in the order of filling of the trigonal prisms by metal atoms (see Fig. 3 and Table II). NbS₂ is also known with a structure like 3R-MoS₂.

NbS₂ has a very broad region of homogeneity on the side of increased metal content. The compounds

¹⁾Engineers E. P. Gladchenko and A. A. Golubnichaya participated in the experimental part of this work.

TaSe₂ has a broad homogeneity range from the diselenide to the composition Ta₂Se₃. The phases Ta_{1-x}Se₂ have the 3R-MoS₂ structure when 0.03 ≤ x ≤ 0.21, a 2H(b)-Nb_{1-x}Se₂ structure when x ≈ 0.1, and a 2H-Nb_{1-x}S₂ structure for all other values of x. The other modifications of TaSe₂ are found only in compounds of stoichiometric composition. Since all of the modifications of TaSe₂ have similar internal energies, single-phase preparations are usually not obtained, and there is no reliable information on which is the equilibrium phase.

The only ditelluride that has a layer structure analogous to the disulfides and diselenides is MoTe₂. This compound is remarkable in that it can exist in two modifications: the 2H-MoS₂ type and the Cd(OH)₂ type with small distortions (which is not observed with the other dichalcogenides of W and Mo). The second modification is the equilibrium phase above 850°C, but it can be quenched and exists in the metastable state at room temperature.^[72]

The methods of synthesis of the dichalcogenides are highly varied.^[37,44,45,47,63,66,67,73-80] However, in order to prepare pure compounds of assigned chemical composition, the only suitable method of synthesis is heating the chalcogen and metal or alloy of metals together in evacuated, sealed quartz ampules. The temperature at which the reaction proceeds is 400–800°C. Sometimes the ampules are held at temperatures up to 1200°C to induce ordering of the structures. The reaction time is from several hours to several weeks. Since all these compounds decompose before melting, single crystals are grown by gas-transport reaction methods^[4,57,73-75,77], etc. One can grow by the same method single crystals of the quasibinary alloys of the different dichalcogenides. Here the composition of the single-crystals differs little from the composition of the original compounds. The single crystals grow in the shape of hexagonal plates of transverse width 5–10 mm and thickness 0.1–0.2 mm.

3. OPTICAL PROPERTIES AND BAND STRUCTURE

Formation of an MX₂ crystal involves s_xd_Ms_Mp_X hybridization, and consequently a valence bonding band of σ electrons arises that contains 16 electrons per MX₂ group, i.e., two completely filled s and p shells of selenium or sulfur. Here the W and Mo atoms each have two d electrons that are not involved in valence bonding, and Nb and Ta have one each. This model, which arises from general considerations of valence theory, is confirmed by the data of the x-ray spectroscopic studies performed in^[13] on the compounds (NH₄)₂MoO₄, MoO₃, MoS₂, and MoC₂, in which the valence of Mo varies from six to two (Fig. 6). We see from this diagram that the d levels are filled as the valence of Mo decreases, and the spectral pattern becomes impoverished.

As we know, the d states are split in the field of the crystal structure into several bands, in accord with the lattice symmetry.

We can suggest from purely geometrical arguments (Fig. 7)^[4] that for octahedral coordination the d_{z²} and d_{x²-y²} states of the metal atoms are preferable for hybridization with the p states of the chalcogen. Since

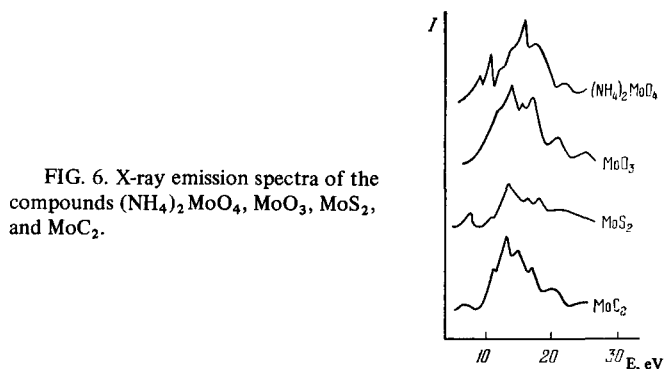


FIG. 6. X-ray emission spectra of the compounds (NH₄)₂MoO₄, MoO₃, MoS₂, and MoC₂.

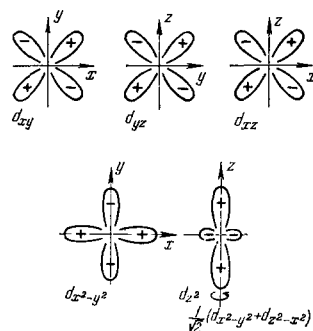


FIG. 7. Spatial orientation of the ψ functions of the d levels.

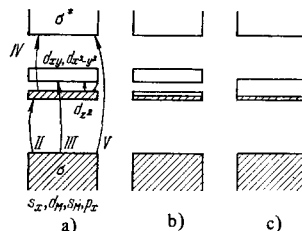
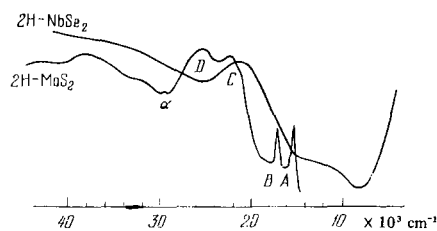
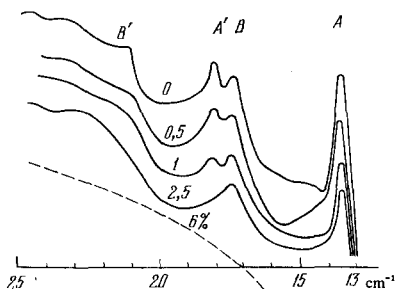


FIG. 8. Band models of the dichalcogenides for structures having trigonal-prismatic coordination of Group VI metals (a); trigonal-prismatic coordination of Group V metals (b), and with octahedral coordination (c).

the remaining d_{xy}, d_{xz}, and d_{yz} states have similar symmetries, the energy bands formed by these states, which lie beneath the valence-bonding band, must overlap (Fig. 8c). The d_{xz} and d_{yz} states are preferable for hybridization in trigonal-prismatic coordination. Hence the band of the d_{z²} states lies above the valence band. The fact that the dichalcogenides of W and Mo having trigonal-prismatic structures are semiconductors permits us to conclude that the d_{z²} band lies below the band formed by the two other states not involved in valence bonding (d_{xy} and d_{x²-y²}) (Fig. 8b).

The absorption spectra of MoS₂ have been studied in^[4,81,82], of WSe₂ in^[4,83,84], and of WS₂ and MoSe₂ in^[4] in the energy range 0.5–5 eV. The reflection spectra of MoS₂ were studied in^[85].

The absorption spectra were studied in ultrathin single crystals cut either from crystals of natural molybdenite or from WS₂, WSe₂, and MoSe₂ grown by the method of gas-transport reactions. The thickness of the specimens was 500–200 Å.

FIG. 9. Absorption spectra of 2H-MoS₂ and 2H-NbSe₂.FIG. 10. Absorption spectra of WSe₂-NbSe₂ crystals.

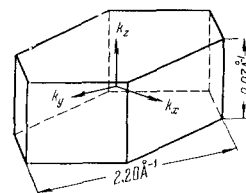
The spectra of all the compounds in the 2H modification proved to be analogous. They are shown for NbSe₂ and MoS₂ in Fig. 9.

The authors of^[4] think that the absorption spectra confirm the correctness of the band models that they proposed (see Fig. 8).

Just like the x-ray spectroscopic data, the optical data indicate that the bonding within the layers is covalent in nature, and four d and s electrons per metal atom participate in bonding. The model of Fig. 8a indicates five fundamental types of transitions that can occur in the trigonal-prismatic dichalcogenides of the Group VI metals. Transition V is a transition across the fundamental bonding energy gap from the filled valence band into the empty one. Such transitions give rise to the exciton α (see Fig. 9). The transition III gives rise to the excitons A and B, which are characteristic of these substances.

The energies of the excitons A and B, which are, e.g., 1.35 and 1.6 eV respectively for WSe₂,^[83,84] agree well with the width of the energy gap determined in^[44] from the increase in concentration of current carriers over the temperature range 400–600°C. Transition IV, having a somewhat greater energy, is reflected in the spectrum by a broad band capped by the peaks C and D. Transition II is impossible in these compounds. Transition I from the filled to the empty d band should have an energy of several tenths of an eV. Such transitions have been observed in MoS₂ in the infrared.

The existence of two excitons A and B of similar energies is due to spin-orbital splitting of the valence-electron levels. Reality of this phenomenon is proved by the fact that the distance between the peaks A and B is directly proportional to the molecular weight of the compounds. Moreover, this distance changes on going from the 2H to the 3R form. Although these modifications are composed of identical layers, they belong to different space groups. This is why the forms of their Brillouin zones differ.

FIG. 11. Brillouin zone of WSe₂.

When we go from the Group VI to the Group V metals, the lower d band becomes only half-filled. This must substantially change the form of the absorption spectrum and the electrical properties of the compounds: metallic conductivity must arise in them, as is actually observed.

First of all, the excitons A and B, which are shielded by the free charges (holes), must disappear from the spectra. It was shown in^[4] that this occurs gradually when the W atoms in WSe₂ are replaced by Nb atoms.

Figure 10 shows the spectra for these systems. We see from these spectra that a very large concentration of holes introduced by Nb atoms is needed in order to shield the A and B excitons (2.5 and 6 atom percent, which corresponds to hole concentrations of the order of 10^{20} – 10^{21} cm⁻³). Since the radius of the excitons is about 10^{-7} cm^[4] the shielding radius is approximately equal to the radius of the excitons. Since half of the states are not filled in the d_{z2} band of NbSe₂, part of the type-IV transitions (Fig. 8a) that occur in WSe₂ proves to be impossible owing to lack of electrons. As the authors of^[4] state, this explains the absence of the peak D in the absorption spectra of the dichalcogenides of the Group V metals. Figure 9 shows a typical absorption spectrum of a dichalcogenide of a Group V metal (NbSe₂), while Fig. 8b shows a model of the energy bands. The reflection spectra of NbSe₂ were studied in^[88].

The Brillouin zone of the dichalcogenides having trigonal-prismatic coordination is a hexagonal prism with a diameter of the base about twice the height. The zone is bounded by planes parallel to the 001 and 100 planes (Fig. 11). The fact that such an anisotropic zone in the W and Mo compounds is completely filled without transition of electrons to the next zone is an important feature of these compounds, which determines their optical, electrical, and galvanomagnetic properties. We should note that the band model proposed in^[4] is questionable with respect to the position of the d_{z2} band. A weak peak in the infrared is found in MoS₂, and on this basis the distance between the d_{z2} and (d_{xy}, d_{x2-y2}) bands has been taken to be of the order of 0.1 eV. It may be due to impurity levels, while this energy gap may actually be considerably larger. We recall that transitions between the stated bands are forbidden. Hence the authors of^[4] had to assume that there is an admixture of p states in the (d_{xy}, d_{x2-y2}) band.

The small effective mass of the charge carriers ($m \approx m_0$) and the low depletion concentration of current carriers in the temperature range 100–500°C in WSe₂ ($\sim 10^{17}$ cm⁻³)^[44] gives us reasons for thinking that free charges arise not only in the d_{z2} band, but also in the valence band. This can occur if the d_{z2} band overlaps the latter.

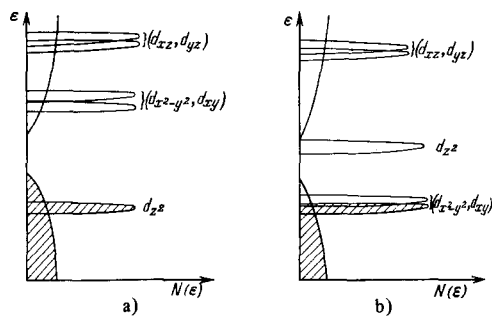


FIG. 12. Band models of dichalcogenides having trigonal-prismatic (a) and octahedral (b) coordinations.

A band model was proposed in^[87] in which the $(d_{xy}, d_{x^2-y^2})$ band lies below the d_{z^2} band. In this model, the semiconductor properties of the W and Mo compounds are explained by spin-orbital splitting of the $(d_{xy}, d_{x^2-y^2})$ band into two bands of capacity two electrons each per metal atom. However, the spin-orbital splitting required to produce an energy of 1.35 eV (as is the case in WSe_2 ^[4,83]) between the d_{xy} and $d_{x^2-y^2}$ bands is much greater than that found for the 5d electrons of free W ions.^[4,72] Hence, the model proposed in^[87] hardly agrees with reality.

The authors of^[72] have performed calculations by the crystal-field and molecular-orbital methods that showed that the d_{z^2} level is the lowest d energy level in compounds of trigonal-prismatic symmetry, and is followed by the $(d_{x^2-y^2}, d_{xy})$ and (d_{xz}, d_{yz}) levels. The sequence differs in compounds with octahedral coordination: there the lowest level is one of the levels (d_{xz}, d_{yz}) or $(d_{x^2-y^2}, d_{xy})$. Since the capacity of these levels is four electrons per metal atom, then a phase transition from a structure having trigonal-prismatic coordination to one having octahedral coordination must cause the semiconductor properties to transform to metallic. As was noted, such a phase transition has been found at 850°C in $MoTe_2$, and it is actually accompanied by such a change in electrical properties.^[72,102] On the basis of these data, as well as the results of measuring the effective masses of current carriers in^[4,44,83], the band model of the dichalcogenides depicted in Fig. 12 has been proposed. In this model, the valence band overlaps the filled (or only half-filled) d_{z^2} band in the compounds with trigonal-prismatic coordination, or a band of the (d_{xz}, d_{yz}) type in compounds with octahedral coordination. Such a band pattern agrees with the results of measuring the thermoelectric power, the electrical conductivity, the heat capacity, and the Hall effect of the dichalcogenides of Nb and Ta.^[88] This study found a considerable deviation of the concentration of current carriers from one per MX_2 group. We might expect this from the band model proposed in^[4,87]: from 0.1 in TaS_2 to 3 in $TaSe_2$.

Moreover, different signs of the current carriers are found from the Hall effect and the Seebeck effect. These phenomena can be explained only if we assume that the d_{z^2} band overlaps the valence band. This must produce charge carriers having substantially different effective masses ("light" and "heavy"), and hence having different mobilities. Since the Hall effect is de-

termined by the square of the mobility, but the Seebeck effect by its first power, the differing signs of these effects are quite explainable within the framework of this model.

Evidently, the last model is closest to reality. However, one of the (d_{xz}, d_{yz}) -type bands probably also lies within the valence band, owing to hybridization of the orbitals of the metal and the chalcogen.

4. ELECTRICAL AND GALVANOMAGNETIC PROPERTIES

The electrical and galvanomagnetic properties of the dichalcogenides are determined by the group number of the metal atom: the dichalcogenides of W and Mo are semiconductors, and those of Nb and Ta show metallic conduction. Deviations from this rule are found only in TaS_2 and $TaSe_2$ in the modifications with octahedral coordination by the chalcogen atoms, and also in $MoTe_2$.

Some data on the electrical properties of the dichalcogenides of the Group VI metals are collected in Table V. As we see from this table, the compound WS_2 has been practically overlooked by researchers, whereas rather many studies have been concerned with MoS_2 , $MoSe_2$, WSe_2 , and $MoTe_2$.

For all these compounds, the $\ln \sigma = f(1/T)$ and $\ln R = f(1/T)$ relations are characterized by two rectilinear regions having activation energies of 0.03–0.1 eV (at low temperatures) and 0.4–0.9 eV (at high temperatures). These regions are separated by a certain temperature region in which R is almost independent of T (depletion), while σ can even decline with increasing T. As we know, such a temperature-dependence is typical of impurity semiconductors. Evidently, the conductivity of these compounds at low temperatures is due to impurities, rather than being intrinsic, as is implied by the band model proposed in^[4] (see Fig. 8). This is confirmed by the fact that the scatter in value of ΔE at low temperatures is very large for a given compound (probably because of presence of different impurities in it). Moreover, as we have noted, the electron concentration in the depletion region, e.g., in WSe_2 ^[44] amounts to only about 10^{17} cm^{-3} . On the other hand, if the conduction in the d bands were intrinsic, it would have to be at least of the order of 10^{21} cm^{-3} . The authors of^[83] came to the same conclusion.

At 600°K and above, intrinsic conduction begins to set in, and it is characterized by the following activation energies: 0.4–0.9 eV for 2H- MoS_2 , 0.4–0.5 eV for 3R- MoS_2 , 0.6 eV for $MoSe_2$, and 0.85 eV for WSe_2 . Unfortunately, all of the performed studies have been made on low-purity materials, while purification of the prepared compounds presents almost insolvable difficulties because these compounds decompose before melting. Moreover, in none of the research did they study the temperature-dependences $\sigma(T)$ and $R(T)$ over a broad enough temperature range from cryogenic temperatures to the onset of intrinsic conduction. Hence, the presented conclusions have been drawn by comparing the results of different studies. It is of unquestionable interest to perform such measurements. However, the existing data are quite sufficient for

Table V

Compound	Specimen characteristics	Structure type	Activation energy of current carriers, eV	Sign of current carriers	σ (ohm ⁻¹ cm ⁻¹) at 293°K	Carrier concentration (cm ⁻³) at 293°K	Thermo-e.m.f. coefficient, μ V/degree	Reference
MoS ₂	Natural single crystal	2H-MoS ₂	0.03—0.06, < 300 °K; 0.7, > 300 °K	p	—	—	—	89
	Ditto	2H-MoS ₂	0.08, < 400 °K 0.87, > 400 °K	p	5·10 ⁻⁴ c 8·10 ⁻² ⊥ c	—	—	82
	» »	2H-MoS ₂	0.09, < 400 °K	p	2,5·10 ⁻¹ —10 ⁻²	3·10 ¹⁵ —2·10 ¹⁷	600	90
	» »	2H-MoS ₂	0.07—0.16, > 300 °K	n	10 ⁻¹	6·10 ¹⁵	—	91
	Synthetic single crystal	2H-MoS ₂	0.5—0.7, > 400 °K	p	3,2·10 ⁻⁵	2·10 ¹⁶	450—760	92
	Synthetic polycrystal	3R-MoS ₂	0.4—0.5, > 400 °K	p	8·10 ⁻⁶ — —2·10 ⁻⁴	8·10 ¹⁵	400—750	92
WS ₂	Ditto	2H-MoS ₂	—	p	15	3,7·10 ²⁰	120	93
	» »	2H-MoS ₂	0.04—0.18	p	—	—	—	89
	» »	2H-MoS ₂	—	n	7·10 ⁻¹	—	—	94
MoSe ₂	» »	2H-MoS ₂	—	p	10 ⁻⁸	—	300	95
	Synthetic single crystal	2H-MoS ₂	—	n	7·10 ⁻¹	5·10 ¹⁶	—	91
	Synthetic polycrystal	2H-MoS ₂	0.07—0.16, > 300 °K	p	1,2·10 ⁻⁴	—	430—610	96
	Ditto	2H-MoS ₂	—	p	4·10 ⁻²	—	700	97
	Synthetic single crystal	2H-MoS ₂	0.6, > 300 °K	n	3·10 ⁻¹	—	900	100
	Synthetic polycrystal	2H-MoS ₂	—	p	10 ⁻¹ —10 ⁻³	—	400—800	99
	Ditto	2H-MoS ₂	0.1, > 300 °K	n	2·10 ⁻⁴	6·10 ¹⁶	—	44
	WSe ₂	Synthetic single crystal	2H-MoS ₂	—	p	2	—	950
Synthetic polycrystal		2H-MoS ₂	0.85, > 700 °K	p	1,2—4	8·10 ¹⁶	—	44
Ditto		2H-MoS ₂	—	p	2,5·10 ⁻³	—	600	95
» »		2H-MoS ₂	—	p	5·10 ⁻³	—	600	99
Synthetic single crystal		2H-MoS ₂	—	p	2·10 ⁻¹	—	—	78
Synthetic polycrystal		2H-MoS ₂	0.1, < 600 °K	p	2	4·10 ¹⁷	780	98
Synthetic single crystal		2H-MoS ₂	0.07—0.16, > 300 °K	n	1	5·10 ¹⁶	—	91
Ditto		2H-MoS ₂	0.68 (optical) 0.046, < 200 °K	p	0.2	10 ¹⁶	—	83
MoTe ₂	» »	2H-MoS ₂	—	n	—	—	780	100
	» »	2H-MoS ₂	0.61, > 600 °K	n	1	10 ¹⁸	600	101
	Synthetic polycrystal	2H-MoS ₂	—	n	4·10 ⁻² (373 °K)	—	360 (373 °K)	44
	Ditto	2H-MoS ₂	—	p	5·10 ⁻⁴	—	—	99
	» »	2H-MoS ₂	—	p	7·10 ⁻⁵	—	400	95
	» »	2H-MoS ₂	0.6, > 400 °K; metallic conduction	n, p	10 ⁻¹ (500 °K)	—	100—600	72
	» »	CdJ(distorted)	Ditto	p	2·10 ²	—	22	72
	» »	CdJ ₂	—	p	10 ³	—	—	102
» »	2H-MoS ₂	—	p	10 ⁻³	—	—	102	

concluding that the band model of these compounds proposed in^[72] is closer to reality than the model proposed in^[4].

We see from Table V that the electrical conductivity of the dichalcogenides of W and Mo varies over a very wide range. The values of σ for MoS₂ differ by a factor of more than 10⁶, for MoSe₂ by 10⁵, and for WSe₂ by 10³. The reason for such a large spread is mainly the uncontrolled impurities. They note in some of the studies, e.g.,^[99] that increasing the temperature of synthesis from 650° to 1100°C increases the electrical conductivity of MoSe₂ and WSe₂ by two orders of magnitude. This was explained by solution of impurities. However, another reason for this phenomenon can be increased in grain size, which decreases the number of intergrain contacts, the resistance of which can be quite significant. Solution of impurities owing to temperature increase might be proved by an increase in the concentration of current carriers. However, it has not been possible to find such data. Therefore we have

tried with the example of MoS₂ to find what role these phenomena play. To do this, we pressed natural MoS₂ with well-formed, relatively coarse grains, and held it at 600—1100°C. The electrical conductivity of the compound was increased by three orders of magnitude by holding at 1100°C, but the concentration of current carriers was increased only twenty times.

In^[91], single crystals of MoSe₂ with a concentration of current carriers of 5×10^{16} cm⁻³ had an electrical conductivity 3.5×10^3 larger than the polycrystalline specimens in^[44] with the same carrier concentration.

All of this indicates that we must treat critically the large spread of values: to a considerable extent, it can be due to the technique of synthesis and preparation of specimens for measurements and their microstructure (for a given purity of the compounds).

The electrical conductivity of MoS₂ shows extremely large crystallographic anisotropy. In the direction of the c axis, $\sigma = 4.6 \times 10^{-4}$ ohm⁻¹·cm⁻¹, and in the perpendicular direction $\sigma = 7.8 \times 10^{-2}$ ohm⁻¹·cm⁻¹ (for the

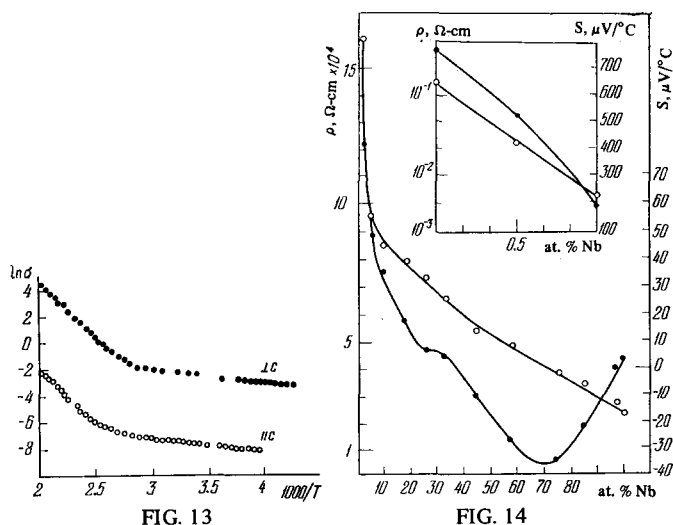


FIG. 13

FIG. 14

FIG. 13. The temperature-dependence of the electrical conductivity of a single crystal of molybdenite along the c axis and perpendicular to the c axis.

FIG. 14. Concentration dependence of $\rho(\circ)$ and $S(\circ)$ of WSe_2-NbSe_2 quasibinary alloys.

same single crystal). However, the activation energy of the current carriers is the same in both cases (Fig. 13).^[82]

Experiments performed to study the dependence of σ along the c axis on the a.c. frequency showed that σ is proportional to the frequency in the range 10^5-10^7 Hz. This indicates that the charges migrate jumpwise from layer to layer.^[4]

As we see from Table V, all the compounds of W and Mo are thermoelectric materials of both p and n types with rather high Seebeck coefficients. The value of S depends on the impurities dissolved in the dichalcogenides. Hence, it cannot be predicted unless one has performed a special doping, although the p type is found oftener than the n type. The low electrical conductivity of these compounds rules out using them in the pure form as thermoelements. In order to increase the electrical conductivity of the dichalcogenides of W and Mo, compounds have been synthesized in a number of studies in which part of the W or Mo atoms were replaced by Nb or Ta atoms (quasibinary alloys $M\gamma X_2-M\gamma IX_2$). The Nb or Ta atoms in these alloys play the role of acceptor impurities.

The quasibinary solid solutions WSe_2-NbSe_2 remain semiconductors as long as the concentration of $NbSe_2$ is less than 1 mole percent. Replacement of this amount of the W atoms by Nb atoms gives rise to an acceptor impurity level with an energy gap of 0.09 eV. Further replacement gives rise to a hole-type conduction band, and about 70% of the Nb atoms lead to hole formation, beginning at 2% of replaced W atoms (Table VI^[98]).

This replacement leads to^[98] a sharp decrease in the electrical resistance, and not a very strong decline in S (Fig. 14).

Replacement of W atoms in WSe_2 by Ta atoms gives an analogous effect. WSe_2-TaSe_2 alloys containing up to 5 mole percent $TaSe_2$ show pure hole conduc-

Table VI

Compound	x	ρ , Megohm·cm	n, cm ⁻³	μ , cm ² /V·sec	n/n ₀ (reference)
$W_{1-x}Ta_xSe_2$	0	780	$8 \cdot 10^{18}$	99.0	} 44
	0.005	30.2	$1.6 \cdot 10^{19}$	12.9	
	0.01	11.7	$8.4 \cdot 10^{19}$	6.3	
	0.02	4.3	$2.5 \cdot 10^{20}$	5.8	
	0.03	3.2	$3.5 \cdot 10^{20}$	5.6	
$W_{1-x}Ta_xSe_2$	0	500	$4 \cdot 10^{17}$	31.0	} *
	0.005	40	$7 \cdot 10^{18}$	22.5	
	0.01	18	$2.4 \cdot 10^{19}$	13.5	
	0.02	4.3	$1.7 \cdot 10^{20}$	8.5	
	0.04	2.3	$3.2 \cdot 10^{20}$	8.6	
$W_{1-x}Nb_xSe_2$	0	1.1	$8 \cdot 10^{20}$	7.0	} 98
	0.005	50	$3 \cdot 10^{18}$	41.0	
	0.01	5	$1.2 \cdot 10^{20}$	10.4	
$Mo_{1-x}Re_xSe_2$	0	1.6	$3.2 \cdot 10^{20}$	12.4	} 44
	0.02	5000	$6 \cdot 10^{18}$	50.0	
		43	$4.5 \cdot 10^{19}$	4.0	

*Unpublished data of V. L. Kalikhman and L. L. Pravoverova (see [98]) for the methodology of specimen preparation.

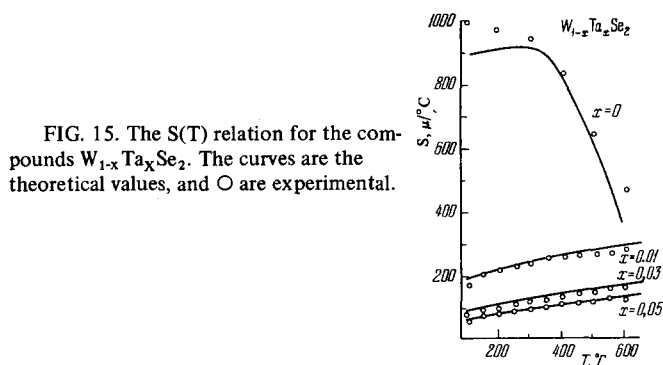


FIG. 15. The $S(T)$ relation for the compounds $W_{1-x}Ta_xSe_2$. The curves are the theoretical values, and \circ are experimental.

tion with an effective mass of the current carriers close to unity. The mechanism of scattering involves ionized impurities when the $TaSe_2$ content is less than 1 mole percent, and phonons when the $TaSe_2$ content is more than 1%. The $S(T)$ relation calculated for them agrees excellently with the experimental data (Fig. 15^[44]). In this study, the procedure for determining the Fermi level ϵ and the effective mass m^*/m_0 consisted in establishing the type of scattering from the temperature-dependence of the mobility $\mu(T)$, measuring S at 350°K, and determining ϵ from the known relations^[103]:

$$S = 86 \left[\frac{4F_3(\epsilon^*)}{3F_2(\epsilon^*)} - \epsilon^* \right] \mu \text{ V/deg}$$

for $TaSe_2 \leq 1$ mole percent, and

$$S = 86 [2F_1(\epsilon^*)/F(\epsilon^*) - \epsilon^*] \mu \text{ V/deg}$$

for $TaSe_2 > 1$ mole percent, where F_3 , F_2 , F_1 , and F_0 are the Fermi integrals, and $\epsilon^* = \epsilon/kT$. Then the $S(T)$ relation was calculated from the known value of ϵ . The effective mass was determined by substituting ϵ^* into the relation

$$p = 4\pi (2m^*kT/h^2)^{3/2} F_{1/2}(\epsilon^*),$$

Here p is the charge concentration measured by the Hall effect, and ϵ denotes the distance of the Fermi level from the edge of the valence band. Alloys that contain from one to several mole percent $NbSe_2$ or $TaSe_2$ have a relatively high coefficient S (about 200 μ V/degree at room temperature), which increases

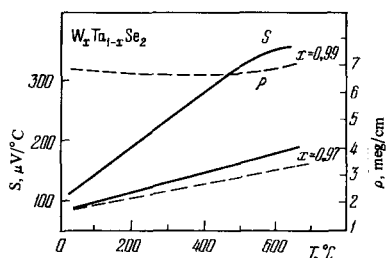


FIG. 16. The $S(T)$ and $\rho(T)$ relations for the compounds $W_{0.99}Ta_{0.01}Se_2$ and $W_{0.97}Ta_{0.03}Se_2$.

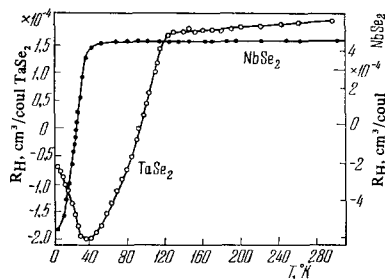


FIG. 17. The $R_H(T)$ relation for $NbSe_2$.

with rising temperature (Fig. 16^[47,98]). Along with this, they have relatively high electrical conductivity (10^2 – $2 \times 10^2 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$) and low heat conductivity (about $0.02 \text{ W}^\circ\text{C}^{-1}/\text{cm}$). This makes them very promising for use as thermoelements at moderate temperatures.

Owing to their texture, pressed quasibinary alloys show rather great anisotropy in their properties. The particles pack during the pressing process in such a way that their c -axis direction lies predominantly parallel to the direction of application of pressure. For example, the electrical conductivity of the alloy $W_{0.97}Ta_{0.09}Se_2$ is four times lower, the heat conductivity 3.5 times lower, and S is 1.4 times lower than in the perpendicular direction. Perhaps if one could grow large enough crystals of WSe_2 and its alloys, then their anisotropy of properties would be of the same order of magnitude as in MoS_2 .

Our measurements on the alloys $MoSe_2$ – $NbSe_2$, $MoSe_2$ – $TaSe_2$, WS_2 – NbS_2 , WS_2 – TaS_2 , MoS_2 – NbS_2 , and MoS_2 – TaS_2 have shown that the properties of these alloys vary with increasing concentration of the second component in about the same way as for the quasibinary alloys mentioned above.

WSe_2 – $ReSe_2$ alloys are also known. In contrast to those mentioned above, they show electron conduction, as do the $MoSe_2$ – $ReSe_2$ alloys.^[44,83]

The electrical properties of the dichalcogenides of Nb and Ta have been studied in less detail. Most of the studies in this field have dealt with the superconductivity of these compounds. As is known, 2H- NbS_2 has metallic conduction with $\sigma = 3 \times 10^2 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ (at 293°K).^[94]

Removing part of the sulfur from NbS_2 up to the concentration $NbS_{1.6}$ (the structure of this compound is of the 3R- NbS_2 type) causes a slight decline in the conductivity (to $2 \times 10^2 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$), but it changes the

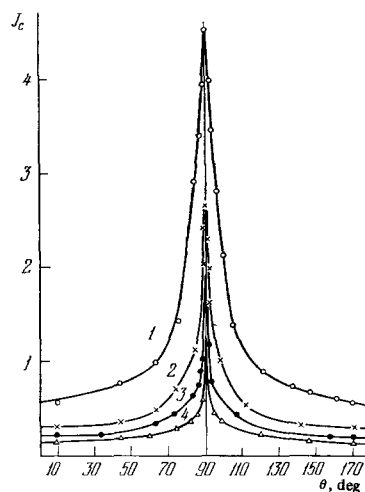


FIG. 18. Anisotropy of the critical currents for superconductivity in $NbSe_2$. θ is the angle between the magnetic field and the c axis; the current flows \perp to the c axis; 1–783 Oe, 2–2758 Oe, 3–3691 Oe, 4–8500 Oe; T @ 4.21°K .

type of conduction to semiconduction. 2H- NbS_2 transforms to the superconducting state at 6.1 – 6.3°K , while 3R- NbS_2 transforms at 5 – 5.5°K .^[104]

Tantalum disulfide in the 2H modification is also a metallic conductor having electrical conductivity $3 \times 10^2 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ at 293°K . In the temperature range 1.3 – 2.1°K , a mixture of all the known modifications of TaS_2 also transforms to the superconducting state, while 1H- TaS_2 transforms at 0.8°K .^[108]

The electrical properties of $NbSe_2$ have been studied in rather good detail, especially its superconductivity, which in the 2H modification sets in at 7.1°K .^[78,106,109-111] 2H- $NbSe_2$ is a metallic conductor with hole conduction at temperatures above 26°K . The hole concentration determined by Hall-effect measurements on single crystals grown by the method of gas-transport reactions is $1.4 \times 10^{22} \text{ cm}^{-3}$.^[77] The concentration of electrons at 7°K is $1.1 \times 10^{22} \text{ cm}^{-3}$ (Fig. 17). This corresponds approximately to the concentration of Nb atoms.

The electrical conductivity of 2H- $NbSe_2$ in a direction perpendicular to the c axis (single crystals) is about $7 \times 10^3 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. In specimens pressed from powders and baked, $\sigma = 5 \times 10^3$.^[98]

Deviation of the composition of $NbSe_2$ from stoichiometric (toward an increased Nb content) markedly decreases the electrical conductivity: it is less by a factor by almost 50 at the composition $Nb_{1.2}Se_2$ than for $NbSe_2$, and it increases with rising temperature.^[63]

Since one can grow single crystals of $NbSe_2$ only as thin plates whose surfaces are perpendicular to c , it has not yet proved possible to measure σ along the c axis. However, it is evidently much smaller than in the perpendicular direction. Owing to the texture that arises in pressed specimens, they have $\sigma_{\perp c}/\sigma_{\parallel c} \approx 4$.^[107] 4H- $NbSe_2$ has an electrical conductivity smaller by a factor of 1.5 than 2H- $NbSe_2$. The superconducting state in this modification of $NbSe_2$ sets in at 6.3°K .^[108,110] As the composition deviates from stoichiometric, the transition temperature to the superconducting state (T_c) for 4H- $NbSe_2$ declines to 5.9°K

at the composition $Nb_{1.09}Se_2$.^[97] The decline is much more substantial for $2H-NbSe_2$: to $2.2^\circ K$.^[110,111] Evidently this involves the fact that the layer stacking rearranges at the composition $Nb_{1.09}Se_2$ to form the phase $2H(b)-Nb_{1+x}Se_2$ (see Fig. 3 and Table II). The authors of^[110,111] did not make note of this, nor did they give a plausible explanation for such a marked decline in T_C .

The critical currents in $NbSe_2$ are strongly anisotropic with respect to the direction of the magnetic field applied to the specimen. The maximum currents are observed when the field is applied in a direction perpendicular to the c axis of the single crystal (Fig. 18).

In the absence of a field, the critical current density is about $10^4 A/cm^2$. It is about $500 A/cm^2$ in a field of 7000 gauss, and $200 A/cm^2$ in a field of 18,000 gauss.^[108,109,112] Superconductivity in the c axis direction also arises at $T_C = 7.1^\circ K$.^[109]

Substitution of Te for Se atoms sharply lowers T_C .^[113] $NbSe_2$ in the 3R modification does not show superconductivity.^[110] In all probability, this is because the distances between Nb atoms in adjacent layers in this modification are considerably larger than in $2H-NbSe_2$, and Se atoms lie between them.

All of this indicates that the niobium selenides are not purely two-dimensional structures, and it confirms the conclusions of^[114], which cast doubt on the possible existence of superconductivity in two-dimensional systems. The electrical properties of single crystals of $2H-TaSe_2$ are analogous to those of $2H-NbSe_2$. At $T > 90^\circ K$, the sign of the current carriers determined from the Hall effect is positive, but negative at $T < 90^\circ K$ (see Fig. 17^[115]). (The carrier concentration in $TaSe_2$ is approximately three times as great as in $NbSe_2$, but ρ is almost the same: about 1.2×10^{-4} ohm \cdot cm at $300^\circ K$ ^[115]).

There is evidence that the sign of the carriers in $TaSe_2$ and $NbSe_2$ as determined from the sign of S is negative at $T = 300^\circ K$.^[88] In polycrystalline $2H-TaSe_2$, $\rho = 4 \times 10^{-4}$ ohm \cdot cm, while it is approximately 1.5 times as great in $4H(b)-TaSe_2$. Evidently, ρ is still greater in $1H-TaSe_2$.^[4] According to a number of the experimental data for octahedral coordination by the Se atoms (which is fully realized in $1H-TaSe_2$ and partially in $4H-TaSe_2$), the overlap of the d levels of the metal atoms is much weaker than for trigonal-prismatic coordination, and the number of carriers in the conduction band is smaller.^[4] This phenomenon has not yet been studied enough. In all probability, it arises from the superstructure that has been found in $TaSe_2$.^[4]

The same holds also for TaS_2 ; T_C for $3R-TaSe_2$ is only $0.2^\circ K$, and $0.14^\circ K$ for $2H-TaSe_2$.^[106]

As we know, within the framework of the Bardeen-Cooper-Schrieffer (BCS) theory, the transition temperature to the superconducting state is given for a phonon mechanism by the expression

$$T_c = 1.14 \theta_D \exp [-1/N(0) V],$$

Here θ_D is the characteristic temperature, $N(0)$ is the density of states at $T = 0$, $N(0) \sim m^* n^{1/3}$ (m^* is the effective mass of the current carriers and n is the carrier concentration), and V is the value of the effective electron-electron interaction.

A set of experimental data is given in^[4] that indi-

cates that the product $N(0) \cdot V$ (and hence also T_0) has a maximum at some definite n . For this reason, the authors of^[4] consider quasibinary alloys of the dichalcogenides of the group V and VI metals to be of considerable interest from the standpoint of developing materials having high transition temperatures to the superconducting state. It would be especially interesting to find superconductivity in alloys of composition not very far from the Group VI dichalcogenides, since the existence in them of stable excitons might lead to appearance of an exciton mechanism of superconductivity which was recently proposed by V. L. Ginzburg. Whenever this mechanism arises, θ_D in the BCS formula is an electron temperature rather than a lattice temperature. Hence, the authors of^[4] think that T_C in such compounds could be higher than the boiling point of liquid hydrogen ($20.4^\circ K$).

5. ANTIFRICTION PROPERTIES

All the dichalcogenides of W, Mo, Nb, and Ta show strong adhesion to metallic surfaces. When combined with the layered nature of their structures and the fact that the bonds between layers are very weak, this property makes them excellent solid lubricants. The mechanism of easy sliding of the dichalcogenides having trigonal-prismatic atomic coordination on metallic surfaces that is now generally recognized consists in the idea that a thin (several hundred Å) highly-textured film of the dichalcogenide is formed on the metal with the 0001 planes of the crystals parallel to the surface of the metal. The bonding forces of this film with the metal considerably exceed the bonding forces of the layers of dichalcogenide with one another. Thus, dichalcogenide slides on dichalcogenide, rather than dichalcogenide on metal.^[116-119] Owing to this friction mechanism, the antifriction characteristics of these materials appear to a very high degree in a vacuum. The presence of any atmosphere, especially water vapor, impairs these characteristics, since it gives rise to adsorbed films or oxides that hinder sliding.^[120-123] However, some of the dichalcogenides of W and Mo, especially WSe_2 , retain rather good antifriction properties even in a moist atmosphere. This is also true of compounds of these metals in which a small part of the W or Mo atoms is replaced by Nb or Ta.^[123]

If we bear in mind the relatively high electrical conductivity of the dichalcogenides of Nb and Ta, as well as of the substituted dichalcogenides of W and Mo, we should note that, until these compounds had been prepared, there was only one material in nature that possessed a similar set of electrical and antifriction properties: graphite. Existence of this material made it possible to develop such an important branch of modern technology as machine design of direct-current motors. Moreover, graphite has been widely applied in various sorts of sliding contacts.

However, it turned out with the development of aviation and cosmonautics that the antifriction properties of graphite deteriorate sharply in the absence of water (or any other) vapors in the atmosphere where it is being used. Detailed studies on single crystals of graphite^[124] have shown that the crystalline anisotropy

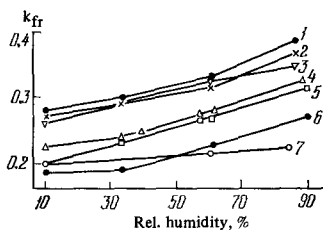


FIG. 19. Relation of the frictional coefficient to the humidity of the atmosphere for the compounds: NbS₂ (1), TaSe₂ (2), TaS₂ (3), MoS₂ (4), NbSe₂ (5), MoSe₂ (6), and WSe₂ (7).

of its mechanical properties can be quite insignificant. The anisotropy of its electrical properties can also be insignificant.^[125]

However, the anisotropy of properties is very high in graphite specimens of perfect structure (e.g., single crystals of pyrolytic or natural graphite^[119]). Hence, evidently, we should consider the reason for the poor antifriction properties of graphite in vacuo to be the numerous distortions that are characteristic of its structure, as well as the ease with which these distortions arise with various types of mechanical agents.

Apparently, the adhesion of the dichalcogenides, e.g., NbSe₂, to metallic counterobjects proves to be much stronger than that of graphite. Thus, electron-diffraction analysis of a film rubbed onto a copper ring by a briquet containing 70 volume percent graphite and the rest NbSe₂ showed that it consisted practically completely of NbSe₂.^[126]

For the reasons presented above, an entire series of motors and devices whose operation depended on parts containing graphite as an electrically-conductive solid lubricant has proved inapplicable under high-altitude and space conditions, and in general, in instruments that operate in a high vacuum.^[5-7,117,120]

This problem could be solved radically only after the dichalcogenides of Nb and Ta, as well as the dichalcogenides of W and Mo substituted with Nb or Ta, could be prepared.

The dichalcogenides of W, Mo, Nb, and Ta are stable to radiation. Radiation doses of 10¹⁷ neutrons/cm² do not produce detectable changes in them. This gives them an important advantage over most antifriction materials under space conditions, especially over any type of organic compound.^[5-7,120] The diselenides of Nb and Ta show catastrophically rapid abrasion under normal conditions because of moisture in the air.^[120] The frictional coefficients of all the dichalcogenides but WSe₂ increase with increasing humidity of the air^[121] (Fig. 19). According to the ideas presented above, the frictional coefficients of the dichalcogenides depend little on the counterobject on which they slide.

The antifriction characteristics of the different polymorphic modifications are about the same insofar as they pertain to materials with trigonal-prismatic coordination by the chalcogen atoms. Substances having octahedral coordination have much poorer antifriction characteristics.^[127]

The frictional coefficients of all the trigonal-prismatic dichalcogenides in air of low humidity (30–40% at 20°C) are 0.1–0.2 in dried air, and 0.05–0.01 in vacuo,^[117,119-122,128] provided that the pressure against the counterobject is about 1 kg/cm². Under substantially higher pressures, the frictional coefficient is considerably lower (e.g. the frictional coefficient of

MoS₂ is reduced to 0.025 at a pressure of about 10,000 kg/cm², and that of TaS₂ to 0.009^[5]).

Raising the ambient temperature to 150–200°C somewhat lowers the frictional coefficient, while further increase sharply raises it.^[119,122] Quasibinary solutions MVIX₂–MVX₂ having a concentration of the second component of about 5 mole percent combine a relatively high electrical conductivity (0.5–2 × 10³ ohm⁻¹·cm⁻¹) with good antifriction characteristics, both in vacuo and under normal conditions and in atmospheres of high humidity (up to 100%).^[123]

The antifriction properties of the dichalcogenides with trigonal-prismatic coordination are substantially better than for all other known solid lubricants.^[128]

6. CONCLUSIONS

1) The disulfides and diselenides of W, Mo, Nb, and Ta, and also MoTe₂, consist of close-packed two-dimensional molecules (layers) made of trigonal prisms or octahedra. Atoms of S, Se, or Te lie at the vertices of the prisms, while a metal atom lies at the center of every other prism.

2) The atoms within each layer are bound by strong covalent bonds. The layers are bound to one another by van der Waals forces.

3) Four d and s electrons of each metal atom and the s and p electrons of the chalcogen atom participate in covalent bonding. They form a bonding band that contains 16 electrons per MX₂ group.

4) The free d levels of the metal atoms form two bands separated by an energy gap. The capacity of the first of them is two electrons per MX₂ group, and that of the second is four (for trigonal-prismatic coordination by the chalcogen atoms). One of these bands overlaps the valence band. As a rule, the degree of filling of the d bands determines the electrical properties of the compounds. The dichalcogenides of W and Mo are semiconductors, and those of Nb and Ta show metallic conduction.

5) The layered structure is the reason for their extremely large crystalline anisotropy of properties, and also the reason why the Brillouin zones which are anisotropic in shape can be completely filled, while overlap of bands (except that with the valence band) does not occur.

6) We cannot treat the dichalcogenides of W, Mo, Nb, and Ta as purely two-dimensional systems. This is shown by the superconductivity found in these compounds (especially in the c-axis direction) and its dependence on the manner of stacking of the layers.

7) The compound WSe₂ in which a small part of the W atoms has been replaced by Nb or Ta atoms is a promising material for high-temperature thermoelectric sources.

8) The layered structure is the reason for the infinitesimally small resistance to displacement of the layers over one another. When combined with high adhesion to metal surfaces, this causes the discussed compounds to be materials with outstanding antifriction properties, that do not require any action of the surrounding medium to elicit them.

9) The dichalcogenides of Nb and Ta, and especially those of W and Mo in which a small fraction of the W

or Mo atoms are replaced by Nb or Ta atoms, show a unique combination of good electrical and antifriction properties, both in a high vacuum and in an atmosphere of high humidity. For this reason, these materials are extremely promising for applications for sliding electrical contacts.

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- ¹F. Jellinek, *Ark. Kemi* 20, 447 (1963).
- ²K. Selte, E. Bjerkelund, and A. Kjekshus, *J. Less Common Met.* 11, 14 (1966).
- ³H. Haraldsen, *Z. angew. Chem. (Intern.)* 5, 58 (1969).
- ⁴J. A. Wilson and A. D. Yoffe, *Adv. Phys.* 18, 193 (1969).
- ⁵P. M. Magie, *Lubrication Engineering* 21, 262 (1966).
- ⁶J. Przybyszewski, *Lubrication Engineering* 24, 451 (1968).
- ⁷L. F. Moberly and J. L. Jonson, *IEEE Trans. As-3*, 252 (1965).
- ⁸A. A. Opalovskii and V. E. Fedorov, *Usp. Khimii* 35, 425 (1966).
- ⁹G. B. Bokii, *Kristalokhimiya (Crystal Chemistry)*, *Izd-vo MGU, M.*, 1960, p. 164.
- ¹⁰G. S. Zhdanov, *Fizika tverdogo tela (Solid State Physics)*, *Izd-vo MGU, M.*, 1962, pp. 81, 184 (Engl. Transl., *Crystal Physics*, Academic Press, N. Y., 1965).
- ¹¹W. Goldschmidt, *Osnovnye idei geokhimi (Fundamental Ideas of Geochemistry)*, (Russ. transl.) *Goskhimizdat, M.*, 1933.
- ¹²N. V. Belov, *Kristalokhimiya ionnykh soedinenii i metallicheskih kristallov (Crystal Chemistry of Ionic Compounds and Metallic Crystals)*, *Izd-vo AN SSSR, M.*, 1947, p. 57.
- ¹³R. L. Barinskii and É. E. Vaĭnshteĭn, *Izv. Akad. Nauk SSSR, ser. fiz.* 21, 1387 (1957) [*Bull. Acad. Sci. USSR* 21, 1375 (1957)].
- ¹⁴R. C. Evans, *An Introduction to Crystal Chemistry*, 2nd ed., Cambridge Univ. Press, 1964, p. 160.
- ¹⁵Tang Au Chin, and Lin Yo Chuang, *J. Chinese Chem. Soc.* 18, 54 (1951).
- ¹⁶R. Hultgren, *Phys. Rev.* 40, 891 (1932).
- ¹⁷G. E. Kimball, *J. Chem. Phys.* 8, 188 (1940).
- ¹⁸L. P. Pauling, *J. Am. Chem. Soc.* 53, 1367 (1931).
- ¹⁹R. G. Dickinson and L. Pauling, *J. Am. Chem. Soc.* 45, 1465 (1923).
- ²⁰O. Hassel, *Zs. Krist.* 61, 92 (1925).
- ²¹B. Brown and J. Beerntsen, *Acta Cryst.* 18, 31 (1965).
- ²²F. Jellinek, *Acta Cryst.* 13, 1021 (1960).
- ²³B. B. Zvyagin and S. V. Soboleva, *Kristallografiya* 12, 57 (1967) [*Sov. Phys.-Crystallography* 12, 46 (1967)].
- ²⁴Y. Takeuchi and W. Nowacki, *Schweiz. Miner. Petr. Mitt.* 44, 105 (1964).
- ²⁵F. Jellinek, *J. Less Common Met.* 4, 9 (1962).
- ²⁶E. Bjerkelund and A. Kjekshus, *Acta Chem. Scand.* 21, 513 (1967).
- ²⁷R. Huisman and F. Jellinek, *J. Less Common Met.* 17, 111 (1969).
- ²⁸S. A. Semiletov, *Kristallografiya* 6, 536 (1961) [*Sov. Phys.-Crystallography* 6, 428 (1962)].
- ²⁹R. S. Mitchell, *Zs. Krist.* 108, 296 (1956).
- ³⁰G. Hagg and N. Shonberg, *Ark. Kemi* 7, 371 (1954).
- ³¹R. E. Ball and R. E. Herfert, *J. Am. Chem. Soc.* 79, 3351 (1957).
- ³²F. Jellinek, G. Brauer, and H. Muller, *Nature* 185, 376 (1960).
- ³³V. F. Chukhrov et al., *Geologiya rudnykh mestorozhdenii* 10, No. 2, 12 (1968).
- ³⁴S. Graeser, *Schweiz. Miner. Petr. Mitt.* 44, 121 (1964).
- ³⁵A. A. Opalovskii and V. E. Fedorov, *Dokl. Akad. Nauk SSSR* 163, 900 (1965).
- ³⁶J. Mering and A. Levisi, *Compt. Rend. Ac. Sci.* 213, 798 (1941).
- ³⁷A. N. Zelikman, G. E. Indenbaum, M. E. Teslit-skaya, and V. P. Shelankova, *Kristallografiya* 14, 795 (1969) [*Sov. Phys.-Crystallography* 14, 687 (1970)].
- ³⁸A. E. Van Arkel, *Rec. Trav. Chim.*
- ³⁹O. Glemser, H. Sauer, and P. König, *Zs. anorg. und allg. Chem.* 257, 241 (1948).
- ⁴⁰S. M. Samoĭlov and A. M. Rubinshteĭn, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 11, 1905 (1959).
- ⁴¹J. C. Wildervanck and F. Jellinek, *Zs. und anorg. allg. Chem.* 328, 309 (1964).
- ⁴²M. S. Silverman, *Inorg. Chem.* 5, 2067 (1966); 6, 1063 (1967).
- ⁴³P. Ehrlich, *Zs. anorg. und allg. Chem.* 257, 247 (1948).
- ⁴⁴V. T. Hicks, *J. Electrochem. Soc.* 111, 1058 (1964).
- ⁴⁵A. N. Zelikman et al., *Izv. Akad. Nauk SSSR (Neorg. mater.)* 6, 1930 (1970).
- ⁴⁶V. L. Kalikhman, E. P. Gladchenko, and L. L. Pravoverova, *ibid.* 8, 1163 (1972).
- ⁴⁷L. H. Brixner, *J. Electrochem. Soc.* 110, 289 (1963).
- ⁴⁸E. Wendehorst, *Zs. anorg. und allg. Chem.* 173, 268 (1928).
- ⁴⁹L. C. Towle, V. Oberbeck, B. E. Brown, and R. E. Stajdohar, *Science* 154, 895 (1966).
- ⁵⁰E. P. Gladchenko, A. G. Duksina, V. L. Kalikhman, V. A. Obolonchik, and L. M. Prokoshina, *Poroshkovaya metallurgiya*, No. 3, 76 (1970).
- ⁵¹L. H. Brixner and G. Teufer, *Inorg. Chem.* 2, 992 (1963).
- ⁵²W. Biltz and A. Köcher, *Zs. anorg. und allg. Chem.* 237, 369 (1938).
- ⁵³F. Kadijk and F. Jellinek, *J. Less. Common Met.* 19, 421 (1969).
- ⁵⁴H. Biltz and C. Kircher, *Ber. deutsch. Chem. Ges.* 43, 1636 (1910).
- ⁵⁵W. Biltz and A. Kocher, *Zs. anorg. und allg. Chem.* 238, 81 (1938).
- ⁵⁶V. L. Kalikhman, S. V. Radzikovskaya, and V. F. Bukhanevich, *Poroshkovaya metallurgiya*, No. 10, 55 (1970).
- ⁵⁷L. H. Brixner, *J. Inorg. and Nucl. Chem.* 24, 257 (1962).
- ⁵⁸F. Kadijk, R. Huisman, and F. Jellinek, *Rec. Trav. Chim.* 83, 768 (1964).
- ⁵⁹K. Koerts, *Acta Cryst.* 16, 432 (1963).
- ⁶⁰R. Huisman, F. Kadijk, and F. Jellinek, *J. Less Common Met.* 12, 423 (1963).
- ⁶¹E. Revolinsky, B. E. Brown, D. J. Beerntsen, C. H. Armitage, *J. Less. Common Met.* 48, 63 (1965).
- ⁶²K. Selte, E. Bjerkelund, and A. Kjekshus, *J. Less.*

- Common Met 11, 14 (1966).
- ⁶³ V. L. Kalikhman and A. G. Duksina, *Izv. Akad. Nauk SSSR (Neorg. mater.)* 7, 1127 (1971).
- ⁶⁴ R. Huisman, F. Kadijk, and F. Jellinek, *Acta Cryst.* 24, 1102 (1968).
- ⁶⁵ K. Seite and A. Kjekshus, *Acta Chem. Scand.* 18, 697 (1964).
- ⁶⁶ S. M. Ariya, A. I. Zaslavskii, and I. I. Matveeva, *Zh. Obshchei Khim.* 26, 2373 (1956).
- ⁶⁷ L. A. Aslanov, Yu. M. Ukrainskii, and Yu. P. Simanov, *Zh. Neorg. Khim.* 8, 1801 (1963) [Russ. J. Inorg. Chem. 8, 937 (1963)].
- ⁶⁸ E. Bjerkelund and A. Kjekshus, *Acta Chem. Scand.* 21, 513 (1967).
- ⁶⁹ H. E. Swanson, N. T. Gilfrich, and G. M. Ugrnic, *NBS Circ. No. 539*, 5, 47 (1955).
- ⁷⁰ H. E. Swanson, N. T. Gilfrich, and G. M. Ugrnic, *NBS Circ. No. 539*, 8, 65 (1958).
- ⁷¹ P. B. James and M. Lavik, *Acta Cryst.* 16, 1183 (1963).
- ⁷² a) M. B. Vellinga, R. de Jonge, and C. Haas, *J. Sol. State Chem.* 2, 299 (1970); b) R. Huisman, R. de Jonge, C. Haas, and F. Jellinek, *J. Sol. State Chem.* 3, 56 (1971).
- ⁷³ V. L. Kalikhman et al., *Izv. Akad. Nauk SSSR (Neorg. mater.)* 7, 1165 (1971).
- ⁷⁴ H. Shafer, *Zs. anorg. Chem.* 286, 27 (1956).
- ⁷⁵ H. Shafer, *Zs. anorg. Chem.* 290, 219 (1957).
- ⁷⁶ R. Nitsche, *J. Phys. Chem. Solids* 21, 199 (1961).
- ⁷⁷ N. H. Lee, H. McKinzie, D. S. Tannhauser, and A. Wold, *J. Appl. Phys.* 40, 602 (1969).
- ⁷⁸ R. Kershaw, M. Vlasse, and A. Wold, *Inorg. Chem.* 6, 1599 (1967).
- ⁷⁹ A. de Shulten, *Bull. Soc. Min. France* 12, 545 (1889).
- ⁸⁰ V. A. Obolonchik, S. V. Radzikovskaya, and V. F. Bukhanevich, *Poroshkovaya metallurgiya*, No. 11, 9 (1965).
- ⁸¹ R. F. Frindt and A. D. Yoffe, *Proc. Roy. Soc.* A273, 69 (1963).
- ⁸² B. L. Evans and P. A. Young, *Proc. Roy. Soc.* A284, 402 (1965).
- ⁸³ L. C. Upadhyayula, J. J. Loferski, A. Wold, W. Giriat, and R. Kershaw, *J. Appl. Phys.* 39, 4736 (1968).
- ⁸⁴ R. F. Frindt, *J. Phys. Chem. Solids* 24, 1107 (1963).
- ⁸⁵ V. V. Sobolev, *Optika i Spektroskopiya* 18, 334 (1965) [Optics and Spectroscopy 18, 187 (1965)].
- ⁸⁶ E. A. Antonova, V. G. Vorob'ev, T. A. Kalyuzhnaya, and V. V. Sobolev, *Fiz. Tekh. Poluprovodnikov* 3, 922 (1969) [Sov. Phys.-Semiconductors 3, 777 (1969)].
- ⁸⁷ J. B. Goodenough, *Mat. Res. Bull.* 3, 409 (1968).
- ⁸⁸ M. H. von Maaren and H. B. Harland, *Phys. Lett.* A29, 571 (1969).
- ⁸⁹ J. Lagrenoudie, *J. de Phys.* 15, 299 (1964).
- ⁹⁰ R. Mansfield and S. A. Salaam, *Proc. Phys. Soc.* B66, 377 (1953).
- ⁹¹ R. Fivaz and E. Mooser, *Phys. Rev.* 163, 743 (1967).
- ⁹² M. V. Teslitskaya, Candidate's Dissertation, Moscow Institute of Steel and Alloys, 1968.
- ⁹³ G. V. Samsonov and V. Kh. Oganessian, *Dokl. Akad. Nauk UkrSSR* 10, 1317 (1965).
- ⁹⁴ D. Boes, *Fuses Rech. Astron.*, Nr. 26 (1964).
- ⁹⁵ J. A. Champion, *Brit. J. Appl. Phys.* 16, 1035 (1965).
- ⁹⁶ Yu. M. Ukrainskii and A. V. Novoselova, *Dokl. Akad. Nauk SSSR* 139, 1136 (1961).
- ⁹⁷ V. A. Obolonchik, L. M. Prokoshina, and V. P. Fedorchenko, in *Khalkogenidy (Chalcogenides)*, No. 2, "Naukova dumka", Kiev, 1970, p. 130.
- ⁹⁸ V. L. Kalikhman and L. L. Pravoverova, *Izv. Akad. Nauk SSSR (Neorg. mater.)* 7, 2162 (1971).
- ⁹⁹ E. Revolinsky and D. Beerntsen, *J. Appl. Phys.* 35, 2086 (1964).
- ¹⁰⁰ L. H. Brixner, *J. Inorg. and Nucl. Chem.* 24, 257 (1962).
- ¹⁰¹ P. A. Lepetit, *J. de Phys.* 26, 175 (1965).
- ¹⁰² E. Revolinsky and D. J. Beerntsen, *J. Phys. Chem. Solids* 27, 523 (1966).
- ¹⁰³ V. I. Fistul', *Sil'no legirovannye poluprovodniki (Heavily Doped Semiconductors)*, "Nauka", M., 1967, pp. 141-150 (Engl. Transl., Plenum, New York, 1969).
- ¹⁰⁴ M. H. van Maaren and G. M. Schaeffer, *Phys. Lett.* 20, 131 (1966).
- ¹⁰⁵ M. H. van Maaren and G. M. Schaeffer, *Phys. Lett.* A24, 645 (1966).
- ¹⁰⁶ E. Revolinsky, E. P. Lautenschlager, and C. H. Armitage, *Sol. State Comm.* 1, 59 (1963).
- ¹⁰⁷ V. L. Kalikhman and A. G. Duksina, *Elektrotekhnik, No. 8*, 58 (1971).
- ¹⁰⁸ D. J. Beerntsen, G. A. Spiering, and C. H. Armitage, *IEEE Trans. As-2*, 813 (1964).
- ¹⁰⁹ G. A. Spiering, E. Revolinsky, and D. J. Beerntsen, *J. Phys. Chem. Sol.* 27, 535 (1966).
- ¹¹⁰ E. Revolinsky, G. A. Spiering, and D. J. Beerntsen, *J. Phys. Chem. Sol.* 26, 1029 (1965).
- ¹¹¹ E. A. Antonova, K. V. Kiseleva, and S. A. Medvedev, *FMM* 24, 441 (1969).
- ¹¹² E. A. Antonova, S. A. Medvedev, and I. Yu. Shebalin, *Zh. Eksp. Teor. Fiz.* 57, 329 (1969) [Sov. Phys.-JETP].
- ¹¹³ E. A. Antonova, K. V. Kiselev, and S. A. Medvedev, *Zh. Eksp. Teor. Fiz.* 59, 54 (1970) [Sov. Phys.-JETP].
- ¹¹⁴ R. A. Ferrel, *Phys. Rev. Lett.* 13, 330 (1964).
- ¹¹⁵ N. H. Lee, et al., *J. Sol. State Chem.* 1, 190 (1970).
- ¹¹⁶ J. M. Feng, *Lubric Engineering* 8, 285 (1952).
- ¹¹⁷ U. S. Patent (Cl. 310-228) No. 3300667 (1967).
- ¹¹⁸ W. Winer, *Wear* 10, 422 (1967).
- ¹¹⁹ A. Ya. Artamonov, Sh. E. Bersegyan, and Yu. D. Repkin, *Poroshkovaya metallurgiya*, No. 9, 64 (1968).
- ¹²⁰ D. Boes, *IEEE Trans. As-2*, 457 (1964).
- ¹²¹ J. P. Giltrow, *J. Appl. Phys.* 18, 831 (1967).
- ¹²² A. Ya. Artamonov, Sh. E. Bersegyan, and Yu. D. Repkin, *Poroshkovaya metallurgiya*, No. 9, 64 (1968).
- ¹²³ V. L. Kalikhman and L. L. Pravoverova, *Poroshkovaya metallurgiya*, No. 7, 193 (1972).
- ¹²⁴ P. J. Braiant, P. Z. Gutshall, L. H. Taylor, *Wear* 7, 118 (1964).
- ¹²⁵ E. R. Braithwaite, *Solid Lubricants and Surfaces*, Macmillan, N. Y., 1964 (Russ. Transl., "Khimiya", M., 1967, p. 62).
- ¹²⁶ V. L. Kalikhman, A. G. Duksina, E. B. Granovskii, and V. M. Titov, *Elektrotekhnik, No. 11* (1972).
- ¹²⁷ W. E. Jamison and S. L. Cosgrove, *ASIE Trans.* 14, 62 (1971).
- ¹²⁸ M. T. Lavik, T. B. Daniel, and A. N. Abott, *J. Appl. Phys.* 32, 1795 (1961).