Atomic-volume deviations and occurrence of semiconducting properties in transition metal sulphides

While all the sulphides of non-transition elements are semiconductors [1], many sulphides of transition metals are metals. The aim of the present note is to consider the relationship between the occurence of semiconducting properties and the deviations of atomic volume from additivity in the sulphides of transition metals having three-dimensional networks of metal atoms. The compounds Mo_6S_8 [2] and Nb_3S_4 [3] and the disulphides ZrS_2, NbS_2, MoS_2, etc. [4], since they are built up of clusters of atoms or of layers or having large holes, are omitted from consideration.

The percentage deviation of the atomic volume, V, from the sum of its components, $\Sigma\Omega$, is given by

$$K = \frac{m+n}{2n}\,\frac{\Sigma\Omega - V}{V}\,100 = \alpha\frac{\Delta V}{V}, \qquad (1)$$

where ΔV is given by $\Sigma\Omega - V$, α is equal to $100[(m+n)/2n]$, and m and n are the numbers of atoms of transition metal, $\mathscr{T}$, and of sulphur, S in the compound $\mathscr{T}_m S_n$, respectively. The coefficient $(m+n)/2n$ provides the normalization to the case of equiatomic compounds, $\mathscr{T}S$, since the contraction of the compound is due mainly to the presence of the sulphur atoms. Information on the type of conductivity was taken mainly from the available reviews [3, 5, 6] and from data on atomic

TABLE I Sulphides of non-magnetic transition metals (with the exception of Rn, Os, Rn, Os, Rh and Ir sulphides)

Compound	Structure	$\alpha\frac{\Delta V}{V}$	Type of conductor	T_c (K)
La_5S_7	tetragonal	4	–	–
Re_2S_7	tetragonal	5	semiconducting	–
VS_4	monoclinic	6	semiconducting	–
Zr_9S_2	tetragonal	8	–	–
Hf_2S_3	CdI_2	8	semiconducting	–
PtS	tetragonal	10	semiconducting	–
Hf_3S_4	monoclinic	11	semiconducting	–
PdS_2	orthorhombic	12	semiconducting	–
Lu_2S_3	hexagonal	12	semiconducting	–
V_7S_8	orthorhombic	13	–	–
ZrS_3	monoclinic	14	semiconducting	–
La_2S_3	Cd_2S_3	14	semiconducting	< 1.3
Sc_2S_3	orthorhombic	14	semiconducting	–
HfS_3	$ZrSe_3$	14	semiconducting	–
Mo_2S_3	monoclinic	14	–	–
TaS_3	orthorhombic	15	semiconducting	–
PtS_2	CdI_2	16	semiconducting	–
NbS_3	monoclinic	16	semiconducting	–
Y_2S_3	monoclinic	17	semiconducting	–
PdS	tetragonal	17	semiconducting	< 0.3
La_2S_3	Ce_2S_3	17	semiconducting	–
Zr_3S_4	cubic	19	–	–
TiS_3	monoclinic	19	semiconducting	–
Hf_3S_4	cubic	20	–	–
LaS_2	orthorhombic	21	semiconducting	–
$Pd_{2.2}S$	cubic	21	metallic	1.6
La_2S_4	cubic	21	–	–
Ti_5S_8	rhombic	21	metallic	–
ZrS	CuTi	22	–	–
Y_5S_7	monoclinic	23	metallic	–
V_5S_8	monoclinic	23	metallic	–
Ti_8S_{12}	rhombic	24	metallic	–
LaS	NaCl	24	metallic	0.84
$Pd_{16}S_7$	cubic	25	–	–
La_3S_4	Th_3P_4	25	metallic	8.1
Ta_2S	orthorhombic	27	metallic	–
V_5S_4	Ti_5Te_4	28	metallic	–
Ti_3S_4	rhombic	28	metallic	–
Pd_3S	orthorhombic	29	metallic	–
Ti_4S_5	Ti_4S_5	30	metallic	–
V_3S_4	monoclinic	30	metallic	–
Hf_2S	Hf_2S	31	metallic	–
$VS_{0.9}$	orthorhombic	31	–	–
Ta_6S	monoclinic	33	–	–
Y_4S_3	NaCl	34	metallic	–
$Nb_{0.9}S$	NiAs	34	metallic	–
ZrS	NaCl	35	metallic	4.0
TiS	NiAs	37	metallic	< 1.0
NbS	MnP	39	metallic	< 1.3
VS	MnP	39	metallic	–
ScS	NaCl	39	metallic	< 0.3
Pd_4S	Pd_4Se	39	metallic	< 0.3
$Nb_{21}S_8$	tetragonal	41	metallic	–
HfS	WC	41	metallic	–
YS	NaCl	42	metallic	1.9
$TiS_{0.5}$	WC	42	metallic	–
Ti_3S_4	monoclinic	43	metallic	–
$ZrS_{0.5}$	WC	43	metallic	–
$Nb_{14}S_5$	orthorhombic	43	metallic	–
V_3S	tetragonal	46	metallic	< 1.1
LuS	NaCl	46	metallic	1.0
V_3S	tetragonal	47	metallic	–
Ti_8S_3	monoclinic	52	–	–
Ti_2S	Ta_2S	47	metallic	–
Zr_2S	Ta_2S	59	metallic	–

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volumes. Critical temperature, T_c, values were taken from [7, 8]. For the atomic volume of sulphur a value of 25.52 $Å^3$ was adopted.

Table I shows that metallic properties (apart from the case of pnictides [8]) are associated with a large atomic volume contraction ($K \geqslant 21$), while semiconducting properties are associated with a small atomic volume contraction ($K \leqslant 21$). There are however some exceptions to this rule, which are related to the position of the given transition metal in the Periodic Table. For instance, such violations appear for sulphides of metals with 6 (Cr, U), 8 (Ru, Os) and 9 (Rh, Ir) outer electrons. While metallic compounds $Rh_{17}S_{15}$ ($K = 28$, $T_c = 5.8$ K) and IrS_2 (FeS_2 structure, $K = 31$) obey the rule, the semiconducting compounds IrS_2 ($IrSe_2$ structure, $K = 24$), Ir_2S_3 ($K = 28$), Rh_2S_3 ($K = 28$), RuS_2 ($K = 35$, $T_c < 0.3$ K) and OsS_2 ($K = 35$) violate the rule. Since these compounds are difficult to prepare stoichiometrically [10], they are insufficiently investigated [3]. One explanation of these exceptions to the rule is that the compounds are in fact metallic, and that the semiconducting behaviour is due to the precipitation of thin layers of sulphur on the grain boundaries. An alternative explanation is based on the possibility that in these compounds the valency of (and therefore the number of electrons provided for bonding by) sulphur atoms is higher than usual (see [1]). Other deviations from the rule are observed in chromium (for non-magnetic chromium $V = 11.9$ $Å^3$ [11]) and uranium sulphides having atomic magnetic moments and forming metallic compounds; for instance, for Cr_3S_4, $K = 16$; for Cr_5S_6, $K = 18$; for US, $K = 7$; and for U_3S_5, $K = 7$. These anomalies could be explained by taking into consideration that, for example, in US (magnetic moment per U atom, $\bar{p}$, equals 1.7 μB [12]), the number of U-atom electrons, $\bar{n}_k$, involved in bounding, is 4.3 [13, 14], while for metallic U, $\bar{n}_k = 6$. Therefore, in calculating $\bar{K}$ for US the value of atomic volume, V, for U ought to be found by interpolation between atomic volumes of Th and Pa, corresponding to the average number of valence electrons 4.3 (i.e. $V = 30.4$ $Å^3$), leading, for the metallic US, to the value $\bar{K} = 36$ in agreement with the rule. It should be noted, however, that the value for atomic magnetic moment should be calculated from the saturation magnetization for ferromagnetics, which can sometines differ from data from neutron measurements [12].

It is interesting in this connection to also consider transition metal compounds of other classes: aluminides, silicides and oxides.

The case of the antiferromagnetic alloy Cr_3Al ($p = 1.07$ μB, $\bar{K} = 13$) has been discussed already in the previous note [15]. In silicides, apart from $ReSi_2$ [15], an anomalous, large value of K is observed in the non-magnetic compound $CrSi_2$ ($K = 33$), reported as being semiconducting in a series of papers [16]. In spite of these data it is still possible that the intrinsic properties of this compound are metallic, but that the semiconducting behaviour is caused by the precipitation of very thin layers of Si or SiO_2 on the grain boundaries. This supposition is supported by the fact that in some samples with metallic lustre the resistivity, ρ, was found to be very small ($\rho = 7$ $\mu\Omega$ cm) [14]. Moreover, the dependence of both resistivity and thermoelectric power on composition shows a sharp minimum corresponding to the compound $CrSi_2$ which is characteristic for metallic compounds, but not for semiconducting compounds [17].

The very small change of atomic volume in the metal–semiconductor transition in VO_2 [18] is inconsistent with the point of view considered above. However this could be explained by the assumption that in metallic state the oxygen valency (and the number of bonding electrons provided by oxygen atoms) is 2, while in the semiconducting state oxygen atoms display valency of 4, leading to the additional contraction and compensating for the expansion that is characteristic to the semiconducting state.

It seems, therefore, that in the compound of given composition the atomic volume of the semiconducting state is bigger than that in the metallic state, provided that the valences of the components and the total number of bonding electrons are the same.

Anomalous increases (by three orders of magnitude) in the resistivity of polycrystals compared with that of the single crystals has been found in Sm-doped barium titanate [19]. The increase was attributed to the grain boundary effect. Small single crystals of $CrSi_2$, having a size of about 1 mm^3, have been produced by means of chemical transport reaction [20], but the electrical properties of these crystals have not been investigated. The specimens prepared by sintering [21] and by the floating zone technique [22] show a decrease in their resistivity with temperature from 660 K to the lower temperature and an increase in resistivity (up to three orders of magnitude) due to doping with a small amount of Mn, which is characteristic of metallic rather than semiconducting compounds. Although the author of the work [22] assumes that the specimens prepared by zone-melting are single crystals, no detailed metallographic and X-ray investigations, confirming this supposition, were mentioned. Detailed characterization is necessary since the crystallization of compounds with high melting points infrequently produces many blocks of size over 1 mm. As a result such specimens also show regular Laue patterns characteristic of a single crystal (the dimension of the X-ray beam is about 1 mm^2) in spite of the presence of grain boundaries.

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