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Bonding Schemes for Compounds with the Pyrite, Marcasite, and Arsenopyrite Type Structures

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Tentative bonding schemes for compounds with the pyrite, marcasite, and arsenopyrite type structures are presented and compared with experimental data. The occurrence of three different classes of binary and ternary phases with the marcasite type structure (including also the pseudo-marcasite arrangement of the arsenopyrites) is explained in terms of the spatial orientation, mutual energy-splitting, and filling of the essentially non-bonding d orbitals of the metal atoms. The classes, which are denoted as A, A/B, and B, may be specified by the axial proportions of the unit cell or more conveniently defined by the configuration (d^j) of localized d electrons on the metal atoms. According to the latter definition, class A corresponds to $0 \leqq j \leqq 4$ in d^j, class A/B to $4 < j < 6$, and class B to $6 \leqq j \leqq 10$. The relative expansion of the c axis of the marcasite cell in going from class A to class B is accounted for. This *expansion model* also provides a qualitative explanation of the occurrence of the three structure types in relation to the configurations of localized d electrons on the metal atoms. The majority of the experimental data for the magnetic and electrical properties of the compounds in question are also consistent with this model.

In the current bonding schemes for transition metal compounds with the structure types: pyrite, marcasite, and arsenopyrite, the valence electrons are distributed as bonding and non-bonding (and in some cases anti-bonding) electrons according to the different bond-theoretical models used by various authors. The present discussion makes use of a band-theory (BT) description, which is in all essentials based on molecular orbital (MO) considerations.

MO's are normally constructed by a linear combination of atomic orbitals (AO's), in such a way that there are formed *in toto* the same number of (bonding and anti-bonding) MO's as the number of AO's used for their construction. In inorganic macromolecules of the type which are the subject of this discussion, the bonding as well as the anti-bonding MO's form bands comprising ranges of energy levels.

If one includes the spin-parameter, each band contains twice as many possible electron states as the number of MO's contained in the band.

Table 1. Structural, magnetic, and electrical data for compounds with pyrite, marcasite, Ir refer to the pseudo-marcasite cell, their monoclinic angles (90.35—91.11°) being $OsTe_{1.9}Sb_{0.1}$. The following abbreviations are used: D=diamagnetic, P=paramagnetic, antiferromagnetic, S=semiconductor, (degen.=degenerate,) M=metallic conductor, of marcasites. (Relevant ref-

d^j	Compounds	Pyrite type				
		Structural data			Magnetic data State; $2S$	Electrical data Type; ΔE(eV)
		a (Å)	$T-X$(Å)	$X-X$(Å)		
d^0	$Mo_{2/3}As_2$					
d^1	—					
d^2	$CrSb_2$					
d^3	—					
d^2/d^4	$Cr_{0.5}Fe_{0.5}As_2$ $Cr_{0.5}Fe_{0.5}Sb_2$					
d^4	FeP_2 $FeAs_2$ $FeSb_2$ RuP_2 $RuAs_2$ $RuSb_2$ OsP_2 $OsAs_2$ $OsSb_2$					
d^4/d^6	$Fe_{0.5}Ni_{0.5}As_2$ $Fe_{0.5}Ni_{0.5}Sb_2$					
d^5	$CoAs_2$ $CoSb_2$ RhP_2 $RhAs_2$ $RhSb_2$ $RhBi_2$ IrP_2 $IrAs_2$ $IrSb_2$ $IrBi_2$					
	MnS_2	6.1016	2.592	2.09	A,P; 5	S; ~ 1
	$MnSe_2$	6.417	2.709	2.33	A,P; 5	S; > 0.2
	$MnTe_2$	6.951	2.907	2.75	A,P; 5	S; 0.11

and arsenopyrite type structure. Unit cell dimensions for the dipnictides of Co, Rh, and omitted. The data for the marcasite modification of $OsTe_2$ refer to the ternary phase (t.i.=temperature independent, C-W=the Curie-Weiss Law,) F=ferromagnetic, A= and SC=superconductor at low temperatures. A, A/B, and B refer to the different classes erences are given in the text.)

Marcasite type									
Structural data							Magnetic data State; $2S$	Electrical data Type; ΔE(eV)	Class
a (Å)	b (Å)	c (Å)	$\overline{T-X}$(Å)	$X-X$(Å)	c/a	c/b			
5.299	5.983	2.885	2.379	2.489	0.544	0.482			A
6.0275	6.8738	3.2715	2.708	2.84	0.543	0.476	A,P;2	S; 0.32	A
5.37	6.13	2.93			0.55	0.48	P;∼1	S	A
5.9569	6.7250	3.2199			0.541	0.479			
4.9732	5.6570	2.7235	2.259	2.237	0.548	0.481		S; 0.4	
5.3013	5.9859	2.8822	2.40	2.41	0.544	0.482	P,∼t.i.	S;∼0.2	
5.8328	6.5376	3.1973	2.590	2.887	0.548	0.489	P, not C-W	S; 0.17	
5.1173	5.8932	2.8711	2.35	2.30	0.561	0.487	D; 0	S;∼1	
5.4302	6.1834	2.9714	2.48	2.36	0.547	0.481	D; 0	S;∼0.8	A
5.9524	6.6737	3.1803	2.643	2.86	0.534	0.477	D; 0	S;>0.3	
5.1001	5.9012	2.9182	2.34	2.35	0.572	0.495	D; 0	S;∼1.2	
5.4129	6.1910	3.0126	2.468	2.48	0.557	0.487	D; 0	S;∼0.9	
5.9409	6.6880	3.2112	2.650	2.85	0.541	0.480	D; 0	S;>0.3	
5.1424	5.9277	3.1017			0.603	0.523			A/B
5.643	6.441	3.382			0.599	0.525			
5.0447	5.8680	3.1260	2.360	2.462	0.620	0.533	D; 0	S;>0.2	
5.5833	6.3879	3.3774	2.56	2.82	0.605	0.529	D; 0	S; 0.2	
4.8260	5.7951	3.1999	2.37	2.24	0.663	0.552	D; 0	S; ∼ 1	
5.1417	6.0816	3.2943	2.45	2.49	0.641	0.542	D; 0	S; ∼ 1	
5.6652	6.5596	3.4840	2.63	2.84	0.615	0.531	D; 0	S	
5.9413	6.7945	3.5887	2.72	3.00	0.604	0.528	D; 0	M	
4.7943	5.7915	3.2599	2.37	2.25	0.680	0.563	D; 0	S; ∼ 1	A/B
5.0982	6.0717	3.3621	2.46	2.48	0.660	0.554	D; 0	S; ∼ 1	
5.6091	6.5492	3.5628	2.64	2.81	0.635	0.544	D; 0	S	
6.0	6.9	3.7			0.6_1	0.5_3			

d^j	Compounds	Pyrite type				
		Structural data			Magnetic data State; $2S$	Electrical data Type; ΔE(eV)
		a (Å)	$T-X$(Å)	$X-X$(Å)		
d^6	FeS_2	5.4179	2.262	2.177	D; 0	S; 0.9
	$FeSe_2$	5.7859			~ 0	S; 0.1
	$FeTe_2$	6.2937			~ 0	S-degen./M?
	RuS_2	5.6095	2.351	2.18	D; 0	S; ~ 1.8
	$RuSe_2$	5.9336	2.475	2.41	D; 0	S; ~ 1
	$RuTe_2$	6.3906	2.647	2.79	D; 0	S; 0.25
	OsS_2	5.6196	2.352	2.21	D; 0	S; ~ 2
	$OsSe_2$	5.9449	2.477	2.44	D; 0	S
	$OsTe_2$	6.3968	2.647	2.83	D; 0	S; > 0.2
	$Ir_{2/3}Se_2$	5.9293	2.472	2.42	D; 0	S; $\geqq 0.45$
	NiP_2	5.4788	2.290	2.12	P, t.i.	M
	$NiAs_2$	5.7634				M
	$NiSb_2$					
	$PdAs_2$	5.9855	2.497	2.43	D; 0	M
	$PdSb_2$	6.4584	2.670	2.89	D; 0	M
	PtP_2	5.6956	2.391	2.17	D; 0	S; > 0.6
	$PtAs_2$	5.9665	2.489	2.42	D; 0	S; 0.55
	$PtSb_2$	6.4400	2.670	2.79	D; 0	S; 0.07
	$PtBi_2$	6.7022	2.771	3.00		M, SC
d^7	CoS_2	5.528	2.319	2.13	F, P; 1	M
	$CoSe_2$	5.5893	2.438	2.45	P; ~ 1	M
	$CoTe_2$	6.3182			P, t.i.	M
	$AuSb_2$	6.6583	2.763	2.86	D; 0	M, SC
d^8	NiS_2	5.6873	2.401	2.06	P; ~ 2	S; 0.32
	$NiSe_2$	5.9629	2.488	2.42	P, not C-W	M
	$NiTe_2$	6.374				M
d^9	CuS_2	5.7898			P, t.i.	M, SC
	$CuSe_2$	6.1166			P, t.i.	M, SC
	$CuTe_2$	6.6052			D; 0	M, SC
d^{10}	ZnS_2	5.9542			D; 0	
	$ZnSe_2$	6.2930				S; 0.24
	CdS_2	6.3032			D; 0	S; 0.23
	$CdSe_2$	6.615				

Fig. 1 shows a hypothetical energy band diagram for compounds with pyrite, marcasite, and arsenopyrite type structures. The diagram must be viewed as a rather simplified illustration of the distribution of the most important bonding, non-bonding, and anti-bonding bands. Levels with lower energy than those of the valence electrons are omitted for the purpose of simplification, since electrons in these levels belong to closed shells which are relatively unperturbed by the chemical bonding.

Marcasite type									
Structural data							Magnetic data State: $2S$	Electrical data Type; ΔE(eV)	Class
a (Å)	b (Å)	c (Å)	$\overline{T-X}$(Å)	$X-X$(Å)	c/a	c/b			
4.4431	5.4245	3.3871	2.247	2.223	0.762	0.624	D; 0	S	
4.7987	5.7806	3.5827	2.3_8	2.5_1	0.747	0.620	D; 0	S; 0.6	
5.2655	6.2679	3.8738	2.567	2.926	0.736	0.618	P; ~ 0.6	S; 0.4_6	
6.404	5.281	4.046			0.766	0.632		S	B
4.7583	5.7954	3.5449	2.378	2.45	0.745	0.612	P, ~ t.i.	S; >0.05	
5.1837	6.3184	3.8408	2.560	2.86	0.741	0.608	D; 0	M	
4.84	5.72	3.60			0.74	0.63		M	
5.3294	6.3223	3.9080	2.597	2.914	0.733	0.618	P; 1(2)	M	B
5.103	6.292	3.812	2.61	2.29	0.747	0.606		M, SC	B

Concerning the details of Fig. 1, it must be emphasized that the diagram shows only in a general way the mutual sequence of the individual bands, and the different band-gaps and band-widths. The important question of possible overlapping of two or more bands is also neglected in the diagram. In particular, the positioning of the $X-X$ bands relative to the $T-X$ bands is almost arbitrarily chosen, since the location of these bands (which represent bonding and anti-bonding MO's for the $X-X$ pairs) in the diagram will depend on the relevant combination of elements.* Even the order of sequence of the $T-X$ bands is somewhat uncertain.

* In the general formula TX_2 of these compounds the symbols T and X are used to denote the (transition) metal and non-metal atoms, respectively.

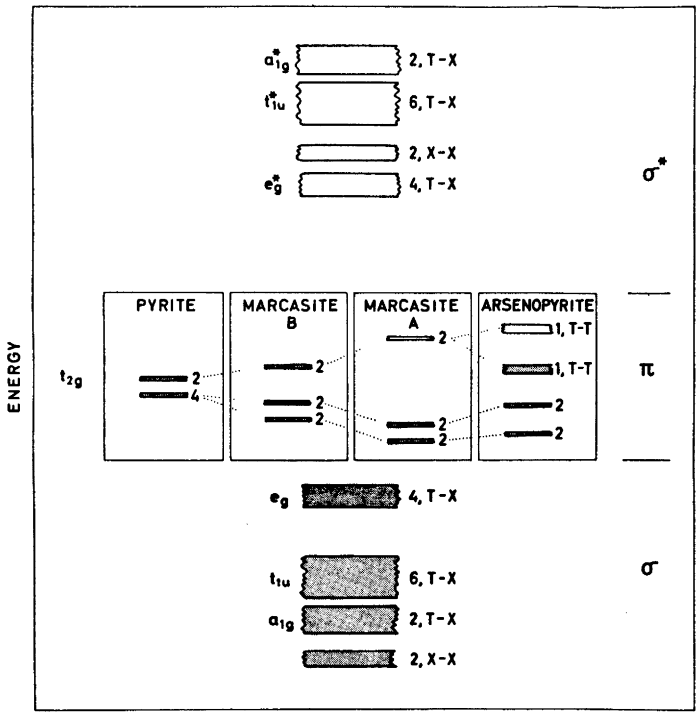

Fig. 1. A hypothetical energy band diagram for compounds with pyrite, marcasite, and arsenopyrite type structure. The numbers indicate the possible electron states per formula unit. The filling of the bonding (σ) $X-X$ and $T-X$ bands is shown shaded. Also shown, for example, is the filling of localized t_{2g} levels.

The $T-X$ bands are contemplated as involving ns, np, and $(n-1)d$ (or nd; *vide infra*) orbitals from the T atom. The s, p, and two of the d orbitals ($d_{x^2-y^2}$ and d_{z^2}) have σ-symmetry with respect to the bond directions in octahedral coordination, and their symmetry type is denoted a_{1g}, t_{1u}, and e_g, respectively. The three remaining d orbitals (d_{xy}, d_{yz}, and d_{zx}) have π symmetry with respect to the axes of the octahedron and belong to the symmetry class t_{2g}.

Six σ orbitals per octahedron of the symmetry types $a_{1g}(\times 1)$, $t_{1u}(\times 3)$, and $e_g(\times 2)$ are obtained by linear combination of orbitals from the X atoms. Hence, the T and X atoms form six bonding (σ) and six anti-bonding (σ^*) orbitals. These twelve orbitals (per formula unit) are represented as bands in Fig. 1 and denoted $T-X$ and the above symmetry types are furthermore indicated together with the number of electron states contained in each band per formula unit.

The establishment of bonding (by 14 electrons per formula unit in the one $X-X$ and six $T-X$ bands) will fix the coordinate system which describes the location of the d orbitals of the T atom. The e_g orbitals lie along the axes of the octahedron, whereas the t_{2g} orbitals point towards the mid points of the edges of the octahedron. It is assumed (*cf.* Bither *et al.*[1]) that π bonding between the t_{2g} orbitals on the T atoms and corresponding orbitals on the X atoms is of subordinate importance in the compounds in question, and the t_{2g} orbitals of the T atoms are accordingly considered as essentially localized atomic orbitals in the following discussion, except for the compounds with the arsenopyrite type structure (*vide infra*). However, a narrow band width is indicated in Fig. 1

for each of the approximately non-bonding t_{2g} orbitals in the respective sub-diagrams for pyrite and marcasite (classes A and B), the situation being somewhat more complicated in the case of arsenopyrite.

The location in space and mutual splitting of the t_{2g} orbitals play major parts in understanding the peculiarities of the marcasite family (*vide infra*). However, it must again be emphasized that the location of the t_{2g} orbitals on the energy level diagram (Fig. 1) is uncertain. The expected differences between the individual compounds and structure types do not, for example, justify an attempt to place the t_{2g} orbitals with a common centre of gravity with respect to the energy scale.

In what follows, the number of valence electrons used for bonding in the compounds in question will be accounted for (see Table 1) and hence the number of electrons which must be distributed on non-bonding and anti-bonding bands. In accordance with common chemical experience each X atom is ascribed a number of valence electrons (v_X) equal to the Group number of the element in the Periodic system, *i.e.*:

$v_X = 5$ for P, As, Sb, and Bi, and
$v_X = 6$ for S, Se, and Te.

The shortest $X-X$ distances in the compounds under consideration (Table 1) show good agreement with the corresponding expectation values for $X-X$ single bonds. One electron from each X atom is thus formally used for filling the bonding $X-X$ band, and thus two electrons are employed per formula unit.

The remaining $(v_X - 1)$ valence electrons from each X atom can accordingly contribute to the filling of the three bonding $T-X$ bands. According to Fig. 1 there are twelve electron states per formula unit in these bands, which, in accordance with the observed $T-X$ distances (Table 1) can also be regarded as six single bonds. In order to fill the bonding $T-X$ bands completely, each T atom must therefore contribute $v_T = 12 - 2(v_X - 1)$ electrons, *i.e.* $v_X = 5$ gives $v_T = 4$ and $v_X = 6$ leads to $v_T = 2$. In a ternary phase as for example FeAsS $\bar{v}_X = 5.5$ and $v_T = 3$. (A number of such ternary phases are known,[2] but they are not listed in Table 1.) If the configuration of valence electrons for the free T atom is described as $(n-1)d^i ns^2$, then the formation of bonding implies the configurations:

$(n-1)d^{i-2}$ when $v_X = 5$,
$(n-1)d^{i-1}$ when $\bar{v}_X = 5.5$, and
$(n-1)d^i$ when $v_X = 6$.

This is the electron configuration d^i listed in the first column of Table 1, except for the compounds $Mo_{2/3}As_2$ and $Ir_{2/3}Se_2$.

For $Mo_{2/3}As_2$ the configuration d^0 is obtained, since each Mo atom ($4d^5 5s^2$ for the free atom) must contribute six valence electrons in order to provide 4 electrons to the $T-X$ bands per 2/3 Mo atom. The configuration on Ir in $Ir_{2/3}Se_2$* is analogously d^6.

* The analogous compounds between Rh and Ir and S, Se, and Te are reported to have compositions which deviate from the general formula $T_{2/3}X_2$ (*cf.*, *e.g.*, Haraldsen [3]). Furthermore, since the compounds probably exhibit ranges of homogeneity of as yet unknown widths, their data are not included in Table 1.

Compounds with arsenopyrite type structure have also an additional bonding in the form of $T-T$ pairs. This formation of pairs can be said to influence the localized valence electrons on the T atoms only, in that their configurations are increased from the formal d^5 (as these compounds are denoted in Table 1) to an apparent d^6.

The effect of the formation of $T-T$ pairs is tentatively indicated in Fig. 1 as a splitting of one of the t_{2g} orbitals (here d_{xy}, *vide infra*) in one bonding and one anti-bonding band. The bonding $T-T$ band becomes completely filled with one electron per formula unit as indicated by the shading in Fig. 1. In this way the 14 electron states per formula unit in the σ bands become completely filled for all compounds and the X atoms obtain formally complete octets.

An equivalent formulation can be given mathematically in terms of the generalized (8−N) rule:[4-7]

$$n+P-Q=8a$$

where the use of the figure 8 is justified by the fact that the X atoms obtain formally complete octets, and (per formula unit) a is the number of X atoms, n the total number of bonding electrons, and P and Q, respectively, the number of electrons engaged in $X-X$ and $T-T$ bonds.

For compounds with pyrite and marcasite type structures, $a=2$, $n=v_T+2v_X=14$, $P=2$, and $Q=0$, implying that the rule is satisfied. Compounds with the arsenopyrite type structure fulfil the rule with $a=2$, $n=15$, $P=2$, and $Q=1$.

The generalized (8−N) rule is often used as a necessary, but insufficient criterion for the prediction of semiconduction. Consistent with the fact that the rule is satisfied, the majority of the compounds listed in Table 1 exhibit semiconduction. This application of the rule is connected with the complete filling of the bonding (σ) bands for a given compound. According to Fig. 1 the non-bonding (localized) electrons on the T atoms have higher energies than the electrons contained in the σ bands. The fact that some of the compounds show a metallic type of conductivity is therefore not inconsistent with the fulfilment of the rule, but emphasizes rather its limited applicability to compounds containing a transition element.

In the published descriptions of the bonding in compounds of the three structure types, individual authors have applied different models for the distribution of the valence electrons. An ionic model has for example been used by Haraldsen [8] (see also Refs. 9, 10) and recently (but more formally) by Hulliger and Mooser.[7,11]

According to the ionic model the compounds are ascribed the formulae $T^{4+}X_2^{4-}$ or $T^{2+}X_2^{2-}$, depending on whether the X atom belongs to Group VB or VIB. These formulae may be used for all of the three structure types in the cases of the binary compounds, since the additional $T-T$ bonds in the arsenopyrite type structure do not require any change of the formula $T^{4+}X_2^{4-}$. However, in the ternary compounds of the type FeAsS the ionic formula becomes $T^{3+}(XX')^{3-}$ where X and X' denote elements from Groups VB and VIB, respectively.

The connection between the ionic and MO−BT descriptions becomes apparent on noting that the 14 valence electrons which according to the former description are localized on the $X-X$ pair, correspond to those contained in the bonding $X-X$ and $T-X$ bands in Fig. 1. In the ionic description these bands ought to be denoted as anion (X_2^{4-} or X_2^{2-}) bands.

The remainder of the valence electrons are then imagined as being localized in d orbitals on the T atom. The number of such electrons is the same as that according to the MO—BT description and the ionic model is therefore completely equivalent also in this respect. (This appears to be the point of view of Hulliger and Mooser.[7,11])

However, the ionic model must be said to give an unrealistic description of the compounds under consideration. None of the compounds listed in Table 1 exhibit an ionic type of conductivity, the observed metallic and semiconducting properties indicate on the contrary that the effective charges on the atoms must be small. The observed interatomic distances in the crystal structures are also inconsistent with an ionic model. Probably the most important objection to the ionic description is associated with the fact that it has to apply the point charge model of the crystal field theory in order to account for the removal of the degeneracy of the d orbitals on the octahedrally coordinated T atom. On going from the point charge model to a more realistic ionic model it is found (*cf.*, *e.g.*, Cotton [12]) that neither quantitative nor qualitative agreement is obtained between the calculated and observed values for the energy splitting of the d levels.

With the notable exception of Schubert,[13,14] no author has hitherto suggested a metallic bonding model for the compounds under consideration. A suggestion which their properties obviously do not invite. Several authors have on the other hand applied an essentially covalent bonding model. Huggins [15] suggested, as early as 1922, a description based on directed valences and the shared electron pairs according to Lewis.[16] This model was naturally carried further in terms of the hybridization model [17] (see also Ref. 18). The latter model ascribes to the X and T atoms, respectively, tetrahedral sp^3 and octahedral d^2sp^3 hybrid orbitals. Localized bonds with one electron pair in each of the bonding orbitals are imagined to be formed by the overlap of the two kinds of hybrid orbitals, in such a way that the six d^2sp^3 orbitals overlap with one of the sp^3 orbitals from each of the six surrounding X atoms. Three of the four sp^3 orbitals from each X participate accordingly in $T-X$ bonding whereas the fourth sp^3 orbital forms a single bond by reason of the overlap with its neighbour in the $X-X$ pair. There are therefore one $X-X$ and six $T-X$ bonds per formula unit, which engage a total of 14 electrons.

In terms of the MO—BT description, this corresponds to the 14 electrons per formula unit contained in the σ bands (Fig. 1), and hence the hybridization model gives the same number of bonding valence electrons as the former one. Both descriptions accordingly imply that the same number of electrons must be imagined as non-bonding and localized on the T atom. However, the hybridization model implies that (regarding the $(n-1)d$ orbitals) only the three t_{2g} orbitals are available for these electrons, since the two e_g orbitals are used in the d^2sp^3 hybridization. For compounds with $j>6$ in d^j, this model therefore demands a discussion of whether the nd orbitals participate in the hybridization instead of the $(n-1)d$ orbitals, or whether the non-bonding electrons are completely or partially located in these outer orbitals. This does not arise as a formal electron distribution problem according to the MO—BT description (see Fig. 1), since here the σ^* orbitals are available.

The question of whether the nd orbitals participate, either in bonding or by absorbing non-bonding electrons, is however not only a formal problem associated with the hybridization model, but is on the contrary a real problem without regard to the particular model chosen.

Coulson [19] has recently discussed the participation of the d orbitals in bonding with regard to the extension in space of the inner $(n-1)$ and the outer (n) d orbitals. Among the many deciding factors, he points out that the extension in space of the d orbitals decreases with increasing number of unpaired electrons, with increasing positive charge, and with increasing number of electrons excited into the orbital in question. Hence, the nd orbitals, whose electron density will normally be too remote to participate in hybridization with the ns and np orbitals, may in certain cases be easily imagined to obtain an appropriate radial distribution. For MnS_2, $MnSe_2$, and $MnTe_2$, which take a high-spin configuration (*cf.* Table 1), it is, for example, not unreasonable to assume that the $4d$ orbitals on Mn participate in bonding. Thus, Mande and Nigavekar [20] conclude from soft X-ray spectroscopic studies that $MnSe_2$ has a $4s4p^34d^2$ hybridization, whereas they ascribe to $CoSe_2$ a $3d^24s4p^3$ hybridization.

This problem will not be subjected to further consideration in the present paper owing to the lack of suitable comparable data. As evident from Fig. 1, the possibility that bands from the outer (n) d orbitals may occur in the same energy range as the σ^*

bands has not been taken into account. For compounds with $j > 6$ it will accordingly only be assumed that the number of non-bonding electrons exceeding six will be accommodated in bands with higher energy than the t_{2g} bands without further specification.

For the structure types in question, the idealized hybridization model, as well as other idealized models will have to be modified in accordance with the observed irregularities of the coordination polyhedra (*cf.* the preceding paper [21]). However, these modifications need not be considered as introducing inconsistencies into either the hybridization model or the MO–BT description preferred here.

As a part of a more complex description Pearson [22] applies notations taken from the hybridization model, whereas Bither *et al.*[1] use a BT model in their discussion of the bonding in the pyrites. The description of Bither *et al.* differs only slightly from that used in this paper and may be considered formally as a mixture of the hybridization and MO–BT models.

Concluding this consideration of the distribution of the valence electrons, it is perhaps relevant to point out that all of the recent descriptions of bonding in the compounds in question (with the exception of Pearson's [22] proposal for $FeSb_2$) give complete octets for the X atoms. Hence the same number of essentially localized d electrons on the T atom is obtained and the d^j configurations ascribed to the compounds in Table 1 may therefore be regarded as commonly accepted. However, concerning the interpretation of the peculiarities of the marcasite family in relation to the non-bonding and/or antibonding valence electrons, the previous bonding descriptions differ, and the explanation proposed in this paper also differs from all of the earlier ones (see Ref. 21).

A NEW MODEL

The existence of the classes A and B of marcasites, and the fact that the axial proportions of compounds of class A can be explained in terms of the pair reorientation model [21] provoke the suggestion that expanding forces act along the c axes of compounds belonging to class B (and A/B). This hypothesis is substantiated by the fact that there exists at least one compound with marcasite type structure which does not belong to class A, and for which it is immediately apparent that there occur expanding forces which are most pronounced along [001].

The compound in question is the marcasite modification of NaO_2.[23] Its axial ratios ($c/a = 0.801$, $c/b = 0.621$) show that on a relative scale ($b = 1$) the c axis is $\sim$ 29 % larger and the a axis $\sim$ 12 % smaller than the respective observations for the class A marcasites. The axial proportions of this compound differ on the other hand much less from the average values in class B.

The structure must clearly be regarded as ionic (Na^+, O_2^-), and its axial proportions can qualitatively be explained by assuming electrostatic repulsion between equally charged ions in those directions in the structure where these charges are uncompensated by intermediate ions of opposite sign. Such compensation is found along [010] and along both diagonal directions in (010), whereas the charges in the directions [001] and [100] will only be partially compensated. Coulomb repulsions will accordingly occur in the latter directions between neighbouring Na^+ as well as between neighbouring O_2^-. As a consequence of the packing of the hyperoxide ion, the c axis must be shorter than the a axis, and the repulsive force must accordingly be considerably

larger along [001] than along [100]. Provided the bond distances $Na^+ - O_2^-$ are maintained, the cell will therefore expand along [001] and contract along [100] until equilibrium between the acting forces is obtained. The structural data for the pyrite modification of NaO_2 [23] are also consistent with this interpretation.

The properties of transition metal compounds with marcasite type structure cannot be accounted for on the basis of a purely ionic model. The spatial orientation of the t_{2g} orbitals provides, however, a simple explanation of the structural peculiarities of the marcasite classes A, A/B, and B. The axes of the coordinate system which describes the d orbitals of the T atom are fixed by the establishment of the $T-X$ bonds. The lobes of the three t_{2g} orbitals are directed towards the mid points of the edges of the octahedron. If (say) the z axis of the coordinate system is chosen along that axis of the octahedron which is parallel * to (001), then two of the lobes of the d_{xy} orbital will point towards the centres of those edges which are shared between neighbouring octahedra. The nearest neighbour T atoms along [001] will accordingly have lobes from the d_{xy} orbitals which point directly towards each other.

This location will therefore give d_{xy} higher energy than d_{yz} and d_{zx}, since the latter orbitals (the degeneracy of which is also removed as a consequence of the deviation from regularity of the octahedron) point towards edges which are not common to two octahedra. Assuming furthermore that the energy difference between d_{xy} and the two other t_{2g} orbitals exceeds the spin-pairing energy, then the d^2 configuration ought to be of high-spin whereas the d^4 configuration should give rise to low-spin.

Up to the configuration d^4 the d_{xy} orbital will accordingly be energetically unfavourable for the localized d electrons. As long as this orbital is unoccupied its higher energy will not impose any stresses upon the structure beyond those which originate from other sources, *e.g.* effects responsible for the general irregularity of the coordination polyhedra.

Any configuration from d^0 up to and including d^4 is accordingly not expected to introduce differences in the axial proportions of the unit cell, since these are determined essentially by the packing of the $X-X$ pairs. However, if the configuration is increased beyond d^4, the d_{xy} orbital must be utilized, in which case a lower energy is to be obtained by expanding the cell along [001] in order to increase the distance between neighbouring T atoms.

At the configuration d^6 the $(n-1)d_{xy}$ orbital is filled with two electrons, and the unit cell is expected to be expanded to a maximum in the c direction. Configurations beyond d^6 (the marcasite type structure is reported up to d^9; *cf.* Table 1) cannot be expected to introduce a further relative expansion, since the excess electrons must occupy other orbitals than nd_{xy}. The latter is the nearest higher orbital which is expected to produce further expansion. These considerations do not imply a decision concerning the actual bands which are to be used when the t_{2g} orbitals are filled (*cf.* Fig. 1).

A calculation of the magnitude of the relative expansion consequent on the two electrons occupying the $(n-1)d_{xy}$ orbital is expected to be difficult.

* This is only approximately correct for the structures of $FeSb_2$, FeS_2, and $FeTe_2$ where the T atoms are found to be displaced from the centre of the octahedron.[24,25]

However, it is possible to make semi-quantitative considerations of the nature of the expansion for configurations between d^4 and d^6 on the basis of the observed axial proportions for class A (d^0-d^4) and class B (d^6-d^9). To explain the expansion as:

(i) Coulomb repulsion between the charges in the d_{xy} orbitals on neighbouring T atoms, or
(ii) to assume that occupied orbitals require space

appear to be equivalent points of view.

According to the Coulomb repulsion view, the relative expansion for class A/B (d^4-d^6) is expected to be proportional to the square of the average number of electrons (t) occupied in the d_{xy} orbital, *i.e.*:

$$(c/a)_t-(c/a)_A=k_1t^2 \quad (1)$$

$$(c/b)_t-(c/b)_A=k_2t^2 \quad (2)$$

where $(c/a)_t$ and $(c/b)_t$ are the axial proportions of a given phase of class A/B; and $(c/a)_A$ and $(c/b)_A$ are the averages of the observed axial ratios in class A. The proportionality constants k_1 and k_2 are determined by the observations for class B, *i.e.* substituting $t=2$, $(c/a)_2=(c/a)_B$, and $(c/b)_2=(c/b)_B$ into eqns. 1 and 2.

The above equations are also obtained on considering the expansion as a consequence of the fact that an occupied orbital requires space. In the interval d^4-d^6 a compound with a formal average of t electrons in the d_{xy} orbital will be realized in a ternary phase of composition $T_{1-u}T'_uX_2$ ($0\leqq u\leqq 1$), where T and T' are ascribed the configurations d^4 and d^6 (*e.g.* $Fe_{1-u}Ni_uAs_2$ where $0\leqq u\leqq\sim 0.69$) and hence $t=2u$.

Provided T and T' are statistically distributed, their distribution within the linear chains along [001] can be treated as an one-dimensional problem. It is here assumed that when a T atom has a T' atom as neighbour in such a chain no expansion will be caused, since the filled d_{xy} orbital of the T' atom receives that space which is available due to the fact that the corresponding orbital on the neighbouring atom is empty. The relative expansion is accordingly expected to be proportional to the probability of obtaining two or more T' atoms as neighbours in the chain. The probability of finding one T' atom at a given place in the chain equals the mole-fraction u. The relative expansion will therefore be proportional to the square of the mole-fraction, and according to the relation $t=2u$ proportional also to t^2, thus implying eqns. 1 and 2.

The statistical point of view may at first sight appear to be inconsistent with the considerations based on Coulomb repulsion. The equivalence of the two views can be clarified by remarking that the Coulomb repulsive force is proportional to the product of the charges as well as being inversely proportional to the square of the distance between them. Assuming an "average" T atom with $t=2u$ electrons in the d_{xy} orbital and a repetition distance of c in the chains the force is $k\times t^2/c^2$. Alternatively a statistical distribution of T and T' atoms is considered within the chain with, respectively, 0 and 2 electrons in the d_{xy} orbital. The average $T'-T'$ distance within the chain is

in this case c/u and the Coulomb repulsive force is $k \times 2^2/(c/u)^2$. The two expressions are identical since $t = 2u$.

The above mechanism, which is based on the assumption that the marcasite cell expands along [001] when the d_{xy} orbital becomes occupied, implies *inter alia:*

(1) constant axial ratios from d^0 to d^4 and from d^6 to d^{10},
(2) the expansion from d^4 to d^6 follows eqns. 1 and 2,
(3) (d^1), d^3, d^4, d^5, d^6, and d^7 will show low-spin, whereas d^2 will show high-spin, and
(4) certain relations between d^j and the probability of formation of pyrite type structure. (Without additional assumptions the relation vis-à-vis the arsenopyrite type structure is undecided.)

This mechanism will be denoted as the *expansion model*, and its consequences will be compared with the experimental facts. Despite the simple basis of the expansion model, it is seen from Fig. 2 that a remarkably good agreement is obtained between the observations and the predictions of points 1 and 2 above. However, as is apparent from point 1, the expansion model does not define the numerical values of the axial ratios for marcasites in the intervals $d^0 - d^4$ and $d^6 - d^{10}$.

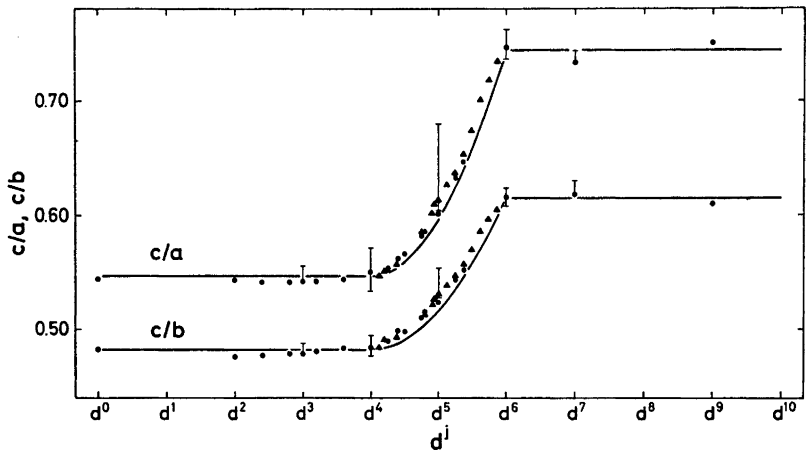

Fig. 2. Axial ratios for compounds with the marcasite type structure as a function of d^j for the T atoms. Filled circles represent c/a and c/b for compounds with configurations $d^0 - d^4$ and $d^6 - d^9$ and ternary phases with configurations corresponding to mixtures of the type d^2/d^4 and d^4/d^6. Filled triangles give the analogous data for mixtures of the type d^4/d^5 and d^5/d^6 together with axial ratios for the pseudo-marcasite cell of binary compounds with arsenopyrite type structure (formal d^5 configuration). When average data are indicated, the total scatter is represented by the length of the vertical bars when the scatter exceeds the size of the symbol. The data which are not evident from Table 1, are taken from Roseboom [26] and Bjerkelund and Kjekshus.[27] The linear sections between d^0 and d^4 and between d^6 and d^9 (d^{10}) correspond to the average axial ratios in the respective intervals. The normalized square law curves between d^4 and d^6 represent eqns. 1 and 2.

From the difference in the packing of the $X-X$ pairs in the pyrite and marcasite type structures the pair reorientation model[21] gives the axial proportions $c/a \approx 0.56$ and $c/b \approx 0.49$ when no other (*i.e.* expanding) forces are acting. The latter supposition is in accordance with the assumptions of the expansion model concerning the interval d^0-d^4, and this limits accordingly the applicability of the pair reorientation model to d^0-d^4 configurations. The mutual consistency of the two models is evident from Fig. 2.

Attempts to explain the deviations from the normalized square law curves shown in Fig. 2 must clearly be somewhat speculative, but it is nevertheless tempting to indicate some factors which may cause the deviations. In the first place the axial proportions for the actual compounds will, to some extent, depend on the mutual size ratio between T and X and hence implicitly upon atomic number, difference in electronegativity, number of unpaired localized electrons, *etc.* From Table 1, systematic variations in the axial proportions are, for example, apparent for the dipnictides of Ru and Os. These tendencies are to some extent counteracted by the averaging of the observations. Furthermore, the assumption of a statistical distribution will probably not be completely satisfied for all compositions throughout the homogeneity range of a ternary phase.

Beyond these and similar circumstances associated with the actual compound, it must be remarked that each of the sketched square law curves applies in the strictest sense only to the mixed configurations d^4/d^6, whereas the corresponding observations for d^4/d^5 and d^5/d^6 (filled triangles in Fig. 2) are expected to match *two* square law curves, one valid from d^4 to d^5, and another from d^5 to d^6; both having the same shape as those shown in the diagram. This is to be expected (and Fig. 2 also gives some indications to this effect), since completely analogous deductions to those which led to eqns. 1 and 2 can be presented for d^4/d^5 and d^5/d^6.

The fact that the d^5 configuration (as opposed to d^4/d^6) gives rise to the monoclinic arsenopyrite type structure represents a problem in this connection, since comparable axial proportions must be taken from the pseudo-marcasite cell which is only approximately orthorhombic. Both the systematic variation of the deviation from a right angle of the pseudo-marcasite cell for the compounds in question,[28] and the fact that the $T-T$ chains (alternating bonding and non-bonding $T-T$ distances) of the structure do not lie on straight lines parallel to the c axis of the pseudo-cell, give rise to a relatively large scatter in the axial proportions. In Fig. 2, where the total scatter of the observations is indicated by the length of the vertical bars, the points shown for d^5 represent averages for $CoAs_2$ and $CoSb_2$ only. This is motivated by the fact that the data shown in the diagram for the ternary phases of the interval d^4-d^6 correspond to solid solutions of diarsenides and diantimonides of Fe, Co, and Ni; and furthermore, that there is demonstrated to be a marked and systematic trend both in the monoclinic angle and the axial ratios for the pseudo-marcasite cell of homologous series (with respect to X as well as T) of the arsenopyrites.

Formal d^j configurations d^4/d^6 may also be obtained by the subtraction of T atoms from a TX_2 compound with $j \geqq 6$. The homogeneity ranges which are found [25] for $FeTe_2$ and $CoTe_2$ represent the only known examples of defect

marcasite structures with a variable composition. The expansion model provides a reasonable explanation of the striking difference in the variation of the unit cell dimensions with composition for these phases.

For $CoTe_x$ a maximum value of $x=2.3$ is obtained (at 450°C) which corresponds to a d^j configuration with $j=9-x=6.7$. In this case, therefore, j always remains >6, the d_{xy} orbital is maintained full, and in accordance with the expansion model, the axial proportions should consequently be constant within the homogeneity range. This is in complete agreement with the observations [25] which show approximately constant axial ratios:

$CoTe_{2.0}$: $c/a=0.733$, $c/b=0.618$;
$CoTe_{2.3}$: $c/a=0.729$, $c/b=0.613$.

The fact that the unit cell dimensions and hence the unit cell volume decrease with increasing x may be trivially attributed to an increasing concentration of vacancies.

It is appropriate to emphasize that the expansion model implies constant axial *ratios* for $j \leqq 4$ and $j \geqq 6$, but it does not convey any information about the absolute dimensions of the axes.

For $FeTe_x$, which at the stoichiometric composition has a d^6 configuration, $j=8-x$ must on the other hand assume values <6 when $x>2$. The c axis for this phase decreases, while the a and b axes increase, with increasing x,[25] which is in qualitative agreement with the expansion model. On extrapolation to a hypothetical phase limit $FeTe_4$, a d^4 configuration is obtained. Linear extrapolation leads to $c/a=0.56$ and $c/b=0.51$ for $x=4$, which are in remarkably good agreement with the axial ratios in class A. Due to the fact that the homogeneity range extends only to $FeTe_{2.067}$ (at 450°C) it must be emphasized that a large degree of uncertainty is associated with the extrapolation. The speculative character of the extrapolation is furthermore stressed by noting the fact that the expansion model implies a square law relationship between axial ratios and composition.

Table 1 shows that the expansion model (with c/a and c/b defined from the pair reorientation model for class A) is in complete accordance with the majority of important data for the compounds in question, whereas some scattered observations may be characterized as not being inconsistent with the model. The model furthermore fulfils the requirement that it allows a prediction of properties which may be tested by experiment, and thus enable one to confirm, modify or reject the model.

The first fact to be considered is that the pyrite type structure does not occur for compounds with configurations from d^0 to d^4, whereas it is found for all d^j configurations from d^5 (high-spin) to d^{10}. With the latter configurations, the compounds will inevitably have electrons in that t_{2g} orbital which has the highest energy. Fig. 1 illustrates clearly that at least for *these electrons* the pyrite type structure will be energetically more favourable than the marcasite type. For compounds with configurations d^0-d^4 the expansion model implies, on the other hand, that this (d_{xy}) orbital is unoccupied and these compounds will accordingly not obtain an energy gain of this kind subject to transformation from the marcasite to the pyrite type structure.

The expansion model implies not only that an occupied d_{xy} orbital will give rise to an increased $T-T$ distance along [001] in the marcasite type structure (classes A/B and B), but it infers also that electrons in this orbital will promote the formation of the pyrite type structure, such that the $T-T$ distance can be further increased. In the pyrite type structure all t_{2g} orbitals, moreover, avoid pointing along the lines connecting neighbouring T atoms.

In order to disclose further factors which are of importance for the relationship between the d^j configuration and the structure type, the relative volume difference as well as the comparable linear dimensions should be analysed. It is appropriate to start out with the average axial proportions for the classes A and B expressed as $a{:}b{:}c$. Putting $b=1$ one obtains for

class A: $a{:}b{:}c \approx 0.880{:}1{:}0.483$ and
class B: $a{:}b{:}c \approx 0.831{:}1{:}0.619$.

With these relative units ($b=1$) there follows for

class A: $\sqrt{a^2+c^2}=1.004$ and
class B: $\sqrt{a^2+c^2}=1.036$.

Hence, the edges of the diagonal plane ($\bar{1}01$) in the marcasite type structure do not differ mutually on the average by more than 0.4 % for class A, whereas the average difference is 3.6 % in class B. For class A the diagonal plane is accordingly more nearly square (as the corresponding plane is in the pyrite type structure [21]) than for class B, and it is therefore not an inherent tendency against forming a square plane which prevents the compounds of class A from crystallizing with the pyrite type structure, as do those of class B.

In terms of the above relative units, the volume of two marcasite unit cells ($4\,TX_2$ units per cell, as in the pyrite type structure) becomes for

class A: $2 \cdot a \cdot b \cdot c = 0.850$ and
class B: $2 \cdot a \cdot b \cdot c = 1.029$.

Provided the b axis remains unchanged during the transformation from marcasite to pyrite type structure, the relation $b = a_P = 1$ gives a pyrite cell with relative volume $a_P{}^3 = 1$.

From this it follows accordingly that the class B marcasites must undergo a relative compression of 2.8 % on the transformation to the pyrite type structure, whereas the class A marcasites would have to increase their volume on the average by 17.6 % in a corresponding transition. The latter figure must be regarded as purely hypothetical, since the pyrite type structure is unknown among compounds with configurations d^0-d^4. For those marcasites of class B where the pyrite modifications are known, the observed cell volume shows that the average compression * amounts to 2.9 %. The good agreement between the observed and predicted compressions for class B indicates that the above considerations for class A may also be qualitatively correct.

In most cases where a transformation from marcasite to pyrite type structure is observed, the compression has been generated by high pressures. On the contrary it is an experimental fact [29] that attempts to produce pyrite modifications of FeP_2 and $FeAs_2$ (the marcasite modifications of which belong to class A) by high pressure syntheses have been unsuccessful. This is in complete accordance with the fact that increased pressure produces volume compression, whereas the model requires the volume to increase.

* The observed compressions vary between 1.7 and 6.5 % when the data for $CoSe_2$ (where values for the marcasite modification are uncertain) are disregarded.

The conclusion is accordingly that the most conspicuous feature of the observations listed in Table 1, the lack of the pyrite type structure for compounds with configurations d^0-d^4, is in complete accordance with the expansion model. The model indicates moreover that it will be impossible or at least very difficult to synthesize pyrite modifications of these compounds.

For configurations between d^6 and d^{10} the expansion model indicates that the pyrite type structure should be more favourable than the marcasite type structure. Nevertheless Table 1 shows that marcasite modifications do exist from d^6 to d^9 (d^{10}) and it is therefore natural to appraise their occurrence in relation to the expansion model.

According to the model, the expanding forces in the marcasite lattice are associated with the number of electrons in the d_{xy} orbital and its extension in space (*vide supra*). For d^6-d^{10} it is expected that:

(i) Compounds with small X atoms (*i.e.* notably S and P) will give rise to relatively short $T-T$ distances along [001] and hence increased forces of expansion. With a given T atom the possibility of realizing the marcasite type structure should accordingly increase with the size of X. As is evident from Table 1 this tendency seems to apply for the compounds of Fe, Ni, Co, and Cu.

(ii) In compounds with a given X atom it must be assumed that the expanding force increases with increasing principal quantum number of the T atom. Consequently, the marcasite modification ought to be easier to realize for T atoms from the first period of transition metals than from the second and third periods. Table 1 shows that this is in accordance with the observations.

(iii) In particular, for T atoms with d^6 configuration the marcasite modification may be stabilized by partial substitution of the X atom with another having a lower Group number. In this way a sufficient reduction in the electron density of the d_{xy} orbital may be obtained to make the marcasite type structure stable. A compound with approximate composition $OsTe_2$ and marcasite type structure is obtained on substitution of 5 atomic % Te by Sb.[30] In a similar way Bhan *et al.*[31] have prepared a ternary phase $PtSn_xSb_{2-x}$ with marcasite type structure. However, in this phase the required substitution of Sn for Sb appears to be considerably larger than in the first example.

While the above considerations in connection with Table 1 have mainly concerned the existence of the different modifications and their structural data, it is relevant to discuss the accord between the model and the available electrical and magnetic data.

For configurations d^0-d^4 the magnetic data show that $CrSb_2$ [32] takes a high-spin configuration. High-spin d^2 and low-spin d^4 probably also occur for, respectively, Cr and Fe in the ternary phase $Cr_{0.5}Fe_{0.5}As_2$.[33] Low-spin configurations are reported for dipnictides of Ru and Os. All these data are in complete accordance with the proposed model.

$CrSb_2$ is particularly suitable for an important test of the model, since the two unpaired electrons on Cr are predicted to occupy the orbitals here denoted by d_{yz} and d_{zx}. A neutron diffraction study of a single crystal of $CrSb_2$ in the antiferromagnetic state may verify that the d_{xy} orbital alone remains unoccupied.

The magnetic data for $FeAs_2$ and $FeSb_2$[34] are not immediately consistent with the model, since their d^4 configurations should give rise to diamagnetism. However, it is not found that localized unpaired electrons occur in these compounds, and in the case of $FeSb_2$ no magnetic ordering was observed at 4°K.[32] It is conceivable that the paramagnetism observed in $FeAs_2$ and $FeSb_2$ results from a thermal distribution of electrons

between states which differ in their magnetic description. However, the form of the susceptibility curves does not support this possibility, and it seems more likely that the kind of temperature dependence observed reflects the presence of discrete and/or dissolved impurities in the measured samples.

The marcasites of class A show semiconducting properties which are in complete accordance with the expansion model and the electron distribution indicated in Fig. 1.

The electrical and magnetic data for the majority of compounds with d^6 configuration are also consistent with the model. Among the exceptions for the d^6 pyrites, three metallic conductors are found, *i.e.* $PdAs_2$, $PdSb_2$, and $PtBi_2$. The systematic trend in the value of the band gap for the platinum dipnictides [35,36] suggests very strongly that an overlap of the valence and conduction bands occurs in $PtBi_2$. The samples of $PdAs_2$ and $PdSb_2$ which have been investigated may possibly have been degenerate semiconductors as a consequence of impurities. However the fact that the semiconductors $PtAs_2$ and $PtSb_2$ do not form solid solutions with the corresponding Pd compounds indicates that there may be an important difference between the band structures of the two groups of compounds.[37] It should be observed that the electrical data are of a more indeterminant type than allows a proper appraisal of the model in this respect.

The situation with respect to the magnetic data for the marcasite modifications of $FeTe_2$ (which show considerable mutual inconsistency [38–41]) and $NiAs_2$ [34] is similar to that discussed for $FeAs_2$ and $FeSb_2$.

The diamagnetism and metallic type of conduction reported for $NiSb_2$ [34,42] suggest that overlap of the valence and conduction bands occurs also in this compound.

The magnetic data for the pyrite modifications of CoS_2 and $CoSe_2$ show that there is one localized unpaired electron per Co atom (see, *e.g.*, Ref. 43) in accordance with a low-spin d^7 configuration. The metallic type of conductivity which is found for these compounds may in principle be given a simple explanation in analogy with that presented for $PtBi_2$ above. However, the results reported by Bither *et al.*[1] may suggest that the band structures of these compounds are rather complicated.

A d^7 configuration with one unpaired electron may also be expected on the basis of a formal distribution of the valence electrons in $AuSb_2$. Hence, the fact that the compound is diamagnetic [44] requires some explanation. The unusually high conductivity [45] clearly shows that this compound must be ascribed a delocalized electron configuration in an incompletely filled conduction band. Further evidence for this assertion lies in the fact that the magnetic susceptibility shows de Haas-van Alphen oscillations at low temperatures,[46] implying that the delocalized electrons have a Fermi surface.

A similar interpretation may tentatively be suggested for the pyrite modification of $CoTe_2$ which exhibits metallic conductivity and weak temperature dependent paramagnetism. According to the model, the marcasite modification of $CoTe_2$ is expected to have one unpaired electron. Indeed Haraldsen *et al.*[47] drew this conclusion from their susceptibility data, attributing the observed moment $\mu_P = 2.81$ B.M. (which corresponds to *two* unpaired electrons per Co atom) to an unquenched orbital contribution by the electron. According to Martin [48] a certain band width (for an unpaired, partially delocalized electron) may give rise to a substantial apparent increase in μ_P. The available data cannot therefore be characterized as being clearly inconsistent with the model which predicts a single unpaired electron per Co atom.

The magnetic and electrical data for the pyrite modification of NiS_2 [1,43] are in complete agreement with the consequences of the model. The corresponding data for the pyrite modifications of $NiSe_2$ [1,43] and $NiTe_2$ [1] suggest an analogous interpretation to that for the pyrite modification of $CoTe_2$.

Delocalized electron configurations are almost certainly also found for the d^9 pyrites. A detailed discussion of the d^8 and d^9 pyrites requires, however, data over and above those available at present.

The unit cell dimensions of the marcasite modification of $CuSe_2$ show that this compound definitely belongs to class B, but it is worth noting that the reported [49] Se—Se pair distance is notably shorter than that expected for a single bond. A careful reexamination of this compound is therefore of considerable interest.

The diamagnetism and semiconducting properties found [1] for the d^{10} pyrites are consistent with the consequences of the model.

The d^5 configuration, which may either adopt a high- or low-spin, demands special attention. The high-spin situation is observed for the dichalcogenides of Mn which show

antiferromagnetism and semiconducting properties. In accordance with the expansion model, these compounds take the pyrite type structure.

A formal d^5 configuration is also found for the dipnictides of Co, Rh, and Ir where the structural arrangement proves to be deformed from the marcasite to the arsenopyrite type. Hence, in these cases the bonding becomes more complex due to the formation of the $T-T$ pairs and the formal d^5 configuration is in fact to be interpreted as an apparent d^6 configuration for the unit T_2X_4. Consistent with this interpretation, the compounds are found to be diamagnetic semiconductors. The only exception is $RhBi_2$ which exhibits metallic type of conduction, probably as a result of an overlap of the valence and conduction bands.

The arsenopyrite type structure also occurs among a number of ternary compounds TXX' where T may be Fe, Ru, or Os, and X and X' are elements from Groups VB and VIB, respectively. (Not all combinations of these elements can be synthesized, owing to incompatibilities introduced by the relative sizes of the components.)

With a d^5 configuration and only one kind of T atom there is accordingly no example of a compound with the marcasite type structure. With the exception of the manganese dichalcogenides these compounds show on the contrary arsenopyrite type structure.

Retaining the requirements of both the marcasite type structure and a compensated spin for the unpaired electron of the formal d^5 low-spin configuration, the repetition of equal $T-T$ distances along [001] would demand a delocalization of the electrons responsible for the bonding within these $T-T$ chains. The fact that none of the compounds in this category crystallize with the marcasite type structure indicates a fundamental reluctance to form the latter type of bonding. This reluctance is apparently not associated with any particular combination of elements.

Among the transition metal compounds there are no definite examples known of this kind of delocalized bond configuration of T atoms in isolated linear chains. Extended linear arrangements of like atoms are also unknown among the simpler molecules. It may perhaps be shown that this kind of bond configuration is generally less favourable than zig-zag chains or such limited units as like-atomic pairs.

The above discussion, which is founded upon structural, magnetic, and electrical data, has shown that there is a promising degree of accordance between the proposed model and the experimental observations. It should, however, be noted that some parameters require reinvestigation and some additional data are desirable.

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