

X-Ray Photoelectron Spectra of 3d Transition Metal Pyrites

H. VAN DER HEIDE, R. HEMMEL, C. F. VAN BRUGGEN,
AND C. HAAS

*Laboratory of Inorganic Chemistry, Materials Science Center of the University,
Nijenborgh 16, 9747 AG Groningen, The Netherlands*

Received April 4, 1979

Photoelectron spectra of the synthetic compounds FeS_2 , CoS_2 , NiS_2 , MnSe_2 , CoSe_2 , and NiSe_2 and of a natural crystal of MnS_2 , all with the pyrite structure, are reported. The sulfur 3s and selenium 4s contributions are split into peaks for bonding and antibonding orbitals due to the covalent bonding in the molecular anion pairs. The difference in lineshape of the peaks for the bonding and antibonding orbitals is attributed to vibronic effects. The metal $2p_{3/2}$ spectra show the effects of multiplet splitting and satellites due to shake-up or shake-off processes. The valence band spectra consist of slightly overlapping contributions of anion p and metal $3d$ electrons. The metal $3d$ spectrum of FeS_2 has a single strong peak of width 0.9 eV. The $3d$ spectra of the other compounds show structure due to several final state configurations.

Introduction

Many of the dichalcogenides of the 3d transition metals MX_2 ($X = \text{S, Se, Te}$) crystallize in the pyrite structure. This structure is cubic, space group T_h^6 (Pa_3), and can be considered as a NaCl-like grouping of metal atoms and chalcogen atom pairs X_2 . The distance in an X_2 pair is short, due to the presence of a covalent bond. Several of the MX_2 compounds with the pyrite structure can be prepared only under high pressure (1).

The magnetic and electrical properties of the 3d transition metal dichalcogenides with the pyrite structure have been studied in considerable detail, and show a large variety in behavior (2-9). Attempts have been made to describe and explain the observed behavior of the pyrites in terms of qualitative energy level schemes or band structure calculations (1, 10-14).

In this paper we report a systematic study of the X-ray photoelectron spectra of the 3d

transition metal dichalcogenides MnS_2 , FeS_2 , CoS_2 , NiS_2 , MnSe_2 , CoSe_2 , and NiSe_2 with the pyrite structure. The valence band spectra of FeS_2 (15-17), NiS_2 (16-18), CoS_2 (17), and ZnS_2 (18) have been reported in the literature. We observed the spectra of the core levels, of the bonding and antibonding orbitals of the anion pairs, and of the valence band region consisting of sulfur 3p (or selenium 4p) and metal 3d orbitals. The structure in the spectra of the 3d electrons is discussed in terms of a ligand-field description of localized $3d^{n-1}$ final states.

Experimental Procedures

As starting materials the pure elements (Koch-Light) were used; the Mn flakes were etched to remove oxide layers. Polycrystalline samples were prepared by heating stoichiometric amounts of the elements in evacuated quartz ampoules for about 2 weeks. The preparation temperatures for the

sulfides and selenides were 400 and 700°C, respectively. In order to obtain a homogeneous product, the samples were crushed and heated again at 700°C for 2 weeks. In this way we were able to obtain pure, homogeneous samples of FeS₂, CoS₂, NiS₂, MnSe₂, NiSe₂, and CoSe₂. Single crystals of FeS₂, CoS₂, and NiS₂ were grown by chemical transport in evacuated quartz ampoules, using Cl₂ as a transport agent (19). The chlorine pressure in the tube was 0.2–0.3 atm, the temperature gradient about 660–715°C. Single crystals of 2–4 mm were formed at the cold site of the tube.

We have not been able to prepare a good sample of MnS₂; the reported spectra are obtained from a natural single crystal.

The purity and crystal structure of the samples were checked by chemical analysis and X-ray powder diffraction.

Photoelectron spectra were collected on an AEI-ES 200 spectrometer, using MgK α (energy 1253.6 eV, linewidth $\approx$ 0.8 eV) and AlK α (energy 1486.3 eV, linewidth $\approx$ 1.0 eV) radiation. In some cases (Fig. 8 only) monochromatized AlK α radiation (linewidth $\approx$ 0.35 eV) was used.

The materials to be investigated were handled in a glove box attached to the spectrometer. Indium foil was mounted on the sample holder and cleaned by argon ion etching until all signs of oxidation had vanished. The samples, which were in sealed tubes, were then brought into the glove box. To remove the remaining oxygen and water in the glove box a copper coil was cooled with liquid nitrogen until all signs of condensation had disappeared. The sample tube was then opened and the sample was powdered to obtain a fresh clean surface. The powder was pressed into the indium foil and inserted into the spectrometer. The result of these precautions was that the oxygen 1s peaks had a very low intensity. The samples were maintained at a temperature of 10°C during the measurement. The vacuum in the sample chamber was typically 10⁻⁹ Torr. The bind-

ing energies are measured relative to the Fermi energy. Some spectra were taken of powdered samples fixed on adhesive tape, in order to avoid interference with In peaks.

The data were corrected for the analyzer transmission, scattered electrons, and K α _{3,4} satellites using a computer program (20).

Core Levels of Anion Pairs

In the pyrites one can clearly distinguish pairs of anions at short distances from one another. Between the anions in such a pair there is a single strong covalent bond. A molecular orbital diagram of an anion pair is given in Fig. 1. The inner core levels 1s, 2s, 2p contribute little to the bonding, due to the small radial extension of these orbitals. The overlap of 3s orbitals of the two sulfur atoms leads to a bonding 3s(σ_g) and an antibonding 3s(σ_u^*) molecular orbital, both occupied by two electrons. The 3p_z orbitals (the line connecting the two sulfur atoms is taken as the z-axis) lead to an occupied bonding 3p_z(σ_g) and an empty 3p_z(σ_u^*) orbital. The 3p_{x,y} orbitals lead to occupied bonding and antibonding Π molecular orbitals. Hybridization causes a mixing of s and p molecular orbitals of the same symmetry. A molecular orbital scheme of this type has been used for a discussion of the electronic energy levels of ZrS₃ (21).

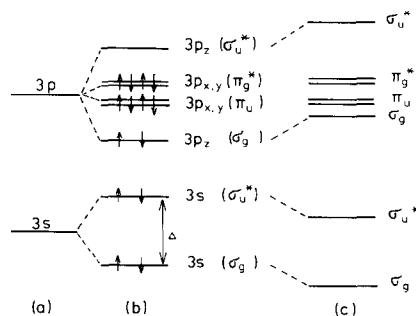


FIG. 1. Molecular orbital diagram of (S₂)²⁻ ion. (a) Atomic energy levels; (b) bonding and antibonding molecular orbitals without s-p hybridization; (c) with s-p hybridization.

Experimental results for the core levels of the anion pairs are given in Figs. 2 and 3 and Table I. The spectra of the sulfur $3s$ and selenium $4s$ electrons show the expected splitting Δ between bonding and antibonding molecular orbitals. The magnitude of Δ correlates quite well with the internuclear distance R in the anion pair: for small R the overlap of the $3s$ orbitals of the two sulfur atoms is large, leading to a large value of Δ . The strong dependence of Δ on R causes coupling of $3s$ electrons with vibrations which modulate R .

The observed spectra show a different shape of the $3s(\sigma_g)$ and $3s(\sigma_u^*)$ peaks: the $3s(\sigma_g)$ peak is much broader and has a lower peak height.¹ We attribute this effect to the strong vibronic coupling of the $3s$ hole in the final state with the interatomic vibrations of the anion pair.

The $3s(\sigma_g)$ peak corresponds to a final state with one hole in the bonding molecular orbital. The bonding in this final state will be weaker and the equilibrium internuclear distance will be larger than in the ground state. The $3s(\sigma_u^*)$ final state has a hole in the antibonding molecular orbital. However, the splitting of the bonding and antibonding levels is not symmetric and the antibonding level is probably close to nonbonding due to s - p hybridization (Fig. 1). As a consequence

¹ This effect has been observed also in ZrS_3 and ZrSe_3 , and was ascribed to covalent interactions (21). The sulfur $3s(\sigma_g)$ orbitals have nonzero overlap with the metal $4d$, $5s$, and $5p$ orbitals. The $3s(\sigma_u^*)$ orbital in ZrS_3 , however, has Π symmetry in the direction of the metal atom due to the "edge-on" coordination of the S_2 group, and can combine only with the $4d$ and $5p$ orbitals of Zr. The band thus formed will be narrower than that due to $3s(\sigma_g)$. In the pyrites, however, each metal atom is surrounded by six anion pairs in such a way that of each pair one atom is much closer to the metal atom than the other. For such an essentially "end-on" coordination one expects overlap of the orbitals of a particular metal atom only with the orbitals of the atom of the pair closest to the metal atom. This leads to equal covalent interactions for $3s(\sigma_g)$ and $3s(\sigma_u^*)$. Therefore this mechanism cannot explain the observed difference of width of the $3s(\sigma_g)$ and $3s(\sigma_u^*)$ peaks in the pyrites.

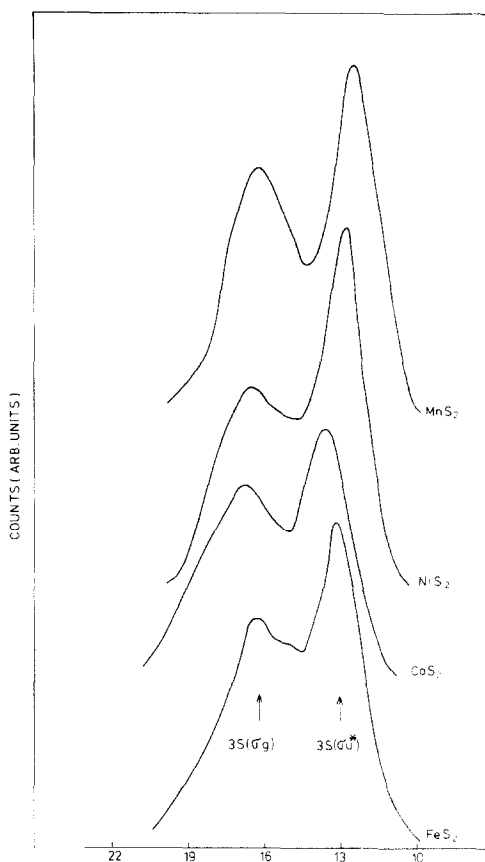


FIG. 2. Photoelectron spectra of sulfur $3s$ electrons in pyrites.

one expects the change of the equilibrium internuclear distance ΔR to be rather small in the $3s(\sigma_u^*)$ final state.

We now consider the effect of vibronic coupling on the lineshape. The XPS phonon linewidth can be calculated using the sudden approximation for the electronic excitation and the Born-Oppenheimer approximation for the electron-phonon interaction (22-24). According to the Franck-Condon principle the zero-point and thermal vibrations in the initial state are directly projected into the final state. In the limit of small vibrational quanta and large values of ΔR this leads to a Gaussian lineshape with a width proportional to ΔR . Because ΔR is expected to be

TABLE I
CORE LEVELS OF ANION PAIRS^a

Compound	$2p_{1/2}$	$2p_{3/2}$	$\sigma_g(3s)$	$\sigma_u^*(3s)$	Δ (eV)	X-X distance R (Å)
MnS ₂	162.9	161.9	16.0	12.4	3.6	2.088
FeS ₂	163.4	162.4	16.4	13.3	3.1	2.135
CoS ₂	163.7	162.6	16.9	13.6	3.3	2.124
NiS ₂	163.7	162.7	16.6	12.9	3.7	2.065
			$\sigma_g(4s)$	$\sigma_u^*(4s)$		
CoSe ₂			16.7	14.2	2.5	2.435
NiSe ₂			16.3	14.0	2.3	2.417

^a Binding energies (eV) are given relative to the Fermi level.

larger for the $3s(\sigma_g)$ than for the $3s(\sigma_u^*)$ final state, one expects a larger vibronic broadening of the $3s(\sigma_g)$ peak, as is observed.

Core Levels of Metal Ions

The photoelectron spectra of the metal $3s$ and $2p_{3/2}$ electrons are given in Figs. 4–7 and

Table II. The structure in these spectra is caused by multiplet splitting of the final state and satellites involving excitations of a second electron. The metal $3s$ electrons are subject to the exchange interaction with the spin of the partly filled $3d$ shell (25–27). For the high-spin $S = \frac{5}{2}$ Mn²⁺ ion this leads to final states ⁵S and ⁷S. In the pyrites MnS₂ and MnSe₂ we observe indeed a well-resolved

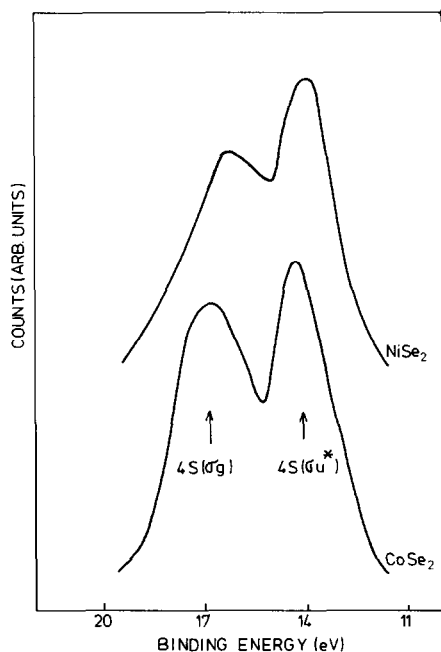


FIG. 3. Photoelectron spectra of selenium $4s$ electrons in pyrites.

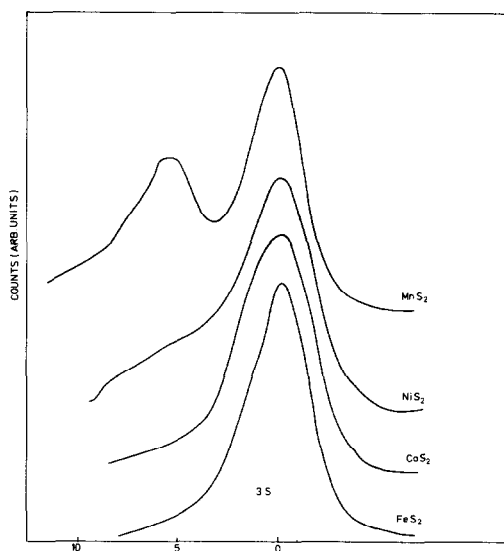


FIG. 4. Photoelectron spectra of metal $3s$ electrons in pyrites. The spectra are shifted so that the maxima of the main peaks coincide.

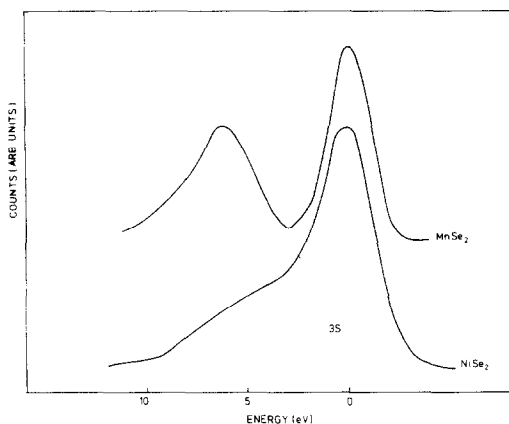


FIG. 5. Photoelectron spectra of metal 3s electrons in pyrites. The spectra are shifted so that the maxima of the main peaks coincide.

splitting of the 3s spectra of 5.5 and 6.2 eV, respectively. In the other pyrites the exchange splitting is not resolved due to the smaller spin density in the 3d shell; the exchange interaction in these cases leads only to a broadening (unresolved splitting) of the 3s lines.

Recent calculations showed that the magnitude of the 3s splitting is strongly influenced by correlation effects due to the reorganization of the *M* shell electrons in the final 3s hole state (28). The 3s splitting is expected to be proportional to the spin density in the 3d shell. Experimental (26) and theoretical (29) evidence indicates that in the Mn^{2+} compounds the 3s splitting decreases with increasing covalency of the metal-ligand bonds. The observed 3s splitting of 5.5 and 6.2 eV for MnS_2 and MnSe_2 are rather high, if compared with the values of 6.3, 6.0, 4.8, and 6.0 eV, reported for MnF_2 , MnCl_2 , MnBr_2 (26), and $\alpha\text{-MnS}$ (30), respectively. Indeed one would expect a smaller splitting for MnS_2 and especially for MnSe_2 , due to the larger covalency of these compounds as compared with the Mn-halides.

The $2p_{3/2}$ spectra of the pyrites consist of a main line and a weaker secondary maximum at a higher binding energy. The width of the

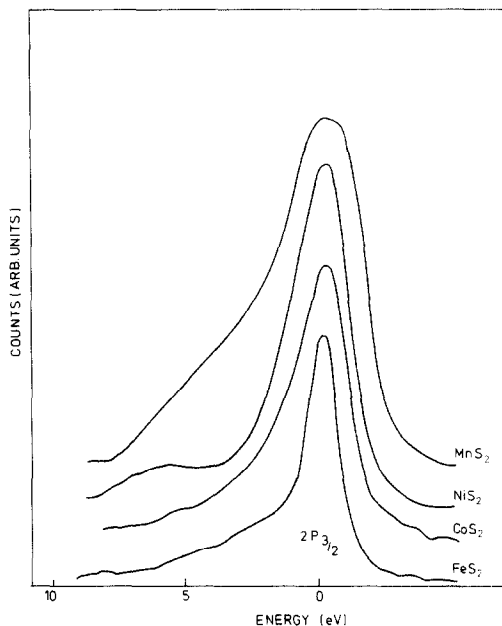


FIG. 6. Photoelectron spectra of metal $2p_{3/2}$ electrons in pyrites. The spectra are shifted so that the maxima of the main peaks coincide.

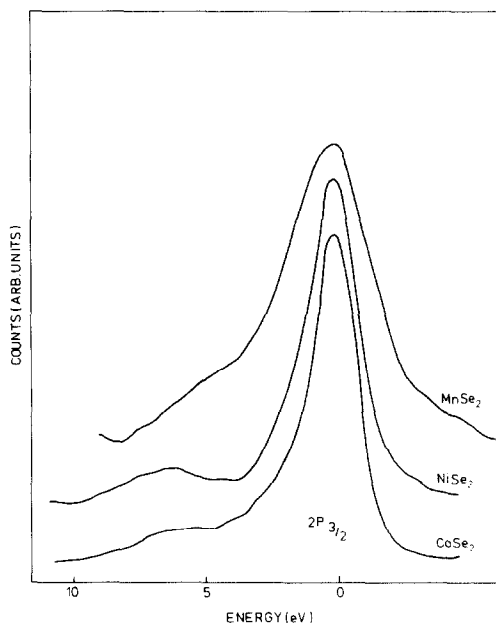


FIG. 7. Photoelectron spectra of metal $2p_{3/2}$ electrons in pyrites. The spectra are shifted so that the maxima of the main peaks coincide.

main line strongly increases in the series FeS_2 – CoS_2 – NiS_2 – MnS_2 and in the series CoSe_2 – NiSe_2 – MnSe_2 (Table II). The effects of multiplet splitting of the $2p_{3/2}$ are complex due to the possibility of coupling both orbital and spin momentum in the final state (25, 31, 32). It was shown that the net effect of multiplet splitting on the main peak of the $2p_{3/2}$ spectrum of Mn^{2+} compounds is an asymmetric broadening at the high-energy side. An asymmetric broadening of this type is observed indeed in the $2p_{3/2}$ spectra of MnS_2 and MnSe_2 (Figs. 6 and 7). In FeS_2 the metal ion is in a low-spin ($3d$)⁶ $S=0$ configuration, only one final state is possible, and no multiplet splitting is expected. This explains the observed small width of the $2p_{3/2}$ peak of FeS_2 . Because of the smaller values of the spin density in the $3d$ shell of the metal ion in CoS_2 , CoSe_2 , NiS_2 , and NiSe_2 one expects in these compounds a broadening of the main $2p_{3/2}$ peak caused by multiplet splitting smaller than that in the Mn dichalcogenides, as is observed.

Several of the $2p_{3/2}$ spectra show satellites at 5–6 eV higher binding energies. It is remarkable that the $2p_{3/2}$ spectrum of FeS_2

shows no satellite structure. For transition metal compounds the origin of the satellite peaks is a controversial topic. Satellites have been attributed to shake-up transitions of metal $3d \rightarrow 4s$ nature (33, 34) or to ligand-orbital to metal-orbital charge transfer (35–37). In the Fe, Co, and Ni pyrites the metal $3d(t_{2g})$ orbitals are fully occupied and charge transfer transitions from ligand orbitals are only possible to unoccupied $3d(e_g)$ orbitals. If satellite structure is due to transitions of this type, one expects strong satellites for ions with unoccupied $3d(e_g)$ orbitals, i.e., for FeS_2 , NiS_2 , CoS_2 , and MnS_2 . However, only the $2p_{3/2}$ spectra of NiS_2 and NiSe_2 (and to a lesser extent that of CoSe_2) show pronounced satellites; satellites in the $2p_{3/2}$ spectra of FeS_2 , MnS_2 , MnSe_2 , and CoSe_2 , if at all present, are weak.

It was noticed that satellites do not occur in low-spin diamagnetic compounds (34). The absence of satellites in FeS_2 agrees with this rule. Yin *et al.* (34) made an attempt to explain this rule and other observed data on satellites in terms of monopole selection rules for metal $3d \rightarrow 4s$ shake-up transitions. However, his approach was criticized by Jørgensen (38), and in our opinion no final answer has been given so far to the problem of the origin of $2p_{3/2}$ satellites in transition metal compounds.

TABLE II
CORE LEVELS OF METALS IONS^a

Compound	$2p_{3/2}$		$(3s)$	
	Binding energy (eV)	Width (eV)	Binding energy (eV)	Width (eV)
MnS_2	640.4	~4.0	82.6 (⁵ S) 88.1 (⁷ S)	
FeS_2	706.7	1.6	92.0	3.5
CoS_2	778.1	2.6	101.9	4.2
NiS_2	853.6	2.7	111.9	4.3
MnSe_2	640.5	~4.0	82.6 (⁵ S) 88.8 (⁷ S)	
CoSe_2	778.3	2.0		
NiSe_2	853.2	2.2	112.0	3.6

^a Binding energies (eV) are given relative to the Fermi level.

Valence Band Spectra

The valence band spectra of the pyrites are shown in Fig. 8. The observed spectra of FeS_2 , CoS_2 , and NiS_2 agree with spectra previously reported (15–17). Some of the valence band spectra have been recorded with and without a monochromator. The noise for spectra with monochromatized radiation is larger due to the lower intensity. The structure in the valence band spectra taken with unmonochromatized radiation is real and reproducible. The valence band spectra consist of contributions of the sulfur $3p$ (selenium $4p$) and metal $3d$ electrons. A

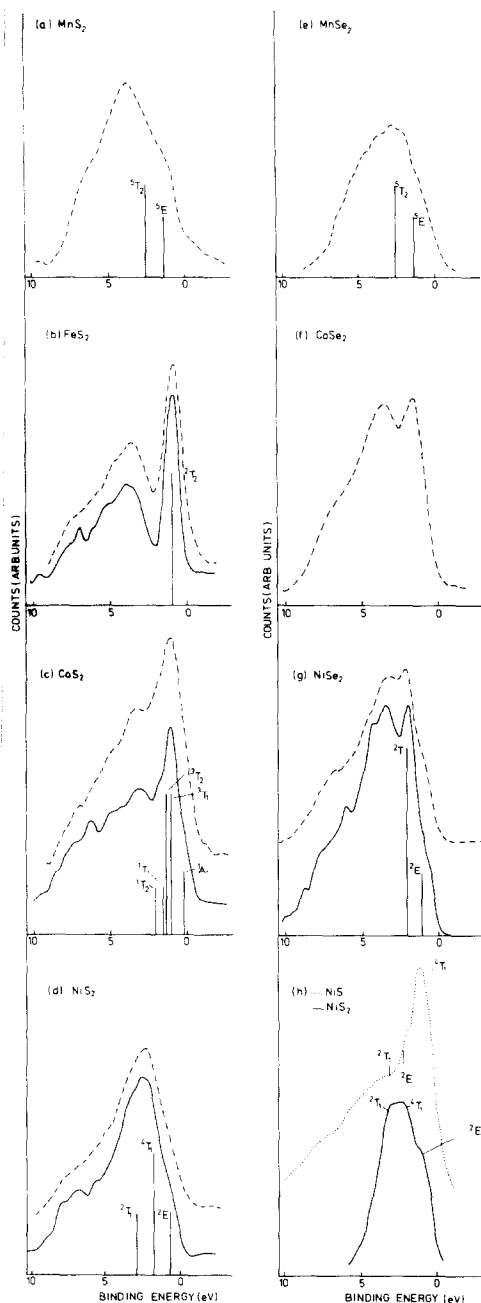


FIG. 8. Valence band spectra of pyrites; spectra marked by solid lines are taken with monochromatized $AlK\alpha$ radiation, those marked by broken lines with unmonochromatized $AlK\alpha$ radiation. Calculated positions (from $10Dq \approx 2.4$ eV, $B \approx 0.06$ eV, and $C = 4B$) and relative intensities of $3d$ peaks are represented by vertical lines. In (h) the $3d$ spectrum of NiS_2 (obtained from (d) by subtracting the $S(3p)$ spectrum of FeS_2) is compared with the valence band of NiS (dotted line).

comparison of XPS and sulfur $K\beta$ X-ray emission showed directly that in FeS_2 , CoS_2 , and NiS_2 the contribution of the d electrons lies at the low-binding-energy side of the valence band (39).

The contribution of sulfur $3p$ electrons, which are best represented by a band-like description, is probably not very different for the different pyrites. The $3d$ electrons are accounted for by a ligand-field description of localized $3d^{n-1}$ final states of the transition metal ions. A description of this type has been successful for the interpretation of several transition metal compounds (40-42). The first coordination sphere of the metal atoms in the pyrite structure is a distorted octahedron of chalcogen atoms. Therefore we expect in first approximation that the interaction with ligands will lead to a ligand-field splitting of octahedral symmetry (O_h). The multiplet splitting then depends only on the Racah parameters, B and C describing the electrostatic repulsion of the d electrons, and the ligand-field parameter $10Dq$ (43).

The photoionization of a d electron in FeS₂ (ground state of metal ion $^1A_{1g}(t_{2g})^6$) leads to a single final state $^2T_{2g}(t_{2g})^5$. Therefore the spectrum of $3d$ electrons in FeS₂ is expected to show a single peak. The observed spectrum shows indeed a strong peak, of width 0.9 eV, at the top of the valence band. The structure below this peak is ascribed to broad energy bands, derived from (mainly) sulfur $3p$ orbitals.

The top of the valence band of CoS_2 shows additional structure, because photoionization of the 2E_g ground state leads to several final states: ${}^1A_{1g}$, ${}^3T_{1g}$, ${}^3T_{2g}$, ${}^1T_{1g}$, ${}^1T_{2g}$. For NiS_2 the ground state is ${}^3A_{2g}$, and the final states are 2E_g , ${}^4T_{1g}$, ${}^2T_{1g}$. The energies and relative intensities, obtained from ligand-field theory (44), account reasonably well for the observed structure. However, the data are not accurate enough to permit a determination of crystal-field and Racah parameters. The spectrum of CoSe_2 shows no resolved structure.

In Fig. 8h the contribution of the 3d electrons of Ni has been obtained by subtracting the sulfur 3p valence band obtained from the FeS₂ spectrum where 3p and 3d bands are clearly separated. The spectrum is rather different from the spectrum of 3d electrons in NiS, NiO, NiF₂, and NiCl₂ (42). This difference is due to the larger crystal-field splitting in NiS₂ which results in a reversal of the peaks due to the ²E_g and ⁴T_{1g} final states. As a consequence one expects that the nature of the top of the valence band of NiS₂ is quite different from that of NiS.

The spectrum of NiSe₂ differs from that of NiS₂ and shows two 3d peaks. However, whereas NiS₂ is an antiferromagnetic semiconductor with well-developed magnetic moments at the Ni atoms (5), NiSe₂ is a nonmagnetic compound and is presumably best described by a low-spin ground state, ¹A_{1g}(t_{2g}⁶e_g²). This leads to only two final states, ²T_{2g} and ²E_g.

For MnS₂ and MnSe₂ two final states, ⁵E_g and ⁵T_{2g}, are expected. The MnS₂ spectrum shows some evidence of this splitting, but the data are not accurate enough to permit a determination of 10Dq.²

Discussion

In this section we compare the photoelectron spectra with other evidence for the electronic structure.

The variation of the electrical and magnetic properties in the series FeS₂-CoS₂-NiS₂-CuS₂ has been ascribed to the increasing number of electrons in the narrow 3d(e_g^{*}) band (1, 13). In this model the 3d levels of the metal are split by the ligand field in a set of 3d(t_{2g}) orbitals, which are (almost) non-bonding and form a narrow band, and a set of 3d(e_g^{*}) orbitals forming an antibonding band. In the semiconductor FeS₂ the 3d(t_{2g})

band is occupied and the 3d(e_g^{*}) is empty. From photoelectron spectra we find the width of the 3d(t_{2g}) band to be about 0.9 eV (width of the observed band including the instrumental linewidth).

The photoelectron spectra of FeS₂ and NiS₂ have been compared with spin-polarized SCF-Xα cluster calculations on octahedral FeS₆¹⁰⁻ and NiS₆¹⁰⁻ clusters (16). However, these calculations do not take into account the presence of (S₂)²⁻ molecular anions and have neither the proper geometry nor the proper charge at the sulfur atom. The energy levels of these calculations are relevant for FeS and NiS, not for FeS₂ and NiS₂.

The only available calculation of the band structure of the pyrites employs a LCAO method to obtain the energy bands of FeS₂ (12). This calculation leads to narrow energy bands t_{2g} and e_g for the 3d orbitals, in agreement with the experimental data. However, the calculations also lead to narrow Π_u and σ_g for the bonding sulfur 3p orbitals. This is not in agreement with the observed photoelectron spectrum which shows a broad band (width about 6 eV) for the sulfur 3p orbitals.

Acknowledgments

We thank Professor Perdok, Laboratory of Solid State Physics, Groningen, for kindly putting at our disposal a single crystal of MnS₂, and Professor F. Jellinek and Dr. G. Sawatzky for helpful discussions.

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² The valence band of MnS₂ is very similar to that of MnS (45). A comparison of the valence band of MnS with that of MgS indicates the assignment of shoulders at 1.5 and 2.5 eV to 3d⁴ final states ⁵E_g and ⁵T_{2g}.

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