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THE CHEMICAL BOND AND THE PROPERTIES OF SULFIDE MINERALS. I. Zn, Fe and Cu IN TETRAHEDRAL AND TRIANGULAR COORDINATIONS WITH SULFUR

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ABSTRACT

Simplified electronic structure models based on molecular orbital calculations are presented for important metal-sulfide minerals that contain Zn, Fe and Cu in tetrahedral or triangular coordination to sulfur (sphalerite, chalcopyrite, covellite and nukundamite). These "one-electron" *MO*/band-theory models are correlated with the properties of the minerals. The models correlate well with electrical properties of pure and iron-bearing sphalerite and with the hardness and stability variations resulting from iron substitution in sphalerite. The reflectance curves of chalcopyrite and covellite, which relate directly to their distinctive appearance under the reflected light microscope, can be explained by using electronic transitions (both sulfur → metal charge-transfer transitions and crystal-field transitions) predicted by the models. If data on properties are not available, the models enable some general predictions regarding electrical, optical and thermochemical behavior to be made.

Keywords: sulfides, bonding, molecular orbitals, sphalerite, chalcopyrite, covellite.

SOMMAIRE

Nous présentons des modèles simplifiés de la structure électronique obtenus par calculs d'orbitales moléculaires pour les principaux minéraux sulfurés qui contiennent Zn, Fe et Cu en coordination tétraédrique ou triangulaire avec le soufre (sphalérite, chalcopyrite, covelline et nukundamite). Ces modèles à un électron, construits d'après les orbitales moléculaires et la théorie des bandes, montrent une bonne corrélation avec les propriétés des minéraux; par exemple, les propriétés électriques de la sphalérite, soit pure, soit ferrifère, et la variation de sa dureté et de sa stabilité en fonction du remplacement (Zn,Fe). Les courbes de réflectance de la chalcopyrite et de la covelline, qui expliquent bien leur apparence au microscope en lumière réfléchie, peuvent s'interpréter en fonction des transitions électroniques que prédit le modèle (impliquant soit un transfert de charge de soufre à métal, soit la nature du champ cristallin). Quand on manque de données sur les propriétés d'un minéral, les modèles permettent de prédire *grosso modo* son comportement électrique, optique ou thermochimique.

(Traduit par la Rédaction)

Mots-clés: sulfures, liaisons, orbitales moléculaires, sphalérite, chalcopyrite, covelline.

INTRODUCTION

Sphalerite and chalcopyrite are important metal-sulfide minerals that contain Zn^{2+}, Fe^{2+}, Cu^{+} and Fe^{3+} in tetrahedral coordination with sulfur. Copper also occurs in tetrahedral and triangular coordinations with sulfur in covellite. The crystal structures of these sulfides are well characterized as are their mineral properties (Vaughan & Craig 1978). There is also a copper–iron sulfide that is apparently isostructural with covellite, and known from syntheses to have a composition ~ Cu_5FeS_6 (or $Cu_{5.5x}Fe_x S_{6.5x}$). Although idaite was originally thought to have this composition, the type material appears to be inadequately described; the name *nukundamite* has recently been applied to what may be another mineral, of composition $Cu_{3.37}Fe_{0.66} S_{3.97}$, which was found to be hexagonal (Rice *et al.* 1979).

Adequate data are now available for these minerals to enable discussion of the chemical bonding or electronic structures and their correlation with properties of mineralogical interest (structural parameters, spectral reflectance, microhardness, thermochemical parameters, electrical and magnetic properties). The approach used in this paper has recently been employed in discussing the properties of major transition-metal oxide minerals (Vaughan & Tossell 1978) and is based on both quantum-mechanics calculations and spectroscopic data.

As previously outlined, we consider a molecular orbital (*MO*) model that incorporates some elements of band theory as the most useful approach to the electronic structures of minerals (Vaughan & Tossell 1978). Calculations using the SCF-X_α scattered wave method have been performed on cluster units of Zn, Fe and Cu coordinated to sulfur (Vaughan *et al.* 1974, Tossell 1977, 1978) and tested against spectroscopic data from X-ray emission, X-ray photoelectron and optical spectroscopies. The same calculations are used here to construct schematic ("one-electron") *MO*/band-theory energy-level diagrams for the sulfides (although modified where necessary in the light of experimental spectroscopic data).

The electronic structures and interpretations of properties will be considered for two major structural types: the sphalerite-type structure of sphalerite itself, ferroan sphalerite and chalcopyrite, and the covellite structure of covellite itself and the ~ Cu_5FeS_6 phase.

SPHALERITE AND CHALCOPYRITE: ELECTRONIC STRUCTURES

Schematic energy-level diagrams for sphalerite, ferroan sphalerite and chalcopyrite are shown in Figure 1. These diagrams have many features in common with the *MO* energy-level diagrams of elementary chemistry texts (Gray 1965, Cotton & Wilkinson 1972), although there are also important differences. Shown to the left of Figure 1 is a set of *MO* energy levels calculated for the ZnS_4^{-6} tetrahedral cluster that can be considered the basic building block of sphalerite. The energy levels for the single tetrahedral unit are labeled according to the irreducible representations of the T_d symmetry group. From the calculations, it is also possible to comment on the compositions of particular molecular orbitals in terms of the contribution of atomic orbitals of metal or sulfur. Thus, the $4t_2$, $1t_1$ and $2e$ molecular orbitals are dominantly sulfur $3p$ in character and nonbonding, whereas the $3t_2$ and $2a_1$ orbitals are the main metal–sulfur bonding orbitals. The $1e$ and $2t_2$ orbitals are the dominantly metal $3d$ "crystal-field"-type orbitals in this system. When large numbers of these tetrahedral units are brought together in a sphalerite crystal, overlap between many of these orbitals can be considered to result in the formation of *bands* of collective electron states. This is illustrated in the simplified "one-electron" band model for sphalerite shown next to Figure 1. Here, the highest energy band shown

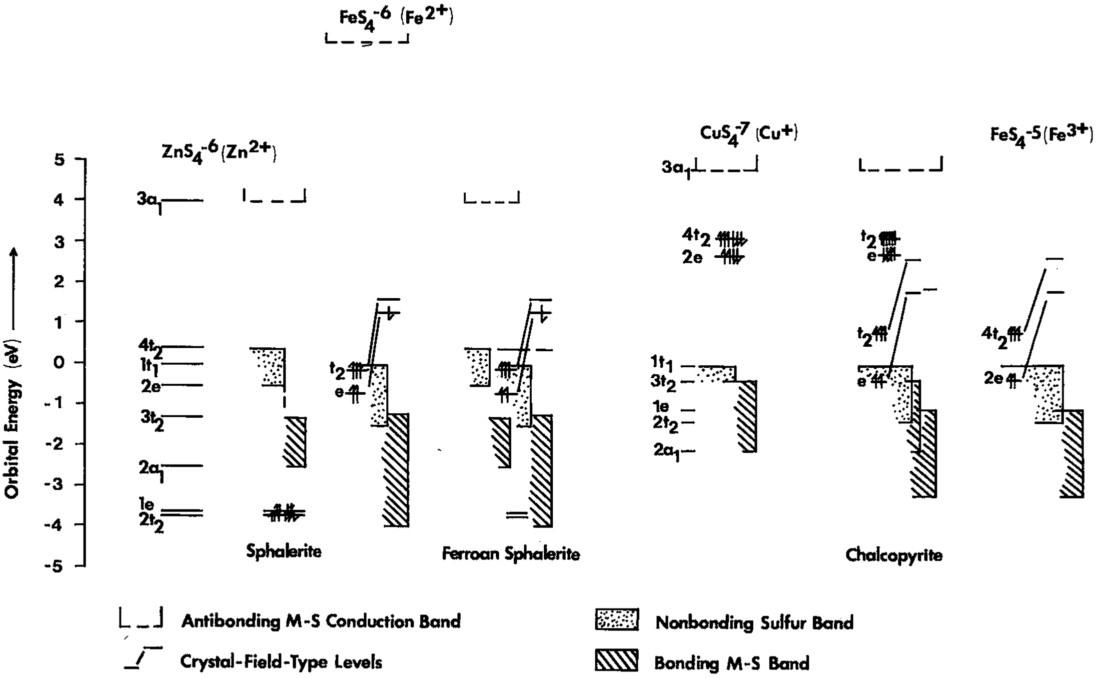

FIG. 1. Electron-structure models for sphalerite, ferroan sphalerite and chalcopyrite. Discrete energy levels are shown for clusters ZnS_4^{6-}, CuS_4^{7-} and FeS_4^{5-} and composite "one-electron"-band model energy level diagrams illustrated for the minerals.

is the empty metal–sulfur antibonding band, beneath which is an energy gap to the filled nonbonding sulfur band. Stabilized relative to this is the main metal–sulfur bonding band, but the crystal-field-type Zn 3*d* levels are shown in this model as not forming a band and remaining localized on the transition-metal cation.

The effect of substantial substitution of Fe^{2+} (high-spin) for Zn^{2+} in pure sphalerite can be examined by adding data from a calculation on an FeS_4^{6-} cluster (Vaughan *et al.* 1974) as shown in Figure 1. The composite one-electron band model for ferroan sphalerite shows significant changes in the relative energies of the sulfur nonbonding band, the metal–sulfur bonding band, and most significantly, of course, in the crystal-field-type levels of mostly Fe 3*d* character. The single unpaired 3*d* electron of Fe^{2+} results in some slight splitting of the valence orbital energy-levels into spin-up (↑) and spin-down (↓) levels, which has only been shown for the crystal-field-type levels since these are most affected.

Chalcopyrite contains both Cu and Fe in tetrahedral coordination with S and, in fact, has the same basic crystal structure as sphalerite. The nature of oxidation states of these transition-metal ions has been a matter of some disagreement. The first solution of the crystal structure (Pauling & Brockway 1932) yielded Cu–S and Fe–S distances that suggested a configuration intermediate between $Cu^+Fe^{3+}(S^{2-})_2$ and $Cu^{2+}Fe^{2+}(S^{2-})_2$. A more recent refinement of the structure (Hall & Stewart 1973) indicated appreciable covalency but could not resolve the question of electronic configuration. A neutron-diffraction study (Donnay *et al.* 1958) showed a magnetic moment of virtually zero on Cu and 3.85 Bohr magnetons on Fe, strongly supporting the Cu^+Fe^{3+} configuration. Mössbauer studies (Vaughan & Craig 1978, p. 139-143) confirmed this result, primarily on the basis of the presence and magnitude of the magnetic hyperfine interaction. Further support for this electronic configuration exists in the Cu 2*p* X-ray photoelectron spectrum (Nakai *et al.* 1978), which shows the low binding-energy and absence of satellite structure characteristic of Cu^+. The electronic structure of chalcopyrite shown in Figure 1 is based on calculations performed on the CuS_4^{7-} and FeS_4^{5-} tetrahedral units (Tossell 1978). Again, the results of calculations for the separate units are shown as well as a composite model for chalcopyrite.

Interpretation of properties

The properties of sphalerite, ferroan sphalerite and chalcopyrite that are of mineralogical interest are summarized in Table 1. Pure ZnS has a very high resistivity, in accordance with its capacity as a semiconductor with a large band-gap. From experimental data (Shuey 1975), this band gap is estimated as 3.6–3.9 eV, which agrees well with the calculated value of 3.6 eV shown in Figure 1. In the absence of impurities it is, of course, diamagnetic. The addition of iron, replacing Zn in the tetrahedral sites and probably entirely as the Fe^{2+} species (Vaughan & Craig 1978), results in the activation energy for conduction dropping to only 0.5 eV (this could result from transitions from the sulfur *p* nonbonding band into Fe^{2+} *d* orbital levels). Iron substitution leads to paramagnetic

TABLE 1. MINERAL PROPERTIES OF SPHALERITE, FERROAN SPHALERITE, CHALCOPYRITE, COVELLITE AND $\sim Cu_5FeS_6$

MINERAL & COMPOSITION	STRUCTURE	CELL DIMENSIONS (Å)	R%(589nm)	$VHN_{100}Kg/mm^2$	THERMAL STABILITY (°C)	ΔH° $(kcal/m)^{298}$	ΔG° $(kcal/m)^{298}$	ELECTRICAL & MAGNETIC DATA
* Sphalerite ZnS	$F\bar{4}\ 3m$	5.43	17.15-19.5	128-276	$\lesssim 1020$	-49.0	-47.9	Semicond. Diamag.
* Ferroan Sphalerite (Zn,Fe)S	$F\bar{4}\ 3m$	(see text)	(see text)	(see text)	(see text)			(see text)
* Chalcopyrite $CuFeS_2$	$I\bar{4}\ 2d$	5.25, 10.32	45.7-50.5	174-219	<550	-44.2	-44.3	Semicond. Antiferro T_N = 550K
* Covellite CuS	$P6_3/mmc$	3.80, 16.36	4.5-21.7	59-129	<500	-12.5	-12.87	Metallic
† Nukundamite Cu_5FeS_6	$(?P6_3/mmc)$	3.78, 11.19	18.8-23.2	103-110 (at 20 newton)	<501?	?	?	?

* Data taken from Vaughan & Craig (1978) † Using data from Rice et al. (1979)

behavior, and at high iron concentrations, antiferromagnetic coupling has been suggested (Keys *et al.* 1968). Chalcopyrite shows antiferromagnetic coupling of the unpaired spins on Fe^{3+} and *n*-type semiconduction with a band gap of ~ 0.6 eV.

Spectra reflectance values throughout the visible region are plotted for sphalerite and iron-rich sphalerite in Figure 2. No electronic transitions occur in pure ZnS at these relatively low energies, but the slight increase in reflectivity towards the higher energy (450 nm) end of the visible region indicates the start of the absorption edge reached at around 3.6 eV. Substitution of Fe^{2+} in sphalerite has a negligible effect on the reflectivity in the visible region. The transition of the single $t_2 \downarrow$ electron into the $e \downarrow$ empty orbital occurs at much lower energy (~ 1,000 nm) and has no effect on the reflectivity profile. Other transitions involving the Fe^{2+} 3*d* electrons are "spin-forbidden", and their very low intensities will have no significant influence on reflectance.

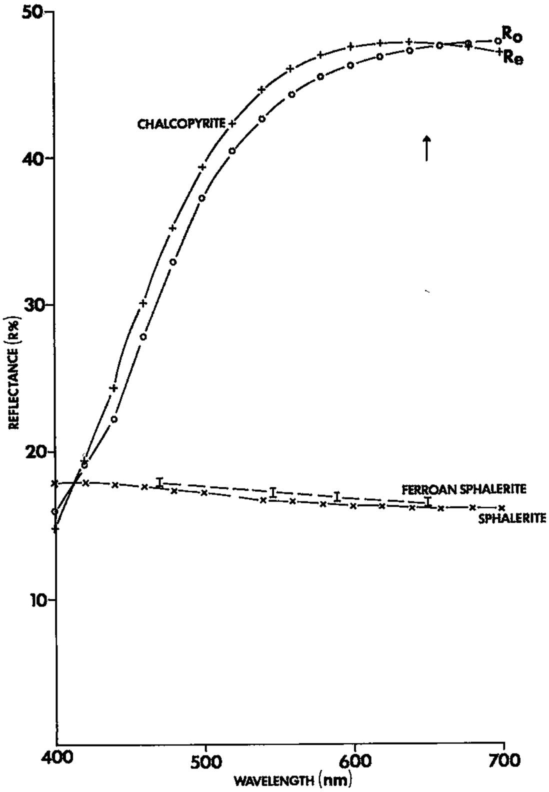

FIG. 2. Reflectance data for chalcopyrite, sphalerite and ferroan sphalerite in the visible region. Data from IMA/COM Data File (Henry 1977).

The reflectance spectrum of chalcopyrite shows a broad peak around 650 nm (indicated by the arrow on Fig. 2), consistent with the absorption peak observed around 620 nm for thin-film $CuFeS_2$ by Sato & Teranishi (1976). In the thin-film spectrum a shoulder also appears at about 1130 nm. Similar features are observed when Fe is doped into GaS_3 (Pivnichny & Brintzinger 1973) or into ZnS (Platonov & Marfunin 1968) and in the ferric-iron protein rubredoxin (Lovenberg & Sobel 1965). These transitions in chalcopyrite probably involve S 3*p*–Fe 3*d* electron transfer ("charge transfer"), although the weaker low-energy shoulder could be a Fe^{3+} spin-forbidden crystal-field transition. The transition at ~ 650 nm (~ 1.9 eV) is responsible for the very pronounced positive feature in the spectral reflectance profile of chalcopyrite, as shown in Figure 2.

The range of Vickers micro-indentation hardness observed in sphalerite and chalcopyrite are virtually the same, but the effects of iron substitution in sphalerite are complex (Young & Millman 1964, Vaughan & Craig 1978). Substitution up to ~ 2 wt. % Fe produces a substantial increase in hardness, whereas further substitution results in decreasing hardness that correlates with the linear increase in unit-cell dimensions. The latter trend correlates with the destabilization inherent in the addition of the $t_2 \downarrow$ electron of Fe^{2+} and the apparent destabilization of iron–sulfur bonding orbitals relative to zinc-sulfur.

Similar arguments can be put forward to explain the thermochemical data for ferroan sphalerite compared with pure ZnS. Iron substitution results in a decrease in stability (Fleet 1975), correlating with decreasing metal–sulfur bonding-orbital stability and the presence of the $t_2 \downarrow$ electron.

COVELLITE AND Cu_5FeS_6: ELECTRONIC STRUCTURE

The crystal structure of covellite is much more complex than that of sphalerite and chalcopyrite. It contains approximately tetrahedrally coordinated copper and copper in triangular coordination. A further complexity is that two thirds of the sulfur atoms are combined in S_2^{2-} anion units. The configuration that has been proposed for covellite is $Cu^{2+}_{III}(Cu^{+}_{IV})_2S^{2-}(S_2^{2-})$ in which, therefore, Cu^{2+} occupies triangular and Cu^{+} tetrahedral sites. Molecular orbital calculations (Tossell 1978) performed using the SCF–X_α scattered wave method on

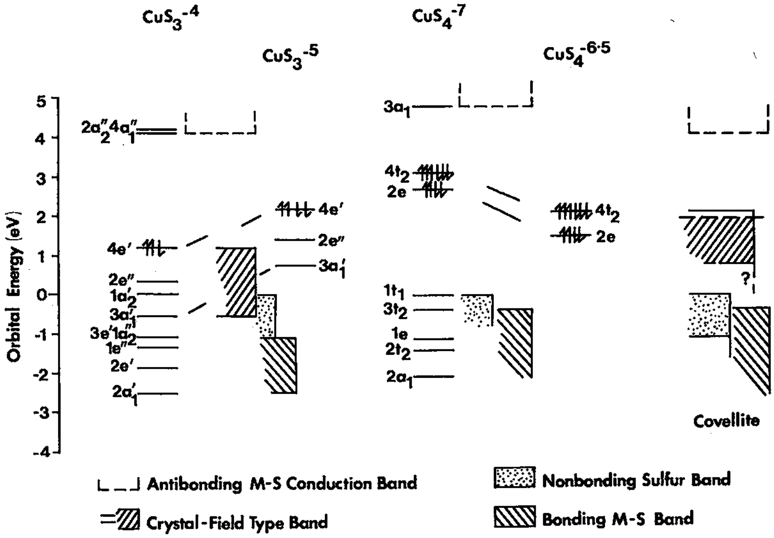

FIG. 3. Electron-structure model for covellite. Discrete energy-levels are shown for clusters CuS_3^{4-}, CuS_3^{5-}, CuS_4^{7-}, $CuS_4^{6.5-}$ and a composite "one-electron"-band model energy-level diagram illustrated for the mineral.

CuS_3^{4-} and CuS_4^{7-} clusters produced the one-electron energy-level diagrams shown in Figure 3. As in the energy-level diagrams of Figure 1, individual molecular orbitals have been labeled according to the irreducible representations of the D_{3h} and T_d symmetry groups. The compositions of the particular groups of orbitals have also been indicated in the simplified band-models shown alongside the energy levels for the isolated clusters. However, the metallic conductivity observed in CuS (Shuey 1975) indicates that the orbitals, dominantly Cu 3*d* in character, also form a collective electron band. Further calculations, in which the transition-state procedure (transfer of half an electron from Cu^+_{IV} to Cu^{2+}_{III}) was employed, indicate that to form such a collective electron band, charge should flow from the $4t_2$ orbital on the tetrahedral Cu^+ to the $4e$ orbital on the triangular Cu^{2+}. The resulting change in electronic structure is then represented by the cluster calculations for CuS_3^{5-} and $CuS_4^{6.5-}$ as shown in Figure 3. These have been combined to give the composite simple band structure model also shown in the triangular sites, there is a closer corres-both a nonbonding sulfur band and metal–sulfur bonding band lies an incompletely filled band dominantly of metal 3*d* orbital character (and minus the equivalent of one third an electron *per* molecule).

The phase of composition Cu_5FeS_6 apparently results from replacement of one sixth of the copper atoms in covellite by iron atoms. Although it would be reasonable to assume that the substitution that occurs involves Fe^{2+} for Cu^{2+}, preliminary Mössbauer-effect measurements on iron in synthetic stoichiometric Cu_5FeS_6 (produced by reaction between high-purity copper, iron and sulfur in sealed, evacuated silica capsules and checked for homogeneity by X-ray diffraction and by examination in polished section) show room-temperature isomer-shift (0.35 mm/s relative to iron foil) and quadrupole-splitting (0.39 mm/s) values indicative of Fe^{3+} rather than Fe^{2+}. This would result in a formal oxidation-state configuration of $Cu^+_4 S^{2-}_2 Cu^+_1 Fe^{3+}_1 (S^{2-}_2)_2$ for Cu_5FeS_6 and implies substitution of Fe^{3+} for Cu^{2+} in the triangularly coordinated sites. Such triangularly coordinated Fe^{3+} has been suggested to occur in tetrahedrite-group minerals on the basis of Mössbauer data (Vaughan & Burns 1972), although the isomer shift (0.29 mm/s) is appreciably smaller than that found for Cu_5FeS_6. Although this does not eliminate the possibility that Fe^{3+} may occur in the triangular sites, there is a closer correspondence with results for phases in which Fe^{3+} occurs in tetrahedral coordination (*e.g.*, bornite, which has isomer shift 0.39 mm/s relative to iron foil and quadrupole splitting 0.16 mm/s at room temperature: Vaughan & Burns 1972). Interestingly, however, quite good correspondence is given with results for phases in which a Fe^{2+}–Fe^{3+} exchange couple is known to be present (*e.g.*, cubanite, with isomer shift 0.40 mm/s and quadrupole spltting 0.27 mm/s: Vaugh & Burns 1972). If an electronic structure model is proposed using calculation results already presented in Figures 1 and 3 for the cluster units CuS_4^{7-}, CuS_3^{5-} and FeS_4^{5-}, one might expect charge to flow from Cu^+ to Fe^{3+} by analogy with the mechanism proposed for covellite. The result might be an intermediate oxidation state for iron. Such a model would be very similar to that presented in Figure 3 for covellite but with the contribution from the more stabilized Fe–S bonding band and a more destabilized, partly filled collective electron band comprised of crystal-field-type levels.

Interpretation of properties

Covellite is a *p*-type metal with a very low resistivity (Table 1, Shuey 1975) that correlates with the model shown in Figure 3. The conduction result from the holes in the band predominantly metal 3*d* orbital in character. Data for the electrical properties of Cu_5FeS_6 and the magnetic properties of both phases are lacking.

Reflectance profiles for covellite are shown in Figure 4. Data are presented for the two major vibration directions in these uniaxial phases. For covellite, data are available extending into both the infrared and the ultraviolet regions of the spectrum. Since the spectrum of covellite is highly anisotropic, it probably arises from transitions within the anisotropic CuS_3^{5-} groups rather than from transitions involving tetrahedral copper. Cluster calculations on $CuS_3^{4,5-}$ yield an energy for the $3a_1'$–$4e'$ crystal-field transition of about 1.5 eV, corresponding to a wavelength of 770 nm. Dipole-selection rules allow this transition only for the R_o spectrum, which is indeed considerably more intense than the R_e spectrum in the wavelength region above 700 nm. The transition yielding the peak in R_e at ~ 400 nm is more difficult to assign, since S 3*p* → Cu 3*d* charge transfer and Cu 3*d* conduction-band transitions are expected in this region. A probable contributor to this part of the spectrum is the $1e'' \rightarrow 4e'$ S 3*p* → Cu 3*d* charge-transfer transition in CuS_3^{5-} with a calculated maximum-intensity wavelength of ~ 450 nm and R_e polarization. All other charge-transfer transitions of the CuS_3^{5-} group in this energy range are symmetry-forbidden.

The insufficient reflectance data available for nukundamite (Fig. 4) and the uncertainties regarding its electronic structure restrict meaningful discussion of this mineral. However, the increase in reflectance toward 700 nm may again relate to a crystal-field transition in copper in the CuS_3^{5-} groups, and an interpretation based upon that for covellite may be possible when data become available. The absence of thermochemical data for the Cu_5FeS_6 phase or for nukundamite also prevents discussion of its stability relative to covellite. However, its rarity

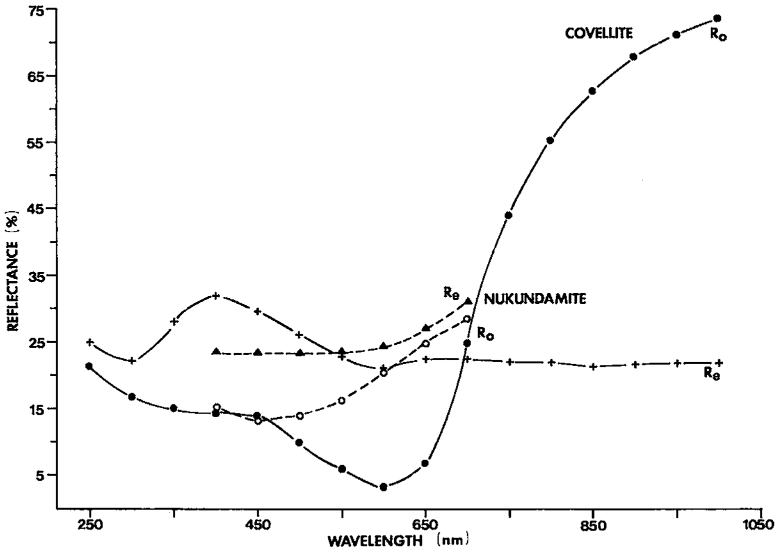

FIG. 4. Reflectance data for covellite and nukundamite. Data from IMA/COM Data File (Henry 1977) and Rice *et al.* (1979).

in nature relative to covellite, bornite and chalcopyrite and uncertainty regarding its phase relations in the Cu–Fe–S system (Vaughan & Craig 1978) suggest it may be metastable. In terms of electronic structure, this may result from the relative destabilization of the partly filled band of crystal-field-type energy levels or from the possible presence of Fe^{3+} in triangular coordination.

DISCUSSION

Quantitative "one-electron" models of the electronic structures of sulfide minerals containing Zn, Fe and Cu in tetrahedral and triangular coordination have been presented and correlated with the properties of these minerals. These models are currently the most satisfactory simplified approach to an understanding of the chemical bond in these complex materials, although they represent only the first stage in a complete understanding of them. Further calculations, particularly on larger cluster units, and spectroscopic measurements employing X-ray emission and photoelectron techniques will enable refinement of these models and extension to other major sulfides.

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