THE AMERICAN MINERALOGIST, VOL. 55, SEPTEMBER-OCTOBER, 1970

INTERPRETATION OF THE REFLECTIVITY BEHAVIOR OF ORE MINERALS

ROGER G. BURNS[1] AND DAVID J. VAUGHAN, *Department of Geology and Mineralogy, University of Oxford, England.*

ABSTRACT

A correlation exists between the percent reflectivity (R) of pyrite-type compounds and the effective number of free electrons (N_{eff}) in the visible region, obtained from specular reflectance spectral measurements. Both R and N_{eff} decrease in each of the series FeS_2—CoS_2—NiS_2—CuS_2 and $CuTe_2$—$CuSe_2$—CuS_2. A molecular orbital model is described which relates the concept of N_{eff} to the delocalisation of excited transition metal electrons into antibonding molecular orbitals of pyrite. The values of N_{eff} are shown to depend on the number and proximity of empty energy levels above the Fermi level. The model is extended to explain reflectivity variations in other isomorphous and isochemical series of ore minerals.

INTRODUCTION

This paper describes a correlation that has been observed in recent literature data on reflectivity measurements of pyrite-type compounds, which forms a basis for explaining reflectivity variations in isomorphous ore minerals.

Although techniques for quantitative measurements of reflectivity have been described (Singh, 1965; Freund, 1966) and data have been tabulated for most opaque minerals at various wavelengths in the visible region, few attempts have been made to explain compositional variations of reflectivity. Such reflectivity variations are exemplified by the pyrite group. Electron microprobe measurements (Springer, Schachner-Korn and Long, 1964; Vaughan, 1969) have shown that most bravoites, (Fe, Co, Ni)S_2, are compositionally zoned, and that the zoned bravoites display a pronounced variation in reflectivity (Vaughan, 1969; Demirsoy, 1969). Thus, iron-rich regions have high reflectivity, nickel-rich zones have relatively low reflectivity and cobalt-rich areas have intermediate reflectivities.

Recently Bither, Bouchard, Cloud, Donohue and Siemons (1968) described specular reflectivity spectra of several pyrite-type transition metal dichalcogenides. These measurements yielded values of the optical constants n (refractive index) and k (absorption coefficient) of each pyrite-type compound over a range of energies (0–5 eV). From the absorption coefficients a parameter n_{eff}, representing the effective number of free electrons per molecule, was calculated at each excitation energy. Bither *et al.* (1968) found that the order of decreasing n_{eff} is

---

[1] Present Address: Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

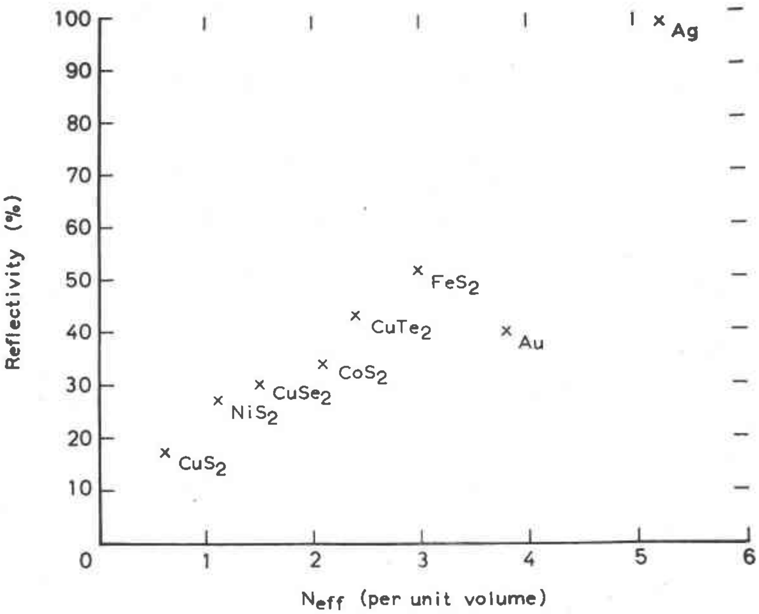

FIG. 1. Plot of percent reflectivity (R) against effective number of free electrons per unit volume (N_{eff}) for pyrite-type compounds. Data for Ag and Au are also shows.

$FeS_2 > CoS_2 > NiS_2 > CuS_2$ which parallels the order of decreasing reflectivities.

These two sets of data, the values of reflectivity and the effective number of free electrons at specific energies, led us to plot percent reflectivity against N_{eff} per unit volume at 496 nm (2.50 eV) for the range of transition metal dichalcogenides measured by Bither *et al.* (1968). This graph is shown in Figure 1. Additional data were available for the metals Au and Ag (Mott and Jones, 1936; Squair, 1965). The data plotted in Figure 1 show that reflectivity increases with the effective number of free electrons. It is this correlation that we wish to discuss further.

THEORY OF REFLECTIVITY

The behavior of light incident on a flat, solid surface is expressed by the Maxwell field equations for electromagnetic waves. Solutions to these equations show that for all media the reflection, refraction and polarization of radiation depend on the geometry and index of refraction, N, of adjoining media.

The index of refraction, N, is a complex number and is defined by

$$N = n + ik \tag{1}$$

where n is the relative refractive index or the ratio of the velocities of light in the two adjoining media; k is the absorption coefficient; and i is the complex conjugate (Jenkins and White, 1957).

The optical constants n and k are related to the reflection coefficient R by the Fresnel equation

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{2}$$

where $R=1$ corresponds to 100 percent reflectivity. The Fresnel equation shows that strongly reflecting substances have both high n and high k.

The index of refraction N depends on the interaction of the light wave with electrons of constituent atoms of the solid medium (Wert and Thomson, 1964). The electrons are accelerated in the electric field of the radiation, but if there are no low-lying energy levels into which the electrons can be excited, the light is emitted with negligible absorption (k is small) but it is slowed down (n is large). Thus, the index of refraction is essentially a real number (since $N \approx n$). Such a situation applies to transparent insulators such as most colorless silicates, in which the index of refraction is determined predominantly by the interaction of radiation with bound electrons surrounding the atoms or forming chemical bonds.

Alternatively, if there are nearby energy levels available to the electrons, they may be excited into these levels by interaction with the electromagnetic wave. Therefore, the electromagnetic wave may be appreciably absorbed (k is large) as well as slowed down (n is large). When this occurs the reflectivity is high (compare equation 2) because light is re-emitted when the excited electrons return to the ground-state. Such a situation applies to metals over a wide range of energies in the electromagnetic spectrum, as well as to most opaque minerals.

Mott and Jones (1936) have given an expression which relates the optical constants of a solid to various types of interaction of the electromagnetic radiation with electrons

$$n^2 - k^2 = 1 - \underbrace{\frac{4\pi n_{\mathrm{eff}} e^2}{m(\omega_0^2 - \omega^2)}}_{(a)} + \underbrace{(\epsilon - 1)_{\mathrm{core}}}_{(b)} + \underbrace{(\epsilon - 1)_{\mathrm{photo}}}_{(c)} \tag{3}$$

where e, m and ω are the charge, mass and angular frequency of an electron, respectively; ϵ is the dielectric constant of the medium; and n_{eff} is the effective number of free electrons per atom or molecule.

The first term (a) in equation 3 is the free electron contribution, which predominates in metals. The second term (b) refers to the interaction with core electrons, such as those surrounding ions in ionic crystals or forming covalent bonds in molecular crystals. The third term (c) takes into account intraelectronic transitions, such as crystal field phenomena in transition elements. It also includes the internal photoelectric effect in metals.

In order to gain an insight into the significance of n_{eff}, the energy levels of electrons in crystals must be considered in terms of band theory of solids and molecular orbital theory.

CONCEPT OF EFFECTIVE NUMBER OF FREE ELECTRONS

Metals. The band theory of metals may be illustrated with reference to sodium, which has the electronic configuration $1s^2 2s^2 2p^6 3s^1$. In the ground-state of an isolated atom, the 3*s* electron occupies a single energy level. However, in a crystal of metallic sodium overlap of orbitals occurs to give a band of closely spaced energy levels. Each sodium atom contributes one atomic orbital to the 3*s* band, and since each orbital can accomodate two electrons, the valence band is half-filled in sodium at absolute zero. This defines the Fermi level, which is the level that divides the filled and vacant energy levels at a particular temperature. Electrons near the top of the filled zone can readily move to and from the unfilled levels within the valence band. The availability of empty levels adjacent to the Fermi level accounts for the high absorption of electromagnetic radiation in the infrared and visible by sodium and hence its high reflectivity. The electrons are delocalized and not located on one sodium atom. In other words, the electrons are effectively free, although n_{eff} is smaller than unity per sodium atom because in the crystal structure the lattice field tends to reduce the freedom of the electrons.

In metals other than sodium and the alkali metals interaction between the uppermost *s* and *p* levels occurs to give a valence band consisting of a hybrid of closely spaced *s–p* energy levels. The high reflectivity is again related to the availability of empty levels in the valence band adjacent to the Fermi level into which electrons may be excited by absorption of electromagnetic radiation. In some metals, transitions are also possible between occupied inner *d* levels and unfilled outer *s–p* levels, leading to color in such metals as Cu and Au. Such effects contribute to the $(\epsilon - 1)$ photo term in equation 3.

Since the contribution from free electrons predominates in metals, reflectivity variations should parallel the effective number of free electrons. Indeed, Figure 1 shows that high reflectivities of Ag and Au may

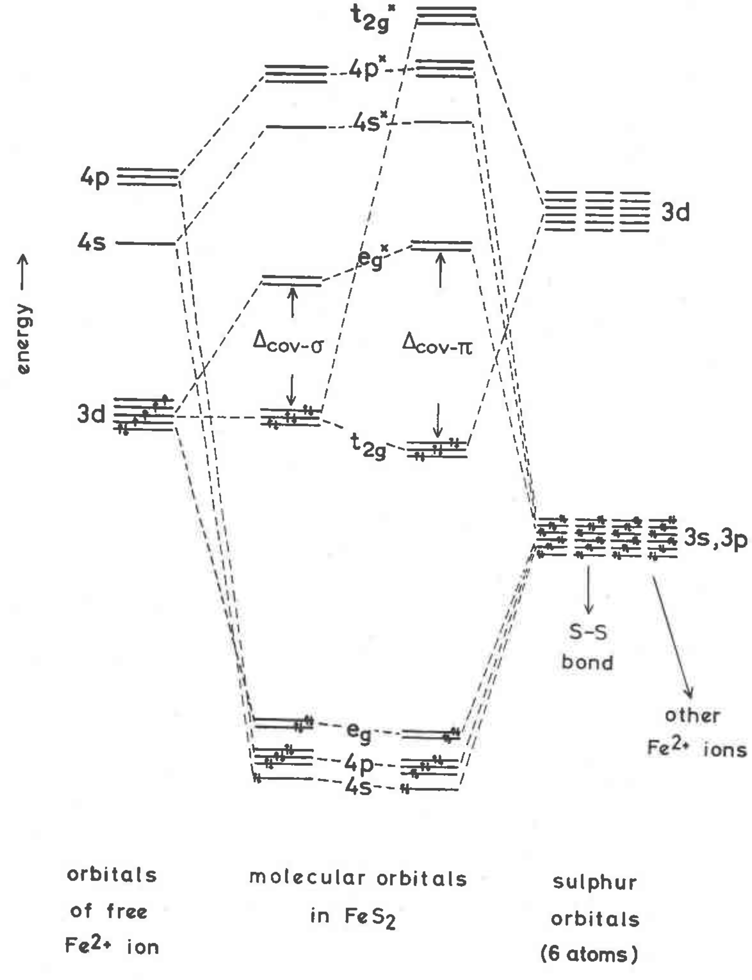

FIG. 2. Molecular orbital energy level diagram for pyrite.

be correlated with large values of N_{eff} recalculated from the n_{eff} data quoted by Mott and Jones (1936), according to the formula

$$N_{\mathrm{eff}} = n_{\mathrm{eff}} \frac{100\,Z}{a^3} \tag{4}$$

where a is the cell edge and Z is the number of atoms, molecules or formula units per unit cell.

TABLE 1. REFLECTIVITIES, EFFECTIVE NUMBER OF FREE ELECTRONS AND ELECTRONIC CONFIGURATIONS OF CATIONS IN THE PYRITE-TYPE DISULPHIDES

		FeS_2	CoS_2	NiS_2	CuS_2
Reflectivity at 496 nm (2.5 eV)[a]		51.6	34	27	17
n_{eff} at 496 nm[b]		1.18	0.88	0.51	0.30
N_{eff} at 496 nm[c]		2.97	2.08	1.11	0.62
electronic configurations of the metal 3*d* orbitals	e_g	—— ——	—— ---- E_F ↑	↑ ↑	---- E_F ↑ ↑ ↓
		---- E_F			
(E_F=Fermi level)	t_{2g}	↑ ↓ ↑ ↓ ↑ ↓	↑ ↓ ↑ ↓ ↑ ↓	↑ ↓ ↑ ↓ ↑ ↓	↑ ↓ ↑ ↓ ↑ ↓

[a] Calculated by the Fresnel equation from the *n* and *k* data of Bither *et al* (1968).

[b] Cited by Bither *et al* (1968)

[c] Calculated from equation 4.

Pyrite-Type Compounds. The energy levels in transition metal dichalcogenides have been discussed by Bither *et al.* (1968). We shall extend their treatment to include the possibility of π-bond formation (Burns, 1970). The pyrite structure is modelled on the halite structure with transition metal ions occupying sodium positions and the midpoints of the $(S—S)^{2-}$ groups located at the chlorine positions. Each cation is in octahedral coordination with one sulphur atom belonging to six different $(S—S)^{2-}$ groups, and the octahedral sites are compressed along a trigonal axis. Each sulphur atom uses hybridised sp^3 orbitals and is tetrahedrally coordinated to three cations and the other sulphur atom of the $(S—S)^{2-}$ group.

The energy level diagram for FeS_2 is shown in Figure 2. One hybrid sp^3 orbital from each of the six sulphur atoms in octahedral coordination forms a σ-bond with the central transition metal ion. The six σ molecular orbitals of the transition metal are formed by d^2sp^3 hybrids consisting of the two e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}), the one 4*s* orbital and the three 4*p* orbitals. Bither *et al.* (1968) assumed that the three t_{2g} orbitals (d_{xy}, d_{yz} and d_{xz}) of the transition metal remain non-bonding. The energy separation between non-bonding t_{2g} and antibonding e_g^* orbitals is designated $\Delta_{cov-\sigma}$, and is analogous to the energy splitting in crystal field theory

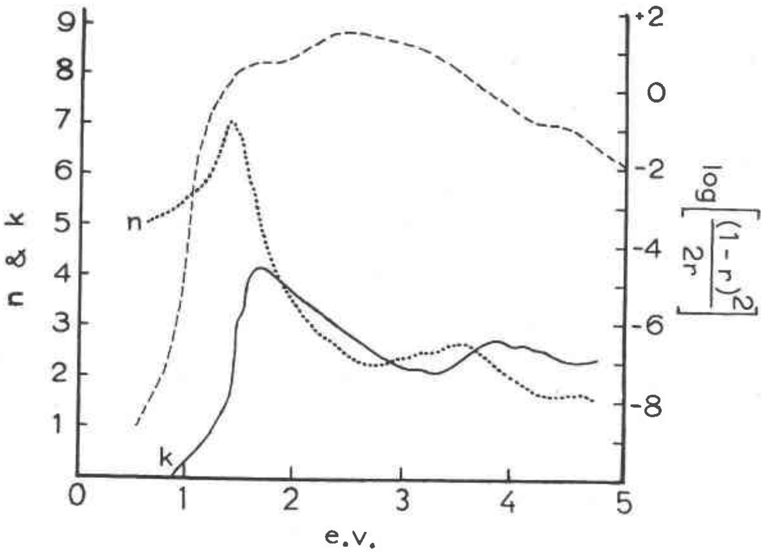

FIG. 3. Plot of n and k for FeS_2 (after Bither *et al*, 1968) The diffuse reflectance spectrum of FeS_2 is also shown, plotted as the Kubelka-Munk function $\log_{10}((1-r)^2/2r)$. This function is derived from the measured absorbance A, where $A = -\log_{10} r$, and is proportional to k.

(Orgel, 1966; Burns, 1970). The two electrons in each sulphur hybrid sp^3 orbital fill completely the σ molecular orbitals, while the $3d$ electrons of the transition metal occupy non-bonding t_{2g} orbitals (and e_g^* orbitals in transition metal ions other than Fe(II)). The electronic configurations of cations in the transition metal (II) disulphides are thus: Mn(II), $(t_{2g})^3(e_g^*)^2$; Fe(II), $(t_{2g})^6$; Co(II), $(t_{2g})^6(e_g^*)^1$; Ni(II), $(t_{2g})^6(e_g^*)^2$; Cu(II), $(t_{2g})^6(e_g^*)^3$ (see Table 1.). Note that Fe(II) and Co(II) have low-spin configurations in the pyrite-type compounds.

The paired electrons in non-bonding t_{2g} orbitals are capable of forming π-bonds with vacant t_{2g}-type $3d$ orbitals of the sulphur atoms (Burns, 1970, p. 181). This results in increased energy separation between non-bonding t_{2g} and anti-bonding e_g^* levels, so that $\Delta_{cov-\pi} > \Delta_{cov-\sigma}$. Since low-spin Fe(II) contains no electrons in e_g^* orbitals which repel sulphur ligands, π-bonding is most efficient in FeS_2. Thus, the order of decreasing $\Delta_{cov-\pi}$ is expected to be $FeS_2 > CoS_2 > NiS_2 > CuS_2 \gg MnS_2$. This interpretation differs from that proposed by Bither *et al.* (1968).

Extensive covalent bonding between transition metal and sulphur atoms leads to delocalization of electrons in antibonding e_g^* and t_{2g}^* orbitals. Electrons excited into e_g^* orbitals become delocalized from the cation and are analogous to the effectively free electrons of metals.

Bither *et al.* (1968) computed values of n and k for a variety of transition metal (II) dichalcogenides from single crystal spectral reflectivity measurements. The data for pyrite are reproduced in Figure 3, together with the diffuse reflectance spectrum obtained in the present study. An absorption maximum is located at about 1.7 eV (730 nm), indicating that pyrite has a higher reflectivity in the red end of the visible spectrum than at the blue-end, accounting for the yellow color of pyrite. Absorption of energy beyond 0.9 eV was attributed by Bither *et al.* (1968) to the onset of $3d$ electron transitions between t_{2g} and $e_g{}^*$ levels. Absorption maxima corresponding to that at 1.7 eV in pyrite are observed at progressively lower energies in the sequence FeS_2-CoS_2-NiS_2-CuS_2 which may be correlated with the order of decreasing $\Delta_{\mathrm{cov}-\pi}$.

From the oscillator strengths of the absorption bands Bither *et al.* (1968) estimated values of n_{eff} (per molecule) at various excitation energies. The values at 496 nm (2.50 eV) are summarized in Table 1, together with the electronic configurations of the transition metals and the Fermi levels. Since reflectivities are measured over selected areas of crystals and light penetrates to at least 100 Å in most opaque solids, the n_{eff} values have been recalculated by equation 4 to give N_{eff} data per unit volume (100 cubic Å). The reflectivities in Table 1 were calculated from the Fresnel equation (equation 2), using the n and k data of Bither *et al.* (1968) at 496 nm. The calculated value for pyrite (51.6%) is in good agreement with the value (51%) calibrated for the pyrite standard N 1915.1.

The data in Table 1, which are also illustrated in Figure 1, show that a comparatively large value of N_{eff} is associated with high reflectivity. More significantly, however, the values of n_{eff} are roughly proportional to the number of energy levels available to the t_{2g} electrons excited into the $e_g{}^*$ orbitals. Thus, Bither *et al.* (1968) noted that the ratios of n_{eff} are $FeS_2:CoS_2:NiS_2:CuS_2 = 1.18:0.88:0.51:0.30 = 4.0:3.0:1.7:1.0$. Alternatively, high values of n_{eff} are associated with electronic configurations in which the Fermi level lies nearby or in the midst of closely spaced energy levels.

Therefore, the comparatively high reflectivity of pyrite is the result of several energy levels lying close to the Fermi level into which t_{2g} electrons may be excited. Electrons in these $e_g{}^*$ orbitals become delocalised (effectively freed from the cation) through the efficiency of covalent bonding between the iron and sulphur atoms.

EXTENSIONS TO OTHER COMPOUNDS

Selenides and Tellurides. Marked variations in reflectivity with anion composition are commonly observed in isostructural compounds and minerals of different metals with sulphur, selenium and tellurium. Such variations may be explained by the increased covalent character and electron delocalisation of the metal-chalcogen bond with rising atomic number in the series S—Se—Te.

Bither *et al.* (1968) calculated values of the effective number of free electrons in synthetic CuS_2, $CuSe_2$ and $CuTe_2$. The values increase in the order $CuS_2 < CuSe_2 < CuTe_2$, which parallels the order of increasing reflectivity (Figure 1). The efficiency of covalent bonding increases with size, and hence polarizibility, of the anions. As a result, delocalisation of excited t_{2g} electrons of copper is increased along the series CuS_2- $CuSe_2$-$CuTe_2$. The increased reflectivity in this series is thus the result of increased electron delocalisation or N_{eff}.

A similar trend might be expected in other series of metal chalcogenide minerals. For example, reflectivities of the isomorphous lead minerals are PbS (galena) 38 percent, PbSe (clausthalite) 50 percent, and PbTe (altaite) 65.5 percent (Travis, 1966). For copper, the ranges of reflectivity are 3.5–21 percent for CuS (covellite) and 10–27 percent for CuSe (klockmannite). In the case of mercury, HgSe (tiemannite) and HgTe (coloradite), each possessing the sphalerite structure, have reflectivities in the ranges 25–27 percent and 37 percent, respectively (de Montreuil Diaz, 1968) whereas the reflectivity range of HgS (cinnabar) having a structure with hexagonal symmetry is only 21–25 percent. The latter example illustrates that semi-quantitative predictions about reflectivity variations are not necessarily confined to a series of isostructural minerals.

Monosulphides. Semiquantitative predictions of relative reflectivity may also be made from a knowledge of the electronic configurations of a series of transition metal ions in minerals. For example, monosulphides with the nickel arsenide structure occur as the minerals troilite (FeS) and jaipurite (CoS). Synthetic isostructural NiS is also known. Magnetic data suggest the following electronic configurations of the divalent cations

Fe(II) in FeS : $(t_{2g})^4(e_g^*)^2$
Co(II) in CoS : $(t_{2g})^6(e_g^*)^1$
Ni(II) in NiS : $(t_{2g})^6(e_g^*)^2$

Thus, only cobalt has a low-spin configuration in this series.

Each of these monosulphides has metallic properties, resulting in part from metal-metal interactions between adjacent cations in nickel arsenide type-structures. By analogy with the pyrite-type disulphides, the position of the Fermi level and efficiency of metal-sulphur covalent bonding should determine the relative reflectivities of the monosulphides. The position of the Fermi level in Co(II) and the greater extent of covalent bonding through π-bond formation leads to a predicted order of reflectivity $FeS < CoS > NiS$, which is in good agreement with the measured values of $FeS \approx 40$, $CoS \approx 50$, and $NiS \approx 47$ percent.

Zinc (II) and manganese (II) have electronic configurations with completely filled and half-filled 3*d* orbitals, respectively, in their sulphide phases. This leads to reduced covalent bonding and high lying Fermi levels compared with iron (II), cobalt (II) and nickel (II). The reflectivities of sphalerite (ZnS), 15.3–15.9, and alabandite (MnS), 20, as well as hauerite (MnS_2), 17.7–19.6 percent, are therefore predictably lower than the corresponding sulphides of iron, cobalt and nickel.

Calculated Reflectivities of Bravoites. The N_{eff} data in Table 1 may be used to estimate the reflectivities of bravoites of known composition. For example, consider the bravoite $(Fe_{0.20}Co_{0.39}Ni_{0.41})S_2$. The reflectivity of this composition may be estimated as follows, using the calculated reflectivity of pyrite, 51.6 percent, obtained from the *n* and *k* data of Bither *et al.* (1968) and the Fresnel equation (equation 2):

20% FeS_2 with reflectivity 51.6 = 10.3%
39% CoS_2 with reflectivity $(51.6 \times 2.08/2.97)$ = 14.1
41% NiS_2 with reflectivity $(51.6 \times 1.11/2.97)$ = 7.9
total 32.3%

The calculated value, 32.3 percent, is in excellent agreement with the measured value of 32.9 percent at 496 nm, for a bravoite of similar composition, which has been interpolated from the reflectivity data of Demirsoy (1969).

Therefore, reflectivities of pyrite-type solid solutions may be estimated accurately from the N_{eff} values of the components.

CONCLUDING REMARKS

The present study indicates how the optical properties of ore minerals may be related to the band structure of solids. Experimentally determined values of *n* and *k*, obtained from specular reflectivity spectra, may be used to calculate percent reflectivities and the effective number of free electrons in the visible region. The compositional variations of reflectivity in solid-solution series are related to changes in the effective number of free electrons in excited energy levels, resulting from delocalisation of cation electrons in antibonding molecular orbitals. High N_{eff} values are associated with a large number of closely spaced energy levels above the Fermi level.

Although only the monosulphides and pyrite-type phases of certain metals have been discussed, the principles described in this paper have application to other mineral groups. For example, the lack of reflectivity variations in skutterudites, pentlandites and iron-containing sphalerites, suggest that only minor changes in the band structure occur in these phases with changing composition. Further semi-quantitative interpretations of reflectivity variations in most ore minerals will depend on the availability of N_{eff} data from specular reflectivity spectral measurements.

ACKNOWLEDGMENTS

We wish to thank Professor A. P. Millman for providing reflectivity data. This work was supported by grants from the Natural Environment Research Council.

REFERENCES

BITHER, T. A., R. J. BOUCHARD, W. H. CLOUD, P. C. DONOHUE, AND W. J. SIEMONS (1968) Transition metal dichalcogenides. High pressure synthesis and correlation of properties. *Inorg. Chem.* **7,** 2208–2220.

BURNS, R. G. (1970) *Mineralogical Applications of Crystal Field Theory.* Cambridge University Press, London.

DEMIRSOY, S. (1969) Untersuchungen über den Einfluss der chemischen Zusammensetzung auf die Spektralen Reflexionsfunktionen und Mikroeindruckhörten im System FeS_2–NiS_2–CoS_2, an Zonen eines naturlichen Bravoit-Kristalls. *Neues Jahrb. Mineral., Monatsh.* **17,** 323–333.

FREUND, H. (ed.) (1966) *Applied Ore Microscopy. Theory and Technique.* Macmillan, New York.

JENKINS, F. AND H. E. WHITE (1957) *Fundamentals of Optics.* McGraw-Hill, New York.

DE MONTREUIL DIAZ, L. A. (1968) *Mineralogy and Geochemistry of Selenides.* M.Sc. Thesis, Univ. of London.

MOTT, N. F., AND H. JONES (1936) *The Theory of the Properties of Metals and Alloys.* Dover, New York.

SINGH, D. S. (1965) Measurement of spectral reflectivity with the Reichert microphotometer. *Trans. Inst. Mining Met.* **74,** 901–916.

SPRINGER, G., D. SCHACHNER-KORN, AND J. V. P. LONG (1964) Metastable solid solution relations in the system FeS_2–CoS_2–NiS_2. *Econ. Geol.* **59,** 475–491.

SQUAIR, H. (1965) A reflectometric method of determining the silver content of natural gold alloys. *Trans. Inst. Mining Met.* **74,** 917–931.

TRAVIS, G. A. (1966) *Gold and Telluride Mineralization at Kalgoorlie, Western Australia.* M.Sc. Thesis, Univ. of London.

VAUGHAN, D. J. (1969) Zonal variation in bravoite. *Amer. Mineral.* **54,** 1075–1083.

WERT, C. A., AND R. M. THOMSON (1964) *Physics of Solids.* McGraw-Hill, New York.

Manuscript received February 28, 1970, accepted for publication, March 16, 1970.