

BOND STRENGTHS IN THE DISULPHIDES OF IRON, COBALT AND NICKEL *

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ABSTRACT

Microhardness values decrease in the sequence $\text{FeS}_2 > \text{CoS}_2 > \text{NiS}_2$. This is attributed to decreasing metal-sulphur bond strengths through the sequence. The decreasing metal-sulphur bond strengths which are attributed largely to ligand-field stabilization effects, are approximately balanced by increasing strength of the sulphur-sulphur bonds, so that the total cohesive energy remains relatively unchanged.

INTRODUCTION

The relationship between the hardness and crystal chemistry of minerals has been explored by various investigators. The most comprehensive works in recent years appear to have been those of Povarennykh, and of Plendl & Gielisse, both having published a number of papers on the subject (Povarennykh 1959; Plendl & Gielisse 1962, 1963).

The disulphides of Fe, Co and Ni, all of which crystallize in the pyrite structure, provide the opportunity of examining the various members of a structural group in which only the metal atom is changed, thereby providing information that permits a systematic development of concepts regarding bond strengths in transition-metal sulphides.

EXPERIMENTAL PROCEDURE

Samples

Samples of pyrite from Spain, and of catterite from Shinkolobwe, Katanga, were obtained from Mr. H. R. Steacy, curator of the systematic reference series of the National Mineral Collection, Ottawa. Synthetic crystals of FeS_2 , CoS_2 and NiS_2 were grown in our laboratories by the procedure outlined below. Synthetic polycrystalline NiS_2 for infrared examination was produced by Dr. L. J. Cabri, of the Mineral Sciences Division, by reaction of the elements in a sealed evacuated silica tube.

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Crystal growth

Crystals of the pyrite-type disulphides of Fe, Co and Ni were grown by two different methods: halogen transport and flux growth. Both methods produced a multitude of single crystals averaging about 1mm in diameter.

In the vapour-transport method, a procedure similar to that of Bouchard (1968) was employed, except that iodine, rather than chlorine was used. The nutrient material was prepared in a two-step procedure: Good-grade metal (Sherritt-Gordon nickel powder; Fisher's reagent-grade cobalt; N.B.S. iron) was heated in a stream of H_2S to form a slightly sulphur-rich monosulphide and also to remove any oxygen from the metals. The resulting monosulphide was placed in a 13-mm-i.d. silica tube with just enough sulphur of 99.999% purity to correspond to a 1:2 metal:sulphur ratio. The tubes were evacuated to 10^{-4} mm Hg, 75 to 100 mg of iodine vapour (I_2) was admitted by sublimation, and then the tubes were sealed to give capsules 12 to 14 cm. long. The tubes were heated for several hours to achieve equilibrium, and were then put in a static temperature gradient for periods ranging from 38 to 68 days, for the actual crystal growth. The temperature gradient was 750° to $620^\circ C$ for the FeS_2 , and 850° to $750^\circ C$ for the CoS_2 and NiS_2 .

In the flux method, a procedure similar to that of Wilke, Schultze & Töpfer (1967) was used. Nutrient material consisting of good-grade metal and 99.999% sulphur (the latter in amounts exceeding the 1:2 stoichiometric ratio by 1 mole) was placed in a quartz tube with reagent-grade lead chloride, and sealed under vacuum. Crystal growth was achieved by heating the flux mixture to $750^\circ C$, then cooling slowly by manually decreasing the temperature $5^\circ C$ per hour during the working day, followed by a period of constant temperature during the night. This cooling cycle was repeated several times until a temperature of $520^\circ C$ was reached, after which the charge was cooled rapidly to room temperature. The flux was removed from the crystals by leaching with a hot acidic solution, followed by hot water, and finally by methanol.

Microhardness determination

The crystals were embedded in cold-setting resin (Araldite 502 with Hardener 956) and polished on a Durener automatic polishing machine, equipped with lead polishing laps and diamond polishing media, followed by final light polishing on a cloth lap with 0.05 micron MgO. The measurements were made with a Leitz Durimet microhardness tester, equipped with a pyramidal indenter corresponding to the Vickers standard.

A 50 g load was used throughout the measurement procedure, this being a compromise between heavier loads, that produced excessive fracturing, and lighter ones that made only small indentations that are difficult to measure accurately. This weight produced indentations with diagonals of the order of 10 microns. Both diagonals were measured, and the Vickers hardness number (VHN) in kg/mm^2 , was calculated from the formula $\text{VHN} = \frac{1854.4P}{d^2}$, where P is the load in grams, and d is the mean length of the diagonals in microns.

For the pyrite measurements, ten indentations were made on a (111) section cut from a large crystal. For the cattierite and the synthetic sulphides, oriented crystals could not be obtained conveniently, so measurements were made on ten randomly selected grains of each sulphide. In a few instances, the grains were severely fractured on impact with the indenter but these values were not included in the results; extra measurements were made to bring the number of acceptable measurements to ten.

Infrared absorption

The infrared spectra were made by Dr. A. H. Gillieson, of the Mineral Sciences Division, on the natural crystals of pyrite and cattierite, and on the synthesized polycrystalline sample of NiS_2 . The measurements were made by transmission through wafers of CsI containing about 0.5% of the sulphides, using a Beckman IR-12 instrument. Details are given by Gillieson (1970).

RESULTS OF MICROHARDNESS DETERMINATIONS

Practically all the indentations, both on the natural and synthetic samples, exhibited some fracturing. This fracturing probably had some effect on the sizes of the indentations obtained, and probably accounts for the rather substantial standard deviations of the measurements.

The results of the microhardness determinations are shown in Table 1, which also includes values for the three minerals reported by Demirsoy (1969). The agreement with Demirsoy's values are quite good for CoS_2 and NiS_2 , but our values for FeS_2 are much lower. Our values fall between those of Demirsoy, which appear to be the highest reported to date, and those of most other investigators (e.g. Bowie & Taylor 1958; Young & Millman 1964); this can probably be attributed chiefly to the difference in indenting weights employed in the determinations since

TABLE I. MICROHARDNESS OF NATURAL AND SYNTHETIC DISULPHIDES OF Fe, Co AND Ni

Sample	Microhardness		(VHN)	Standard Deviation	Values taken from Demirsoy (1969)
	Min.	Max.	Av. of 10		
Pyrite, Spain	1764	2412	1977	185	
FeS ₂ , synthetic	1604	2759	2064 *	292	2894-3548
Cattierite, Katanga	965	1283	1143	91	
CoS ₂ , synthetic	766	1380	1120 *	157	953-1113
NiS ₂ , synthetic	594	1028	883 *	145	733-856

* These values have been reported in a previous paper (Nickel 1970).

the apparent microhardness is known to increase with decreasing indenting load (Young & Millman 1964). Nevertheless, our pyrite value, which is in the neighbourhood of VHN 2000 (\sim 8.0 on Mohs' scale) is still appreciably higher than the hardness value given in standard mineralogical texts (6.0-6.5). To determine whether pyrite is harder or softer than quartz, which is the Mohs' standard for 7.0, we made extensive microhardness measurements on oriented (100), (110) and (111) sections of pyrite and on a basal section of Brazilian quartz, and found that pyrite (in all orientations) gave consistently higher values than quartz, at indenting loads of both 50 g and 100 g. This apparent conflict between our results and those given in the literature can probably be attributed to the different methods employed in the hardness determinations; most older reports were based on scratch tests whereas ours were made by indentation.

The significant aspect of this study, however, is that the hardness values of the investigated minerals decreases in the sequence $\text{FeS}_2 > \text{CoS}_2 > \text{NiS}_2$.

THERMODYNAMIC CONSIDERATIONS

Estimates of the cohesive energies of the disulphides can be obtained from the energy change in the reaction $M(\text{g}) + 2\text{S}(\text{g}) = \text{MS}_2(\text{s})$ where M = the metal under consideration, and (g) and (s) represent the gaseous and solid states, respectively. In other words, this gives the energy liberated when the atoms, initially separated from each other at infinite distance, come together to form the solid. This reaction can be broken down into a series of reactions, for which thermochemical data are available, as shown in Table 2.

The total cohesive energies obtained in this way are all very similar, the slight differences between the values for the different disulphides

TABLE 2. COHESIVE ENERGIES OBTAINED FROM THERMODYNAMIC DATA AT 25°C.

	Fe kcal/mole	Co kcal/mole	Ni kcal/mole	Reference
M(g) → M(s)	- 97	-102.7	-101.8	Samsonov (1968)
2S(g) → 2S(s)	-106.6	-106.6	-106.6	Samsonov (1968)
M(s) + 2S(s) → MS ₂ (s)	- 42.4	- 33.5	- 34.0	Kubaschewski & Evans (1967)
Total Cohesive Energy	-246	-243	-242	

probably not being of any real significance, considering the experimental uncertainties in arriving at the thermochemical values used. In other words, thermodynamic calculations do not mirror the pronounced hardness differences between the three minerals. As will be shown later, this is probably because the thermodynamic calculations give the total cohesive energies, whereas the hardness depends largely on the strengths of the weakest bonds.

ENERGIES OF METAL-SULPHUR BONDS FROM INFRARED DATA

Energies of the metal-sulphur bonds (as distinct from the total cohesive energy) can be obtained from the infrared absorption spectra according to the methods outlined by Plendl (1961). Although Plendl's method is supposed to give the total cohesive energy for simple compounds, in the disulphides considered here the infrared vibrational spectrum can be attributed entirely to the metal-sulphur bonds. Sulphur-sulphur bonds would not be expected to give rise to infrared absorption because the sulphur atoms are structurally identical.

As reported by Gillieson (1970), the infrared absorption spectrum of pyrite gives three sharp peaks at 416, 350 and 293 cm⁻¹, which gives a median frequency of 353 cm⁻¹. The cattierite spectrum shows some similarity to that of pyrite, but contains several extra peaks; the median frequency is 335 cm⁻¹. The NiS₂ spectrum is extremely complicated, perhaps due to structural imperfections, and has a median frequency of 310 cm⁻¹.

Assignment of the individual absorption peaks is beyond the scope of this paper. However, Plendl (1961) has shown that useful information can be obtained from the vibration spectrum as a whole, by the introduction of the concept of the centre of gravity of the lattice vibration spectrum. This involves integration of the vibration spectrum. For the

disulphides considered here, the vibration spectrum is partially superimposed on a steep absorption edge, so that integration in this case would lead to serious errors. The problem was therefore simplified by taking the median of the absorption spectrum as the centre frequency ν_c . The values of ν_c are obtained by multiplying the median wave number values by 2.998×10^{10} , which gives the frequency in Hz. As shown in Table 3, the centre frequency decreases through the sequence $\text{FeS}_2 > \text{CoS}_2 > \text{NiS}_2$.

The cohesive energy (U) can be calculated from the centre frequency by means of Plendl's (1961) formula :

$$U = 0.5 Z m_r (\omega_c r_o X m^{-1/p})^2,$$

where Z is the valency within the molecule (2 in this case)

m_r is the reduced mass of the metal-sulphur pair

$\omega_c = 2\pi\nu_c$ is the mean angular frequency

r_o is metal-sulphur distance in the structure

$Xm = 3.226 \times 10^{22} m_r$

$p = 9$.

The result, in ergs/molecule, when multiplied by the factor $\frac{2.389 \times 10^{-11}}{1.66 \times 10^{-24}}$ gives the cohesive energy in kcal/mole (Table 3). The actual values of the volumetric lattice energies (U/V) obtained by the Plendl calculations are substantially smaller than what might be expected on the basis of the hardness measurements using the relationship between hardness and volumetric lattice energy developed by Plendl & Gielisse (1962, 1963). This is probably because the effect of sulphur-sulphur bonding has not been taken into account in calculating the lattice energies.

TABLE 3. CALCULATION OF METAL-SULPHUR COHESIVE ENERGIES FROM INFRARED DATA

	FeS ₂	CoS ₂	NiS ₂
Median wave number (cm ⁻¹)	353	335	310
ν_c (Hz)	10.56×10^{12}	10.04×10^{12}	9.29×10^{12}
m_r (g)	33.80×10^{-24}	34.46×10^{-24}	34.42×10^{-24}
r_o (cm)	2.259×10^{-8}	2.315×10^{-8}	2.396×10^{-8}
$Xm^{-1/p}$ (g)	0.991	0.990	0.990
U (kcal/mole)	1070	1037	950
Mol. wt. (g)	119.97	123.06	122.83
Density (g/cm ³)	5.013	4.851	4.459
U/V (kcal/cm ³)	44.4	40.9	34.5

DISCUSSION

The thermodynamic calculations show that the total cohesive energies of the disulphides under consideration are approximately equal, but consideration of the metal-sulphur bond strengths and microhardness values indicates a decrease in the sequence $\text{FeS}_2 > \text{CoS}_2 > \text{NiS}_2$. To reconcile these observations it would be reasonable to conclude that the strengths of the sulphur-sulphur bonds must increase through this sequence. Interatomic sulphur-sulphur distances give some indication of bond strengths, shorter distances indicating greater bond strengths. The sulphur-sulphur distances are: FeS_2 2.171, CoS_2 2.124, and NiS_2 2.065 Å (Elliott 1960), which indicates progressive strengthening of the bonds through the sequence. It appears, therefore, that the sulphur-sulphur bonds are strengthened in proportion to the weakening of the metal-sulphur bonds.

The changing metal-sulphur bond strengths can be attributed to ligand-field stabilization, since the stabilization factors for the metals under consideration, in a low-spin state and in octahedral coordination are: Fe 2.4, Co 1.8 and Ni 1.2 (Orgel 1960, p. 47). Added to this is the optical evidence that $10 Dq$, the separation between the e_g and t_{2g} energy levels of the metal atom, also decreases steeply through the series FeS_2 – CoS_2 – NiS_2 (Bither *et al.* 1968). This stabilization has the effect of depressing the energies of the t_{2g} d -electron orbitals of iron more than cobalt, and cobalt more than nickel, so that greater mixing with the sulphur orbitals can occur at the iron end of the series than at the nickel end. The consequence of this is likely to be a decreasing degree of π -bonding (Burns & Vaughan 1970), and hence decreasing bonding strength between metal and sulphur atoms through the series FeS_2 – CoS_2 – NiS_2 .

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