

THE CRYSTAL STRUCTURE OF MILLERITE

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ABSTRACT

The availability of good data on the crystal structures of sulphides is essential for the understanding of sulphide crystal chemistry, but, until recently, few reliable refinements have been published. Because of this, the structure of a single crystal of millerite from Quebec, Canada, with $a = 9.6190(5)$, $c = 3.1499(3)$ Å, space group $R\bar{3}m$, $Z = 9$ and composition $Ni_{1.08}Fe_{0.019}Co_{0.004}S$ has been refined using absorption corrected intensity data to an R factor of 1.4%. The Ni and S atoms are in five-fold coordination (tetragonal pyramidal) with each other. The new interatomic distances are: Ni-S = 2.261(2) Å, 2.261(1) Å (x2) and 2.383(1) Å (x2) and Ni-Ni = 2.534(1) Å (x2) and 3.150 Å (x2). The average Ni-S distance, 2.310 Å, is consistent with a divalent Ni in five-fold coordination. It is suggested that the metal-metal bonding and the formation of the trinuclear cluster are significant in stabilizing the millerite structure.

INTRODUCTION

The transition metals Fe, Co and Ni form several isotypic series of sulphide structures which include monosulphides with the nickel arsenide structure, disulphides with the pyrite structure, thiospinels and the pentlandite series. In addition, each metal is found in special structures in which the solid solution of the other two metals is rather limited. For example, Ni occurs in at least three such structures, millerite (NiS), heazlewoodite (Ni_3S_2) and Ni_7S_6 , all of which contain very small amounts of Fe and Co. The reason for this limited substitution has not been satisfactorily explained, perhaps because of lack of detailed crystal chemical data for these Ni sulphides. Ionic radii have been used to predict solid solution behavior of cations in silicates and oxides. These radii values which are obtained from oxides and fluorides cannot be used with success for sulphide structures because the cation-anion bonding is more covalent and complications exist because of anion-anion repulsion, metal-metal interaction, and variable spin states of cations. Further, valencies of cations in the strict chemical sense have less meaning in sulphides because of the delocalization of electrons. However, we can use interatomic distances, to

some extent, to predict probable cation valencies and spin states for a given coordination number. Thus, we need to have such distances from many different structures to understand the crystal chemistry of transition metal sulphides.

The monosulphide of Ni is dimorphic. The high-temperature form has the NiAs-type structure. The low-temperature form, millerite, is rhombohedral. The transition from NiAs-type to millerite takes place around 400°C (Kullerud & Yund 1962) with concomitant change in electrical and magnetic properties (Jellinek 1970). The structure, based on powder x-ray data (Alsen 1925; Kolmeijer & Moesveld 1931), consists of infinite trigonal prisms of S atoms extending in the c direction with Ni atoms located slightly above the square faces of these prisms. This arrangement of atoms gives rise to a five-fold coordination of Ni which is not very common among sulphide crystal structures. Five-coordinated Ni(II) atoms with sulphur ligands have been observed in the compound $BaNiS_2$ (Grey & Steinfink 1970).

Recently, Fleet (1972) refined the structure of synthetic α Ni_7S_6 using single-crystal diffraction techniques and observed a similarity between the pyramidal site of this structure and the Ni sites in the millerite structure. However, the details of the millerite structure are poorly known and many authors (Wyckoff 1963; Pearson 1972) expressed the need for its structure refinement using modern single x-ray diffraction techniques. Further, although millerite satisfies the criterion for semi-conductivity, it is reported to be metallic and Pauli paramagnetic. The structural reasons for its metallic properties are not clear. As a part of our general study to characterize sulphide structures showing metallic properties and to understand the crystal chemistry and bonding in sulphides, the refinement of the structure of millerite was undertaken and is reported here. The results were presented orally at the A.C.A. Meeting held at Storrs, University of Connecticut, in June, 1973 (Rajamani & Prewitt 1973).

EXPERIMENTAL

Single crystals of millerite* were separated from a massive ore specimen from Quebec, Canada. An approximately rectangular crystal of dimension 0.09 mm × 0.05 mm × 0.03 mm was mounted on the a^* axis and precession photographs were taken. The diffraction symmetry and systematic absences ($-h + k + l = 3n$) indicated three possible space groups, $R\bar{3}m$, $R3m$ and $R32$. The cell dimensions were calculated from 20 values measured on the single-crystal diffractometer. A few x-rayed crystals were mounted and a polished section was made for microprobe analysis using an ARL-electron microprobe. Homogeneous and stoichiometric single crystals of FeS_2 , NiS_2 and CoS_2 were used as standards for Fe, Co, Ni and S. Analyses indicated that millerite is slightly cation-rich, in agreement with the observation made by Misra & Fleet (1973). The composition, cell parameters and calculated density, are listed in Table 1.

Integrated intensities of 435 reflections were collected (within the range of $\sin \theta/\lambda = 0.06 - 0.70$) automatically on a PDP-15/35 controlled Picker diffractometer at room temperature using a graphite monochromator and $MoK\alpha$ radiation. A scan speed of $2^\circ/\text{min}$ was used and background counts were accumulated for five seconds on both sides of each peak. A standard reflection was measured for every 20 reflections. After applying Lorentz and polarization corrections, the intensity data were converted into observed structure factors. As the linear absorption coefficient was 180 cm^{-1} , absorption correction was applied using the method of Wuensch & Prewitt (1965). The resulting transmission factors varied between 0.25 and 0.58. The absorption-corrected, observed structure factors of the symmetry-equivalent reflections were averaged and a total of 92 independent reflections were used for the refinement of the structure. The absorption-corrected observed and calculated structure factors are listed in Table 2.

* The specimen used in this study was kindly supplied by Prof. Gordon E. Brown from the Princeton University mineral collection. The locality was given only as Quebec, Canada.

REFINEMENT

The structure was refined on the previously reported, non-centrosymmetric space group $C_{3v}^n - R3m$ where both Ni and S atoms are located in the same special position, 9b. The starting positional parameters were obtained from Wyckoff (1963). Doyle & Turner's (1968) atomic scattering factors for neutral atoms were used along with correction factors for anomalous dispersion. L. W. Finger's unpublished RFINLE least-squares program was used to refine the structure. The refinement was initialized using unit weights, individual isotropic temperature factors ($B = 1.0$ for S and $B = 0.5$ for Ni) and by fixing the z positional parameter of the Ni atom. The first three cycles of refinement resulted in an R factor of 5.2%. The next four cycles of refinement which included a secondary extinction factor reduced the R factor to 2.9%. Two additional runs using weights based on counting statistics reduced the unweighted R factor to 0.017. Final anisotropic refinement of the structure which included positional parameters and anisotropic temperature factors resulted in an unweighted R factor of 0.014 for the 92 reflections.

The refined positional parameters, temperature factors and r.m.s. amplitude of thermal ellipsoids of vibration are listed in Table 3 and Table 4.

TABLE 1. MILLERITE CRYSTAL DATA

Chemical Formula	$Ni_{1.03}Fe_{0.019}Co_{0.004}S$
Cell Parameters	$a_H = 9.6190(5)$, $c_H = 3.1499(3) \text{ \AA}$, $\gamma = 120.00^\circ$ $a_H = 5.6519 \text{ \AA}$, $\alpha = 116.63^\circ$
Calculated Density	5.267 gm/cc

TABLE 2. STRUCTURE FACTORS FOR MILLERITE

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c			
3	0	0	136	137	5	1	1	26	25	5	0	2	109	109			
6	0	0	89	91	8	1	1	73	73	8	0	2	80	79			
9	0	0	63	58	0	2	1	124	122	0	1	2	150	150			
1	1	0	64	62	3	2	1	80	79	3	1	2	95	95			
4	1	0	113	115	6	2	1	39	36	6	1	2	38	39			
7	1	0	94	92	9	2	1	9	6	9	1	2	28	29			
10	1	0	43	41	1	3	1	164	162	1	2	2	49	48			
2	2	0	61	61	4	3	1	81	79	4	2	2	72	72			
5	2	0	52	51	7	3	1	64	64	7	2	2	51	50			
8	2	0	37	36	2	4	1	18	18	2	3	2	51	51			
3	3	0	149	154	5	4	1	88	87	5	3	2	54	53			
6	3	0	38	37	8	4	1	47	44	8	3	2	88	85			
9	3	0	87	86	0	5	1	48	48	0	4	2	112	111			
4	4	0	116	117	3	5	1	94	96	3	4	2	121	120			
7	4	0	85	83	6	5	1	68	66	6	4	2	27	25			
5	5	0	9	8	1	6	1	78	78	1	5	2	55	55			
8	5	0	34	32	4	6	1	68	67	4	5	2	41	39			
6	6	0	27	24	2	7	1	28	26	2	6	2	59	58			
1	0	1	96	94	5	7	1	62	61	5	6	2	30	30			
4	0	1	169	172	0	8	1	124	121	0	7	2	80	79			
7	0	1	139	127	3	8	1	45	41	3	7	2	39	41			
10	0	1	20	19	1	9	1	26	25	1	8	2	33	35			
2	1	1	95	95	2	0	2	19	19	0.10.2	55	54	1	3	4	33	31

$F_o(0,0,0) = 397$

TABLE 3. POSITIONAL AND THERMAL PARAMETERS IN MILLERITE (STANDARD DEVIATIONS IN PARENTHESES)

Atom	Positional Parameters			Isotropic		Anisotropic Temperature Factors			
	x	y	z	B	B	β_{11}	β_{33}	β_{12}	β_{13}
Ni 9(b)	-0.08781(5)	0.08781(5)	0.088	0.53(2)	0.0017(1)	0.0153(7)	0.0008(1)	0.0000(1)	0.0000(1)
S 9(b)	0.1124(1)	-0.1124(1)	0.6164(5)	0.56(3)	0.0024(1)	0.013(1)	0.0017(2)	0.0000(2)	0.0000(2)

$R = \sum |F_o| - |\sum F_c| / \sum |F_o| = 0.014$ Secondary extinction correction factor $c = 3.6 \times 10^{-6}$

$\beta_{22} = \beta_{11}$, $\beta_{23} = \beta_{13}$

DISCUSSION

Results of our refinement show that the basic structure of millerite is similar to that described earlier on the basis of powder x-ray data. However, there are some differences in the details of the structure. The important interatomic distances and angles are listed in Table 5. Figure 1 shows the structure of millerite projected along the *c* axis of the hexagonal cell.

There are three different Ni-S distances (Fig. 2). The axial Ni-S distance (2.261Å) and two

TABLE 4. MAGNITUDE AND ORIENTATION OF THERMAL ELLIPSOIDS (standard deviations in parentheses)

Atom	Ellipsoid Axis	r.m.s. Amplitude (Å)	Angle (°) w.r.t.		
			<i>a</i>	<i>b</i>	<i>c</i>
Ni 9(<i>b</i>)	<i>x</i> ₁	0.078(3)	60	60	90
	<i>x</i> ₂	0.080(3)	150(2)	30(2)	86(16)
	<i>x</i> ₃	0.088(2)	86(14)	94(14)	4(16)
S 9(<i>b</i>)	<i>x</i> ₁	0.071(6)	30(2)	150(2)	87(20)
	<i>x</i> ₂	0.081(4)	87(18)	93(18)	178(20)
	<i>x</i> ₃	0.098(4)	60	60	90

TABLE 5. IMPORTANT INTERATOMIC DISTANCES AND ANGLES IN MILLERITE (standard deviations in parentheses)

Distances (Å)		Angles (Degrees)	
Ni - S'	2.261(2)	Ni - Ni - Ni(x2)	60.0
- S''(x2)	2.261(1)	Ni - Ni - Ni(x2)	90.0
- S'''(x2)	2.383(1)	S' - Ni - S''(x2)	95.86(5)
- Ni(x2)	2.534(1)	S' - Ni - S'''(x2)	110.58
- Ni(x2)	3.150	S'' - Ni - S'''	91.62(8)
S' - S''(x2)	3.243(3)	S''' - Ni - S'''	85.76(8)
- S'''(x2)	3.150	S'' - Ni - S'''(x2)	85.38(4)

basal Ni-S distances (2.261Å) are similar and are considerably shorter than the other two basal Ni-S distances (2.382Å). The average Ni-S distance, 2.310Å, is consistent with a divalent Ni in five-fold coordination (the distance being intermediate between four- and six-coordinated Ni-S distances, 2.28 and 2.394Å, in heazlewoodite and hexagonal NiS, respectively (Fleet 1972; Trahan *et al.* 1970). There are two sets of S (apical)-Ni-S (equatorial) angles, 95.85° and 110.89°. These distances and angles indicate that the S coordination polyhedron is not a regular square pyramid but a distorted tetragonal pyramid and the four basal S atoms do not lie on the same equatorial plane. This distortion is, perhaps, to overcome anion-anion repulsion and to stabilize the tetragonal pyramidal coordination rather than a trigonal bipyramidal one which should be more stable insofar as ligand-ligand repulsion is concerned (Sacconi 1968). All four equatorial edges of the S polyhedron are shared by adjacent polyhedra and the Ni atoms come closer together across the shared edges. The Ni-Ni distance within the basal plane is 2.534Å, and this distance approximately corresponds to a half metal bond (bond number ~ 0.42, assuming a metallic radius of 1.15Å for Ni). Thus, each Ni can be considered as coordinated to two other Ni atoms, in addition to five S atoms, and the three Ni atoms

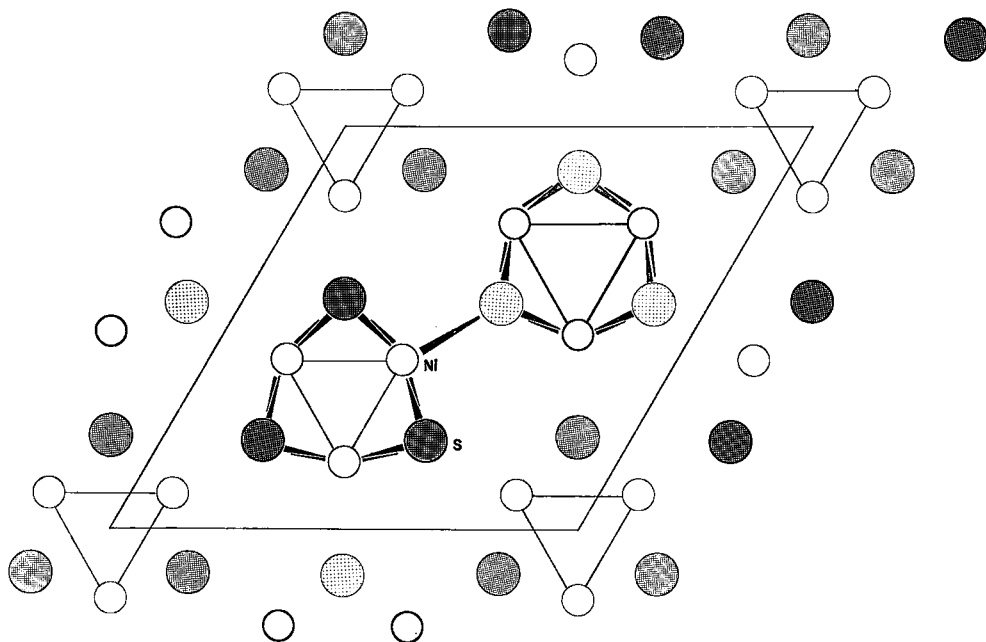


FIG. 1. Projection of the hexagonal cell of millerite along *c*. For Ni: *z* = .75, .42, and .09, respectively, for groups centered around *x*, *y* = 1/3, 2/3, *x*, *y* = 2/3, 1/3, and *x*, *y* = 0, 0. For S: *z* = .95, .62, and .28, respectively, for dark, intermediate, and light circles.

are located at the corners of an equilateral triangle (slightly above the three faces of the S prisms) in the form of a trinuclear cluster. The distance between the clusters, along the *c* axis, is 3.150 Å and this distance is slightly smaller than the critical distance, $R_c = 3.27 \text{ \AA}$ for Ni-Ni interaction in sulphides (Goodenough 1967). Thus, between clusters there could also be weak metal-metal interaction leading to delocalization of *d* electrons throughout the structure. The isotropic temperature factors of the two atoms are in good agreement with previously reported values for other Ni sulphides (Rajamani & Prewitt 1973). The r.m.s. amplitudes of thermal vibration indicate that both Ni and S atoms are slightly anisotropic and the S atom is more anisotropic than the Ni atom.

Millerite satisfies Pearson's (Pearson 1972) general valence rule for valence compounds:

$$\frac{n_a + n_c + b_a - b_c}{N_a} = \frac{6 + 4 - 0 - 2}{1} = 8$$

where n_a is the total number of anion valence electrons, n_c is the number of cation bonding and antibonding valence electrons, b_a is the number of electrons involved in forming anion-anion bonds, b_c is the number of electrons forming cation-cation bonds and N_a is the number of anions (Hulliger 1968; Pearson 1972). However, millerite is reported to be metallic and Pauli paramagnetic (Hulliger 1968). Since the apparent valency of Ni in millerite is 2, as indicated by the average Ni-S distance, only *d* orbitals are involved in metal-metal bonds. The geometry of the S polyhedron and the presence of a trinuclear cluster of Ni atoms suggest that the aspects of bonding in millerite could be similar to that

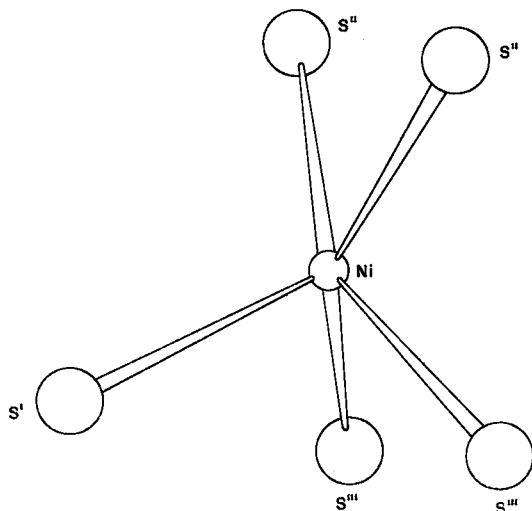


FIG. 2. Coordination of Ni in millerite.

observed in the compound $\text{Co}_3(\text{CO})_9\text{S}$ (Strouse & Dahl 1971). The six antibonding ($3d_{x^2-y^2}$ and $3d_{z^2-y^2}$, σ^* with respect to Ni-S bonding) orbitals of the three Ni atoms in the cluster combine to give three bonding and three antibonding molecular orbitals. The three bonding molecular orbitals form a *d* band and the six *d* electrons of the three Ni atoms could be completely delocalized in this *d* band. In this way, an energetically favorable *d* electron configuration is obtained, as there are no localized electrons in the antibonding molecular orbitals. Thus, the structure of millerite becomes the stable form of Ni monosulphide instead of the common NiAs structure where the nature of bonding leads to two unpaired electrons in the antibonding orbitals for an octahedral Ni(II). Further, Ni-Ni interaction in the NiAs structure involves the nonbonding *d* orbitals which are already completely filled. In the millerite structure, the tendency of Ni to form metal-metal bonds is easily achieved. This qualitative interpretation of bonding in millerite is consistent with its metallic and Pauli paramagnetic behavior.

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