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CRYSTAL STRUCTURE REFINEMENT OF MILLERITE (β-NiS)

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ABSTRACT

Millerite (β-NiS) is rhombohedral with hexagonal axes $a = 9.607(1)$ and $c = 3.143(1)$Å, space group $R3m$, and $Z = 9$. The structure of a millerite crystal from Marbridge Mine, Malartic, Quebec, with composition $(Ni_{0.981}Fe_{0.016}Co_{0.004})S$, has been refined to a weighted R index of 0.056. Within the structure each Ni is coordinated by five S atoms and two Ni atoms. The Ni-S bond lengths observed within the millerite structure are comparable to the expected value for a covalent bond. Molecular orbital theory is invoked to show that the millerite structure with five-fold coordination around Ni is more stable than the nickeline structure (α-NiS) with six-fold coordination about each Ni and thus an explanation is provided for the existence of the former rather than the latter as the low temperature phase found in nature. The Ni-Ni bonding within millerite could be stabilized by the two electrons in the $3d_{z^2}$ orbital which would otherwise be non-bonding if only the S atoms are considered.

INTRODUCTION

Millerite (β-NiS) is the low-temperature polymorph of NiS (Kullerud & Yund 1962). The high temperature form, α-NiS, has not been described in nature. The structure of millerite was first derived by Alsén (1925) and later revised by Kolkmeijer & Moesveld (1931), who found Alsén's atomic positions to be essentially correct but his two atom types to be reversed. The millerite structure is of crystal-chemical interest because of an unusual five-fold coordination of the Ni atoms by S atoms. In this paper we describe a refinement of the millerite structure and we discuss the bonding. This paper has been extracted from the unpublished Ph.D. thesis of Grice (1973) where further details, especially about experimental procedures, may be had. The only other refinement of the millerite structure is the recent one published in abstract form by Rajamani & Prewitt (1973).

EXPERIMENTAL

The millerite whose structure refinement is reported here is from the Marbridge mine, Malartic, Quebec, the geology of which is described by Clark (1965), Buchan & Blowes (1968), and Graterol & Naldrett (1969). This material is massive with a perfect $\{10\bar{1}1\}$ cleavage, and most material is twinned by reflection across $\{01\bar{1}2\}$ which is the common twin law for millerite. The millerite refined by Rajamani & Prewitt (1973) is from "Quebec, Canada" and may be from the Marbridge mine.

Electron microprobe analyses were carried out on the material at the Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, using appropriate standards. The probe data were corrected using a computer program written by Rucklidge & Gasparrini (1969) and the results are given in Table 1. The analysis gives the formula $(Ni_{1.085}Fe_{0.018}Co_{0.004})S_{1.106}$ or for $S = 1$, $(Ni_{0.981}Fe_{0.016}Co_{0.004})S$ which is close to the ideal formula NiS. Rajamani & Prewitt (1973) give the composition $Ni_{1.02}Fe_{0.02}S$ for their millerite.

Difficulty was encountered in trying to find a truly single-crystal fragment of material suitable for x-raying from both Malartic and from several other localities; the fragments from Malartic all showed at least some second twinned individual in the single-crystal photographs. Finally one fragment that showed very little of the twinned individual was ground to a sphere of radius 0.125 mm and used for the analysis. Single-crystal data were collected through the courtesy of Dr. M. J. G. James in the Biochemistry Department, University of Alberta, Edmonton, using a Picker FACS1 four-circle diffractometer and assuming the well-established space group $R3m$. The refined cell dimensions derived and used in the data collection are given in Table 2. Using Zr-filtered Mo$K\alpha$ radiation, intensities were measured out to $2\theta = 60°$, for 155 unique

TABLE 1. MICROPROBE ANALYSIS AND CHEMICAL FORMULA OF MILLERITE

	Weight %	Atomic Proportions		Atomic Proportions For S=1	
Ni	63.68	1.085	1.107	0.981	1.001
Fe	1.03	0.018		0.016	
Co	0.21	0.004		0.004	
Cu	0.00	0.000		0.000	
S	35.47	1.106		1	
Total	100.39				

Chemical formula: $(Ni_{0.981}Fe_{0.016}Co_{0.004})S$

Analysts: J. Grice and S. Jones, 1972.

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reflections, all of which were non-zero. The intensities were collected using 2θ scans with a scanning speed of 2° 2θ per minute and background counts were made for 10 seconds on either side of each peak.

TABLE 2. MILLERITE CELL CONTENT, CELL DIMENSIONS, AND POSITIONAL PARAMETERS

	Hexagonal	Rhombohedral
Space Group	$R3m$ (No. 160)	
Cell Content	$(Ni_{8.83}Fe_{0.14}Co_{0.04})S_9$	$(Ni_{2.94}Fe_{0.04}Co_{0.01})S_3$
Cell Dimensions (this work)	a=9.6071(12)Å c=3.1434(9)	a_r=5.6448 α^r=116°38'
Positional Parameters	9 Ni in (b) $x,\bar{x},z$ 9 S in (b) x,x,z	3 Ni (b) x_1,x_1,x_3 3 S in (b) x_1,x_1,x_3
Kolkmeijer & Moesveld (1931)	x_{Ni}=-0.088, z_{Ni}=0.088 x_S = 0.118, z_S=0.596	x_{Ni}=0 z_{Ni}=0.264 x_S =0.714 z_S =0.361
Kolkmeijer & Moesveld (1931), new origin*	x_{Ni}= 0.912, z_{Ni}=0.492 x_S = 0.114 z_S =0	x_{Ni}=0.404 z_{Ni}=0.668 x_S =0.114 z_S =0.772
This work*	x_{Ni}=0.91225(9) z_{Ni}=0.47546(102) x_S =0.11224(19) z_S =0.	x_{Ni}=0.3877 z_{Ni}=0.6510 x_S=0.1122 z_S =0.7756

*In the present work, the original origin of Kolkmeijer & Moesveld (1931) has been shifted parallel to z to a new origin to set (hexagonal) z_S = 0.

TABLE 3. MAGNITUDES AND ORIENTATIONS OF THERMAL ELLIPSOIDS

Site	Ellipsoid Axes	Equivalent (Å^2)	Angles (in degrees) Between Ellipsoid Axes and Real Axes* A	B	C
Ni	1	0.35(1)	30.0	150.0	91.8
	2	0.41(1)	60.0	60.0	90.0
	3	0.91(1)	88.4	91.6	1.8
S	1	0.39(1)	30.0	150.0	86.1
	2	0.69(1)	60.0	60.0	90.0
	3	0.84(1)	93.4	86.6	3.9

*A,B,C, are the angles between the ellipsoid axes 1,2,3 and the crystallographic axes x,y,z respectively. Standard deviations were not calculated for these angles.

TABLE 4. FINAL F_o AND F_c VALUES

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	3	52	56	2	0	2	17	18	4	3	4	59	57	7	6	1	24	24
0	1	5	21	19	2	0	5	30	26	4	3	1	82	80	7	5	2	37	38
0	1	2	119	147	2	1	1	89	94	4	4	0	130	118	7	4	3	50	51
0	2	1	121	124	2	2	0	74	61	4	4	3	70	70	7	4	0	90	84
0	2	4	13	12	2	2	3	29	30	4	5	2	40	39	7	3	1	63	63
0	3	3	111	121	2	3	2	46	48	4	6	1	72	67	7	2	2	47	49
0	3	0	148	141	2	4	1	21	17	4	7	3	49	49	7	1	0	101	93
0	4	2	101	107	2	4	4	39	38	4	7	0	92	84	7	1	3	50	51
0	5	4	54	52	2	5	3	29	29	4	8	2	80	81	7	0	4	32	30
0	5	1	54	48	2	5	0	60	52	4	9	1	11	11	7	0	1	115	129
0	6	0	107	88	2	6	2	58	56	4	10	0	37	36	8	0	2	72	77
0	6	3	42	42	2	7	4	23	22	5	9	2	23	23	8	1	1	66	72
0	7	2	79	78	2	7	1	31	27	5	8	0	34	33	8	2	0	42	37
0	8	1	135	124	2	8	0	42	37	5	7	1	62	62	8	2	3	22	22
0	8	4	31	30	2	8	3	23	20	5	6	2	31	30	8	3	2	79	85
0	9	3	58	58	2	9	2	47	47	5	5	0	10	8	8	4	1	47	46
0	9	0	64	60	2	10	1	37	35	5	5	3	3	2	8	5	0	34	33
0	10	2	54	52	2	11	0	24	23	5	4	4	10	10	8	6	2	15	15
0	11	1	82	80	3	11	1	55	56	5	4	1	91	87	8	7	1	64	68
0	12	0	57	52	3	10	2	21	21	5	3	2	50	52	9	6	0	35	38
1	12	1	33	34	3	9	0	91	88	5	2	3	30	30	9	5	1	17	18
1	11	2	44	43	3	9	3	15	15	5	2	0	59	52	9	4	2	38	41
1	10	3	33	33	3	8	1	49	43	5	1	1	24	24	9	3	0	88	88
1	10	0	46	43	3	7	2	40	39	5	1	4	26	25	9	3	3	11	12
1	9	1	28	25	3	6	3	48	48	5	0	2	93	105	9	2	1	6	5
1	8	2	34	34	3	6	0	43	37	6	0	3	61	64	9	1	2	26	27
1	7	0	103	93	3	5	1	99	95	6	1	2	34	36	9	0	3	40	40
1	7	3	53	53	3	5	4	44	43	6	2	1	38	37	10	0	1	20	19
1	6	4	34	33	3	4	2	113	117	6	2	4	25	24	10	1	3	32	33
1	6	1	84	77	3	3	0	169	154	6	3	3	49	50	10	1	0	44	43
1	5	2	53	53	3	3	3	23	21	6	3	0	44	37	10	2	2	26	27
1	4	3	51	54	3	2	4	12	11	6	4	2	25	25	10	3	1	23	23
1	4	0	126	115	3	2	1	79	79	6	5	1	70	67	10	4	0	37	36
1	3	1	167	167	3	1	2	81	92	6	6	0	28	23	11	2	0	23	23
1	3	4	29	27	3	0	3	87	94	6	6	3	41	42	11	1	1	65	71
1	2	2	43	46	4	0	1	142	175	6	7	2	27	28	11	0	2	42	47
1	1	0	74	62	4	0	4	67	66	6	8	1	43	45	12	0	1	26	29
1	1	3	26	27	4	1	3	52	55	6	9	0	39	38	13	0	1	32	36
1	0	4	63	62	4	1	0	124	115	7	7	0	42	42	0	0	0	396	396
1	0	1	81	95	4	2	2	64	69										

For 12.0.1 read 12.2.1. The full data on phase angles, l, omitted by editorial decision may be obtainerl from the authors

CRYSTAL STRUCTURE INVESTIGATION

The initial intensities were corrected for Lorentz and polarization effects and absorption (μ = 179.6 cm^{-1} for Mo$K\alpha$ radiation) and were assigned weights based on counting statistics.

The hexagonal cell of the rhombohedral lattice of millerite with the cell dimensions given above contains 9 [NiS]. In the noncentrosymmetric space group, $R3m$, both the Ni and S atoms are in nine-fold special positions, x, $\bar{x}$, z. The starting positional parameters for this refinement were those of Kolkmeijer & Moesveld (1931) transformed from rhombohedral to hexagonal axes and with the origin shifted arbitrarily so that the prototype sulphur would be at (hexagonal) height $z = 0$.

Larson's (1971) computer program GENLES was used for a full-matrix least-squares refinement of the positional and thermal parameters. The scattering factors used for Ni° and S° are those tabulated by Cromer & Mann (1968). The structure refined to weighted and unweighted residual indices of 0.084 and 0.090 with isotropic temperature factors and of 0.056 and 0.066 using anisotropic temperature factors. Table 2 gives the refined positional parameters, Table 3 the anisotropic thermal parameters and Table 4 the observed (F_o) and calculated (F_c) structure factors.

DISCUSSION

The millerite structure is shown in projection along y in Figure 1 and in projection along z as drawn by ORTEP (Johnson 1970) in Figure 2. From these projections it may be seen that the atoms may be regarded as layered parallel to (0001) with six stepped overlapping layers within each c repeat period, three of which consist of Ni atoms at heights 14, 48 and 81 (hundredths of c) and three S atoms at heights 0, 33 and 67. This stepped-layering is reflected in the magnitudes of the thermal vibrations. It can be readily seen in Table 3 that for both the Ni and S atoms the magnitudes of thermal vibration nearly parallel to the z-axis (along ellipsoid axes 3) are considerably larger than they are in the directions parallel and perpendicular to the vertical mirror-planes (axes 1 and 2 respectively). The reason for this might be because the density of atoms in the z-direction is less than in either of the other two directions, and thus a larger amplitude of vibration is possible parallel to z. Similar arguments may be presented to explain the observed differences in amplitudes between vibrational axes 1 and 2 for both the Ni and S atoms. Also in the plane perpendicular to the z-axis both the vibrational magnitudes for S are larger than those for Ni which again reflects the packing of atoms in that the S-S distance (3.23Å) is considerably larger than the corresponding Ni-Ni distance (2.53Å).

The bond distances and interbond angles shown in Table 5 confirm the co-ordination of S atoms around Ni given by Kolkmeijer & Moesveld (1931), namely that each Ni atom is surrounded by five S atoms in the form of a distorted tetragonal pyramid at distances 2.26Å to 2.37Å. In Figure 2 it can be seen that each Ni atom has, besides five S atoms, two other Ni atoms at the same height as itself and at a distance of 2.53Å. This configuration with sevenfold co-ordination around the Ni is illustrated and briefly discussed in Fleet (1972).

Taking Ahrens' (1952) ionic radii for Ni^{2+} (0.69Å) and S^{2-} (1.84Å) the calculated Ni-S ionic bond length would be 2.53Å. The Ni-S bond length in millerite is considerably shorter than this and could reasonably be attributed to extensive covalent bonding. Using the Schomaker-Stevenson (1941) formula revised by

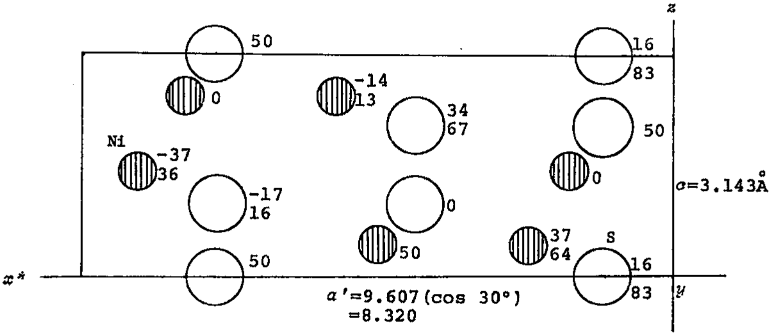

FIG. 1. Projection of the final structure along y. Heights are shown above the plane of projection in hundredths of the b period. Prototype atoms are designated Ni (shaded circle) and S (open circle) respectively. Prototype Ni at height 36 has $y = \bar{x} = 09$, and prototype S at height 83 has $y = \bar{x} = 89$. (See Fig. 2).

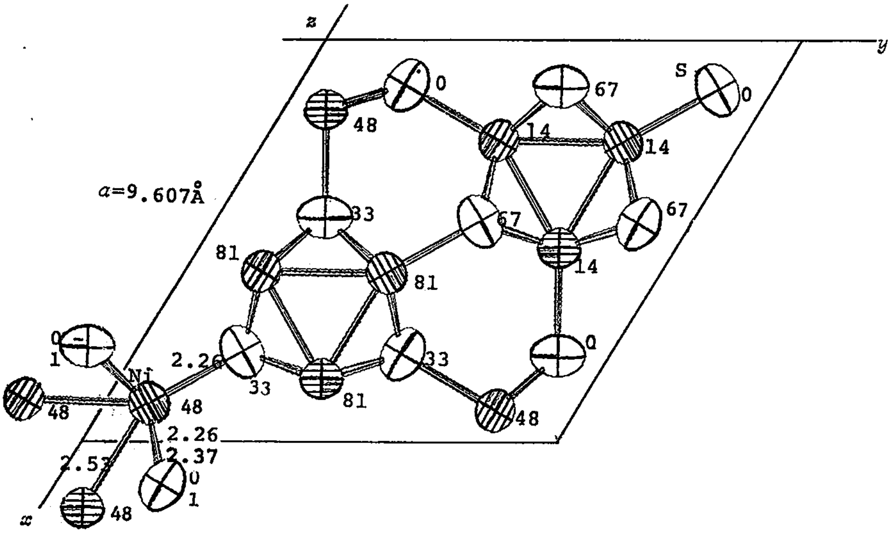

FIG. 2. Projection of the final structure along z. Heights are shown above the plane of projection in hundredths of the c period. Prototype atoms are designated Ni (shaded ellipse) and S (open ellipse) respectively.

Pauling (1960), and Pauling's covalent radii and electronegativities the Ni-S covalent bond length calculates to 2.25Å. This value is close to the minimal Ni-S bond length observed in millerite which further substantiates the idea of covalent bonding in this mineral. In metallic Ni with twelve-fold co-ordination the Ni-Ni distance is 2.48Å (Zhdanov 1965). With a Ni-Ni distance of 2.53Å in millerite it is probably safe to assume there is some metal-metal bond interaction, and Rajamani & Prewitt (1973) suggest that it is significant in stabilizing the millerite structure.

Molecular orbital theory provides the best discussion of bonding for compounds with considerable orbital overlap or covalent bonding. Both σ and π bonds have been taken into consideration for the molecular orbital energy levels. The electronic configuration of the d sub-shell for the free Ni^{2+} ion has three orbitals with paired electrons and two orbitals with unpaired electrons. The orbitals with paired electrons are conducive to π bond formation (Burns 1970).

The NiS_5 configuration in millerite has C_{4v} pseudo-symmetry. Although the true symmetry is C_v the arguments presented here would not change but the application of group theory is simplified somewhat by assuming the higher symmetry. Combining the d^2 electrons available from the Ni^{2+} metal orbitals with the ten electrons for five S^{2-} p orbitals in C_{4v} symmetry it may be shown that the resultant molecular orbitals filled are: σ bonds $4s$, $4p_x$, $4p_y$, $4p_z$ and $3d_{x^2-y^2}$; π bonds $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$; and the remaining two electrons form a non-bonding pair in $3d_{z^2}$. The $3d_{z^2}$ electrons may in fact be incorporated in the bonding of the Ni to two other other Ni's which are symmetrical about the ligand-metal z axis. The pairing of the $3d_{z^2}$ electrons or their involvement in Ni-Ni bonding is supported by the results of a paramagnetic susceptibility measurement carried out by Dr. Maartense, Department of Physics, University of Manitoba, on the Quebec millerite; he found the paramagnetic susceptibility to be negligible, and it is likely that the small value recorded is due to minor amounts of Fe. Thus, millerite can probably be considered as diamagnetic as expected from the occupancy of the molecular orbital energy levels given above.

TABLE 5. INTERATOMIC DISTANCES AND INTERBOND ANGLES

Equivalent Position Code

	x	y	z		x	y	z
a	$1-2x$	$-x$	z	e	$1+x$	$2x$	z
b	$1-2x$	$-x$	$1+z$	f	x	$2x-2$	z
c	$2/3+x$	$1/3-x$	$1/3+z$	g	$3-2x$	$1-x$	z
d	$1+x$	$2x$	$1+z$	h	$2x-2$	x	z

Interatomic Distances

	Distance, Å	Multiplicity	Mean
Ni-S(a,e)	2.264(3)	2	2.306(2)
Ni-S(b,d)	2.369(3)	2	
Ni-S(c)	2.263(2)	1	
Ni			
Ni-Ni(f,h)	2.529(1)	2	2.529(1)
S-S	3.143(4)	1	3.143(4)

Interbond Angles

S(a)-Ni-S(b)	85.41(06)°	S(a)-Ni-Ni(f)	56.05(04)°
S(a)-Ni-S(c)	95.60(08)°	S(a)-Ni-Ni(g)	98.97(02)°
S(a)-Ni-S(e)	91.18(12)°	S(b)-Ni-Ni(f)	57.74(04)°
S(a)-Ni-S(d)	153.58(06)°	S(b)-Ni-Ni(g)	98.57(02)°
S(b)-Ni-S(c)	111.80(07)°	S(c)-Ni-Ni(f)	148.10(04)°
S(b)-Ni-S(d)	86.12(12)°	Ni(f)-Ni-Ni(g)	60°

For comparison it is of interest to look at the molecular orbitals for the high temperature polymorph, α-NiS, which has the nickeline structure. In this phase six atoms surround each nickel (Ni-S distance 2.43Å) with C_{3v} symmetry. The resultant molecular orbitals are: σ bonds $4s$, $4p_x$, $4p_y$, $4p_z$, $3d_{xz}$ and $3d_{yz}$; π bonds $3d_{xy}$, $3d_{x^2-y^2}$ and $3d_{z^2}$; and two unpaired electrons in the antibonding orbitals. These electrons with parallel spin should make α-NiS paramagnetic. Benoit (1955) measured the paramagnetic susceptability of α-NiS and found it to be only weakly but not negligibly paramagnetic. The reason for this low measurement is probably bue to the involvement of the unpaired electrons in a Ni-Ni interaction (Ni-Ni distance 2.67Å) which would greatly supress the paramagnetism.

From the consideration of the Ni-S ligands given above it can be seen that millerite has no anti-bonding molecular orbital energy levels as does α-NiS. Thus the five-fold coordination of S about Ni in millerite requires less energy to form than the six-fold coordination in α-NiS and one would thus expect millerite (β-NiS) to be the stable low temperature phase as observed. Consideration of the Ni-Ni interaction in the two phases would not change these arguments. This increased stability of the millerite structure over the nickeline structure is further evidenced by an appreciable shortening of the Ni-S and Ni-Ni bond lengths in millerite relative to those in α-NiS.

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