

The Crystal Structure of Parkerite ($\text{Ni}_3\text{Bi}_2\text{S}_2$)

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Abstract

Parkerite ($\text{Ni}_3\text{Bi}_2\text{S}_2$) is orthorhombic with $a = 5.545(4)$ Å, $b = 5.731(3)$ Å, $c = 4.052(3)$ Å, space group $Pmam$ (D_{2h}^5), $Z = 1$. The crystal structure, determined on synthetic material, consists of a C centered arrangement of Bi atoms with the Ni in two non-equivalent positions octahedrally coordinated to four Bi and two S and juxtaposed across shared octahedral faces with Ni-Ni distances less than 2.80 Å; the Ni(2) site has an occupancy of 0.5. The S is coordinated to three Ni at the apex of a trigonal pyramid giving Ni-S distances of 2.02 Å and 2.05 Å, which are significantly shorter than in other nickel sulfides. The parkerite structure is shown to be a derivative of the shandite ($\text{Ni}_3\text{Pb}_2\text{S}_2$) structure, the essential differences being the distribution of the Ni atoms about the heavy atoms and the apparent direct coordination of S to the Pb(2) atom in shandite. The short Ni-S distances in parkerite are related to a π bonding contribution to these bonds and further crystal chemical analysis of the compound predicts that only four electrons populate the non-bonding d orbitals on each Ni. The distribution of Ni-Bi and Ni-S bonds readily accounts for the excellent {010} cleavage of parkerite.

Introduction

Parkerite ($\text{Ni}_3\text{Bi}_2\text{S}_2$) occurs in certain arsenide-sulphide assemblages in association with other Bi and Ni phases, such as native bismuth, bismuthinite, niccolite and maucherite. It is an uncommon mineral, having been reported only from Insizwa, South Africa (Scholtz, 1936) and three localities in Canada—Sudbury, Ontario (Michener and Peacock, 1943), Great Slave Lake, Northwest Territories (Thompson, 1951) and Cobalt-Gowganda area, Ontario (Petruk, Harris and Stewart, 1969).

The chemical analyses of the specimens from Ontario correspond quite closely to the ideal composition but the Insizwa parkerite contains a significant amount of Pb (9.5 wt percent) substituting for Bi. Parkerite is orthorhombic; the Sudbury material has $a = 4.03$ Å, $b = 5.53$ Å, $c = 5.73$ Å, possible space group $Pmm2$ (C_{2v}^1), $D_m = 8.4$ gm/cm³, $Z = 1$ (Michener and Peacock, 1943). The lattice parameters reported for the Cobalt-Gowganda parkerite are $a = 4.009$ Å, $b = 5.541$ Å, $c = 5.749$ Å. The orientation of the unit cell as reported by earlier workers does not conform to the present convention for orthorhombic cells. Henceforth, in this article, the conventional orientation will be adopted; the earlier orientation is related to it by the transformation matrix (010/001/100).

$\text{Ni}_3\text{Bi}_2\text{S}_2$ can be synthesized quite readily, the

product being optically and crystallographically equivalent to parkerite. As shown by du Preez (1945), there is extensive solid solution at the Bi end of the $\text{Ni}_3\text{Bi}_2\text{S}_2 - \text{Ni}_3\text{Pb}_2\text{S}_2$ system, extending almost to $\text{Ni}_3\text{BiPbS}_2$. However, the solid solution of Bi in the Pb end member is limited to less than 4 mole percent $\text{Ni}_3\text{Bi}_2\text{S}_2$. Synthetic $\text{Ni}_3\text{Pb}_2\text{S}_2$ is equivalent to the natural phase shandite which is rhombohedral with $r = 5.576$ Å, $\alpha = 60^\circ$ (Peacock and McAndrew, 1950).

Experimental

The present study was made on synthetic material rather than natural material to achieve more rigorous control of composition and, hopefully, a more suitable crystalline product. The parkerite was synthesized by reaction of the pure elements in a sealed silica glass tube heated for seven days at 600°C in a horizontal tube furnace and quenched in water. The commercial Ni sponge was heated at 900°C in a stream of hydrogen gas before use to remove possible oxygen contamination. The product of the synthesis was massive and in the form of a plug. Polished sections show the development of {111} twin lamellae to be much less than in the synthetic material examined by Michener and Peacock, being limited to grains on the margins of the plug.

Preliminary single crystal work on a precession camera essentially confirmed much of the earlier data in the literature. Parkerite is orthorhombic with $a = 5.545(4)$, $b = 5.731(3)$, $c = 4.052(3)$ Å; the lattice parameters were determined by least squares refinement of 12 centered reflections measured in the later, four-circle diffractometer study

with Zr-filtered MoK α ($\lambda = 0.7107$ Å) radiation. The systematic absences, $h0l$ with $h \neq 2n$ (implying $h00$ with $h \neq 2n$), are consistent with space groups $P2_1am$ (C_{2v}^2), $Pma2$ (C_{2v}^4) and $Pmam$ (D_{2h}^8). These are equivalent to the systematic absences reported by Michener and Peacock, although these earlier workers did not recognize the a -glide component.

Some difficulty was encountered in obtaining a single crystal suitable for the collection of the intensity data. Because of the high linear absorption coefficient of parkerite (765.2 cm $^{-1}$), it was clearly necessary to use an equidimensional crystal to realize meaningful absorption corrections on a conventionally-sized crystal, and it was appreciated that, even if this requirement were met, small errors in describing the crystal shape could result in appreciable errors in the corrected data set. However, parkerite has an excellent $\{010\}$ cleavage so that the dominant habit of crystals from the crushed plug was tabular. Moreover, the synthetic parkerite is relatively soft and the crystals bend very readily through a combination of the $\{010\}$ cleavage and $\{111\}$ fracture. Attempts to prepare single crystal spheres in a Bond sphere grinder were frustrated because the crystals cleaved readily on impact with the abrasive. The problem was resolved eventually by choosing a small crystal (calculated volume of $0.31 \cdot 10^{-7}$ cm 3) and mounting it on the b -axis to minimize possible errors in the absorption correction.

The X-ray intensity data for the structure analysis were taken on a Picker FACS 1 four-circle diffractometer system at the University of Western Ontario. All hkl reflections with $2\theta \leq 65^\circ$ were measured using a scintillation detector, Zr-filtered MoK α ($\lambda = 0.7107$ Å) radiation and the 2θ scan technique: 40 second stationary background counts, peak-base widths of 2.0° 2θ (uncorrected for dispersion) and a scanning rate of 0.25° per minute. The resulting data were processed by a data correction routine which corrected for background, Lorentz and polarization effects, and absorption, and assigned standard deviations (σ) to the corrected data based on the summed variances of the counting rates of the peaks and associated backgrounds. Transmission factors for the absorption correction were calculated by the analytical method of de Meulenaer and Tompa (1965). The calculated transmission factors varied from 0.10 for reflection 010 to 0.20 for 280. Each reflection whose intensity was less than the associated background plus 3σ was given zero intensity. The final data list contained 308 reflections of which 78 were 'unobserved'.

Crystal Structure Investigation

The solution of the crystal structure of parkerite was initiated by a Patterson synthesis which showed quite clearly that the expected two Bi atoms per unit cell were arranged approximately on a C centered lattice with some of the Ni content four-coordinated with it at $z = 1/2$ relative to the Bi. Using a trial structure based on the centrosymmetric space group $Pmam$ with Bi in the $2e$ ($1/4, y, 0$; $y = 0.75$) positions and with the Ni distributed over the $2b$ ($0, 0, 1/2$) and $2d$ ($0, 1/2, 1/2$)

positions, an F_0 synthesis suggested an improved set of initial positions (Table 1): the S is eight coordinated with Bi and each Ni is octahedrally coordinated to four Bi and two S. A consequent value of the conventional residual index (R) of 0.22 and an absence of alternate positions on a F_0 map suggested that the basic structural features of parkerite had been outlined at this stage.

The structure was refined further by full-matrix, least-squares refinement using program RFINE (L. Finger, Geophysical Laboratory, Washington). RFINE minimizes the function $\sum w(|F_0| - |F_c|)^2$, where $w = 1/\sigma^2$, and calculates a conventional residual index, $\sum ||F_0| - |F_c||/\sum |F_0|$ and a weighted residual index, $[\sum w(|F_0| - |F_c|)^2/\sum wF_0^2]^{1/2}$. The scattering curves for Ni $^{2+}$ and Bi were taken from Cromer and Mann (1968) and that for S $^{2-}$ computed for a nine parameter fit from data in the International Tables for X-ray Crystallography, Vol. III. The anomalous dispersion coefficients of Cromer (1965) for Ni, Bi and S were included. Isotropic and anisotropic thermal parameters were added successively to the refinement. However, the isotropic thermal parameter for the Ni(2) position refined to a negative value, presumably reflecting limitations in the data set and, as a result, it was constrained to the value of the thermal parameter for Ni(1), since the two sites are quite similar. The refinement, then, was limited to isotropic parameters for Ni and anisotropic parameters for Bi and S and was terminated when the changes to the positional and anisotropic thermal parameters were in the sixth places and the ratios of the changes in these parameters to the errors in the parameters were less than 0.005. The final values of the conventional and weighted residual indices for the non-zero intensities are 0.096 and 0.104 respectively. The refined structure was checked with F_0 and $F_0 - F_c$ Fourier maps; no significant residual peaks were detected. Observed and calculated structure factors are given in Table 2, and positional and thermal parameters and associated standard deviations are given in Table 3.

TABLE 1. Initial Positional Parameters for Parkerite

Atom	Equipoint position	Occupancy	x	y	z
Ni(1)	2b	1.0	0	0	1/2
Ni(2)	2e	0.5	1/4	0.25	0
Bi	2e	1.0	1/4	0.75	0
S	2f	1.0	1/4	0.25	1/2

TABLE 2. Observed and Calculated Structure Factors

K	L	F _o	F _c	K	L	F _o	F _c	K	L	F _o	F _c	K	L	F _o	F _c	K	L	F _o	F _c
H = 0				2	23	19		4	49	41		H = 4			3	0	16		
				3	0	16		5	55	53					4	0	13		
				4	0	11		5	0	21	30				5	0	45	50	
0	1	83	92	5	0	9		1	44	16		0	0	156	158	1	47	53	
				3	0	88	87	2	17	26		1	69	67		2	44	45	
				1	105	103		3	29	12		2	130	131		3	41	42	
				2	72	75		4	0	18		3	58	54		6	0	27	
				3	66	73		6	0	78	77	4	83	84		1	0	19	
				4	50	52		1	44	37		5	42	36		2	20	17	
				5	41	44		2	68	68		1	0	33	29				
				4	0	48	31	3	37	30		1	28	28					
				1	15	31		4	48	48		2	26	24					
				2	32	26		7	0	22	5	3	18	20		0	0	67	
				3	0	23		1	0	24		4	21	15		1	82	85	
				4	25	21		2	22	5		5	0	12		2	61	60	
				5	0	16		3	0	19		2	0	91	84		3	66	
				6	0	11		8	0	25	23	1	113	113		4	45	41	
				2	0	122	123	1	69	75		2	77	72		1	0	25	
				2	95	96		1	50	44		3	85	87		1	19	18	
				3	102	116		3	52	57		4	56	48		2	22	17	
				4	65	59		H = 3				5	56	56		3	0	13	
				5	63	69		6	0	42	28	3	0	31	28		4	0	
				3	0	41	41	1	0	82	79	1	38	22		2	0	92	
				1	55	36		2	73	69		2	22	24		1	46	46	
				2	28	33		3	77	74		3	26	15		2	81	84	
				3	33	23		4	53	49		4	17	16		3	40	39	
				4	0	20		5	44	43		4	0	101	101		4	58	
				5	22	12		2	0	25	18	1	51	48		3	0	19	
				4	0	137	138	2	22	15		2	86	87		1	0	17	
				1	62	61		3	45	39		3	45	39		2	0	12	
				2	108	116		4	62	60		4	62	60		3	0	14	
				3	54	48		5	0	19		5	0	19	12		4	0	
				4	74	75		1	0	22		1	0	22		1	67	65	
				5	37	32		3	0	77	74	2	0	10		2	42	40	
				5	0	25	18	H = 2				3	0	18		3	52	53	
				1	0	30		1	89	88		4	0	7		5	0	19	
				2	20	15		2	62	65		6	0	36	36		1	26	
				3	0	23		3	65	65		1	65	60		2	0	16	
				4	0	9		4	47	46		2	39	32		6	0	47	
				5	0	4		5	39	40		3	52	49					
				6	0	44	43	4	0	38	26	4	0	0	21		H = 7		
				1	74	77		1	0	27		7	0	0	21				
				2	40	38		2	29	22		1	25	4		1	0	40	
				3	62	60		3	15	20		2	0	19		1	52	55	
				4	32	28		4	19	15		H = 5			2	39	40		
				7	0	17	26	5	0	61	63	1	0	59	59		3	44	
				1	38	6		1	61	66		1	0	79	78		2	0	
				2	0	23		2	52	56		1	79	78		1	0	9	
				3	25	5		3	50	51		2	53	53		2	0	8	
				8	0	45	48	2	0	177	187	4	39	40		3	61	58	
				1	31	22		6	0	34	24	3	61	58		3	0	7	
				2	42	43		1	0	24		4	39	40		3	0	41	
				H = 1				2	31	22		2	0	17	13		1	46	
				3	0	88	92	3	0	19		1	0	14		2	35	38	
				5	49	39		7	0	47	47	2	0	11		4	0	14	
				3	0	31	31	1	43	47		3	0	10		1	0	14	
				1	0	96	93	2	45	42		4	0	8					
				1	129	131		3	0	54	57	3	0	54	57		H = 8		
				2	78	81		1	65	67		2	50	51		0	0	66	
				3	87	84		2	50	51		3	51	52		1	32	36	
				4	52	55		3	51	52		4	39	38		1	16	12	
				5	49	48		4	0	26	19	1	0	20		2	0	42	
				6	30	33		1	0	20		1	0	20		1	51	55	
				2	0	38	23	8	0	29	18	2	22	17					
				1	0	24													

Discussion of the Structure

Some interatomic distances and bond angles of interest are given in Tables 4 and 5 respectively (the atom identification labels are consistent with the usage in Figure 1; atoms marked by an asterisk are located in adjacent unit cells). Although the single Ni(2) atom is distributed over two equivalent positions, the X-ray diffraction patterns of parkerite show no evidence that these atoms have any

TABLE 3. Refined Positional and Thermal Parameters for Parkerite*

Atom	Occupancy	x	y	z	B ₁₁ (B)	B ₂₂	B ₃₃
Ni(1)	1.0	0	0	1/2	0.92(13)		
Ni(2)	0.5	1/4	0.204(3)	0	0.92(13)		
Bi	1.0	1/4	0.7423(7)	0	0.79(8)	1.13(10)	1.04(10)
S	1.0	1/4	0.256(9)	1/2	1.2(7)	7.6(1.9)	4.1(1.3)

*Estimated standard deviations (in parentheses) refer to the last decimal place cited. Thus, 0.204(3) means an esd of 0.003.

tendency to long range order. The Ni(1) and Ni(2) sites are quite similar; both are in octahedral coordination with four Bi and two S; each of these coordination octahedra shares four faces so that interatomic distances between Ni atoms related in this way are less than 2.80 Å. The Bi is coordinated to four Ni(1) atoms, arranged to one side of it, and to four of the half-occupied Ni(2) sites. It is anticipated that the Ni(2) sites would exhibit short range ordering in which most of the Bi atoms would be coordinated to two Ni(2) atoms. The average Ni-Bi bond distance is 2.85 Å, which is a little longer than the bond distance in the alloy NiBi (2.71 Å, Hägg and Funke, 1930). The S is coordinated to two Ni(1) and to two of the half-occupied Ni(2) sites so that any specific S atom would be three coordinated to Ni at the apex of a trigonal pyramid.

Parkerite is usually classified as a sulfosalt since its chemistry involves a metal atom in combination with a group V element and S. However, Takéuchi and Sadanaga (1969) have argued that it is the presence of TS₃ pyramids (where T is a group V element) that distinguishes a sulfosalt from a sulfide, and since the present structure determination has shown that Bi is not coordinated to S, parkerite would

TABLE 4. Bond Distances in Parkerite

Atoms*	Distance(Å)**	Atoms*	Distance(Å)**	
Ni(1'')	- Ni(1')	2.772(2)	Bi' - Bi'	4.052(3)
	- Ni(2')	2.718(8)	- Bi''	3.924(4)
	- Bi''	2.865(2)	- S'	3.45(4)
	- S'	2.02(4)	- S*	3.57(4)
			- S''	3.434(2)
Ni(2')	- Bi'	3.09(2)	S' - S'	4.052(3)
	- Bi*	2.64(2)	- S''	3.94(5)
	- Bi''	2.790(3)	- S*''	4.04(5)
	- S'	2.048(8)		

*Atoms marked by asterisks are located in adjacent unit cells.

**Standard deviations (in parentheses) refer to the last decimal place cited.

TABLE 5. Bond Angles in Parkerite

Atoms* forming angle	Angle**	Atoms* forming angle	Angle**
Bi* - Ni(1'') - Bi''	180.0(0) ^o	Ni(1') - Bi' - Ni(1'')	57.9(1) ^o
- Bi''	90.0(1)	- Ni*(1'')	117.9(1)
Bi' - Ni(1'') - Bi''	90.0(1)	- Ni(2')	121.0(1)
- S'	87.6(7)	- Ni*(2')	59.0(1)
- S*''	92.4(7)	Ni*(1') - Bi' - Ni(2')	115.1(3)
S' - Ni(1'') - S*''	180.0(0)	Ni(1'') - Bi' - Ni*(1'')	90.0(1)
		Ni*(1'') - Bi' - Ni(2')	57.5(2)
Bi' - Ni(2') - Bi*''	180.0(0)	Ni(2') - Bi' - Ni*(2')	180.0(0)
- Bi''	83.6(4)	- Ni(2'')	96.4(4)
- S'	81.6(1.6)	Ni*(2') - Bi' - Ni(2'')	83.6(4)
Bi*'' - Ni(2') - Bi''	96.4(4)	Ni(2'') - Bi' - Ni*(2'')	167.3(8)
- S'	98.4(1.6)		
Bi'' - Ni(2') - Bi*''	167.3(8)	Ni(1') - S' - Ni(1'')	86.8(2.0)
- S'	89.1(2)	- Ni(2')	83.9(1.2)
S' - Ni(2') - S'	163.2(3.1) ^o	Ni(2') - S' - Ni(2'')	163.2(3.1) ^o

*Atoms marked by asterisks are located in adjacent unit cells.

**Standard deviations (in parentheses) refer to the last decimal place cited.

not be included as a sulfosalt on the basis of this criterion.

The parkerite structure is a derivative of the shandite ($\text{Ni}_3\text{Pb}_2\text{S}_2$) structure (Peacock and McAndrew, 1950). Although shandite has a rhombohedral unit cell with $r = 5.576 \text{ \AA}$, the rhombohedral angle is 60° and the Pb atoms are arranged on an ideal C centered lattice (Fig. 2), essentially equivalent to the location of the Bi in parkerite. The nearest neighbor Ni environments are quite similar in both structures, differing only in the disposition of the four Ni(1) neighbors about the Ni(2) site of parkerite. The structures differ, principally, in the

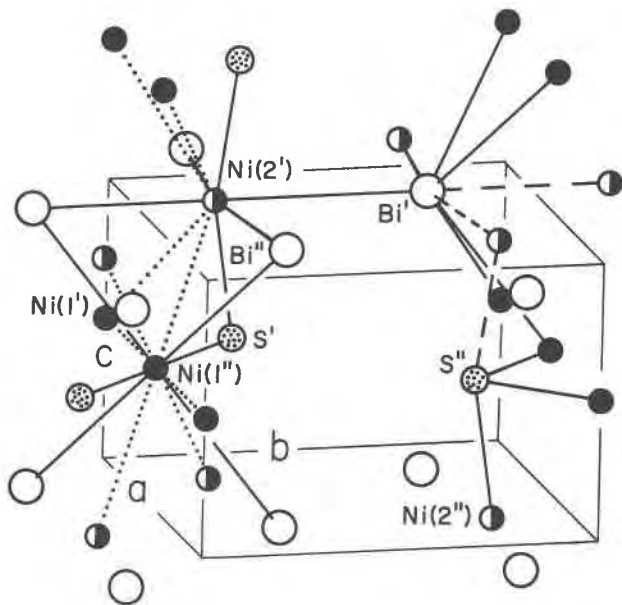


FIG. 1. The crystal structure of parkerite. Ni(1): small full circles; Ni(2): small half-closed circles; Bi: large open circles; S: stippled circles.

arrangements of the Ni atoms about the heavy atoms. In both structures six Ni are coordinated to each heavy atom, but in shandite the Ni atoms form a trigonally-distorted octahedron about the Pb(1) site and a hexagonal ring about the Pb(2) site. In addition each S is coordinated to a Pb(2) atom, as well as to three Ni. However, S was not resolved in the original structure analysis, but it was positioned to give Pb-S and Ni-S distances comparable to the respective data for galena and millerite.

The structure of parkerite requires 18 σ bonds (12 Ni-Bi and 6 Ni-S) per unit cell. Paramagnetic data for parkerite, and hence direct evidence for the $3d$ electron configuration of the Ni atoms and the total number of valence electrons used for bonding, are not available, but analysis of certain aspects of the structure does allow a qualitative treatment of the bonding. The outer electron configurations of the constituent neutral atoms are Ni - $3d^8 4s^2$, Bi - $6s^2 6p^3$ and S - $3s^2 3p^4$.

The nearest Ni-S distances in parkerite (2.02 \AA

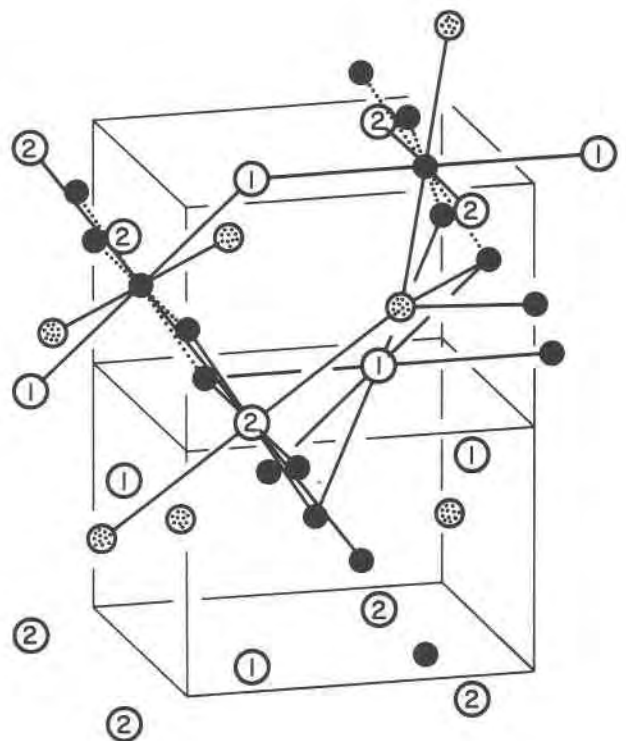


FIG. 2. The crystal structure of shandite, arranged to emphasize the relation of the parkerite structure to it; two unit cell volumes of parkerite are outlined. Ni: small full circles; Bi: large open circles; Pb: large open circles—enclosed numbers differentiate between the Pb(1) and Pb(2) sites; S: stippled circles.

and 2.05 Å) are significantly shorter than the average value (about 2.3 Å) for nickel sulfides, although Ni-S distances of 2.15 Å and 2.19 Å have been reported for α -Ni₇S₆ and millerite respectively (Fleet, 1972). The Ni-S-Ni bond angles approach 90°, suggesting that the σ bonds to the Ni are formed with p orbitals. The short Ni-S bond distances suggest some degree of multiple bond formation, the σ bonds being augmented by π bonding between the $3s$ orbital on the S and the d_{xy} , d_{xz} , and d_{yz} orbitals on the Ni atoms. The bond distance in metallic Ni is 2.492 Å, and it has been suggested that similar Ni-Ni distances in α -Ni₇S₆, heazlewoodite and millerite represent bond numbers of unity (Fleet, 1972). The nearest Ni-Ni distances in parkerite (2.72 Å and 2.77 Å) are too long for full bonds but clearly represent some degree of orbital interaction. The geometry of the Ni sites requires that this interaction must take place in the form of σ bonding between the d_{xy} , d_{xz} , and d_{yz} orbitals. Now, both Ni-S π bonding and Ni-Ni σ bonding possibilities would be prohibited if these $3d$ orbitals were filled; indeed the close approach of the Ni atoms is itself good evidence that these orbitals are not filled. The disposition of the four Ni(1) atoms coordinated to each Bi would require participation of the $6s$ electrons on the Bi atoms in the Ni-Bi σ bonds. The Bi and S atoms, then, contribute 18 electrons to the 12 Ni-Bi and 6 Ni-S σ bonds so that each Ni must contribute 6 electrons, two $4s$ and four $3d$. The four $3d$ electrons on the Ni atoms can be contributed to these bonds only via the $d_{x^2-y^2}$ and d_{z^2} orbitals; it is assumed that the actual bonding orbitals to the Bi and S atoms are octahedral d^2sp^3 hybrid orbitals. This argument requires that only four $3d$ electrons remain to populate the d_{xy} , d_{xz} , and d_{yz} orbitals, allowing these to participate in the Ni-S π bonding and Ni-Ni σ bonding interactions.

The Ni atoms in parkerite are distributed so that the structure is reduced essentially to (010) layers of Ni-(Bi, S) octahedra at $y = 0, 1$ etc. (Fig. 1). Of the 18 Ni-Bi and Ni-S σ bonds per unit cell, only one (a stretched Ni(2)-Bi bond) bridges these layers and this readily explains the excellent {010} cleavage of parkerite.

The extensive solid solution of Pb in parkerite and the very limited solid solution of Bi in shandite must, in part, relate to the disordered structure of parkerite; intuitively, a disordered structure would accommodate a foreign atom more readily than an ordered one. Beyond this statement, further crystal chemical comparisons between the two structures

are hindered by the uncertainty in the S positions in shandite. In this regard, though, crystal chemical analysis of the structure does favor the positions suggested by Peacock and McAndrew. The P_z orbital on the Pb(2) atom would not participate in the σ bonding to the Ni atoms, since all of the Ni atoms coordinated to Pb(2) form a hexagonal ring in the plane normal to this orbital, and would be available to form a σ bond with the $3s$ orbital on the S. This, in turn, would exclude π bonding between S and Ni (unless it involved the empty d orbitals on the S) resulting in conventional Ni-S bond lengths in shandite.

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