

ON PARKERITE AND SHANDITE AND THE CRYSTAL  
STRUCTURE OF  $\text{Ni}_3\text{Pb}_2\text{S}_2$ \*

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ABSTRACT

By quantitative spectrographic analysis parkerite from Sudbury carries  $1.5 \pm 0.1$  per cent Pb, giving the composition  $\text{Ni}_3\text{Bi}_{1.95}\text{Pb}_{0.05}\text{S}_2$ . If the composition  $\text{Ni}_3\text{Bi}_{1.2}\text{Pb}_{0.8}\text{S}_2$  attributed to the original parkerite from Insizwa should be verified, it would be proper to use the name parkerite for the natural equivalent of the isostructural  $\alpha$ -phase  $\text{Ni}_3\text{Bi}_2\text{S}_2 - \text{Ni}_3\text{BiPbS}_2$ , of the artificial system, and to distinguish the Canadian and South African examples as bismuthian and plumbian varieties.

*Shandite* (Ramdohr, 1950) from Trial Harbour, Tasmania, gives the distinctive  $x$ -ray powder pattern of pure  $\text{Ni}_3\text{Pb}_2\text{S}_2$ , the artificial  $\beta$ -phase which will hold almost no Bi in solid solution. In keeping with a face-centered "cubic" lattice and strong optical anisotropism  $\text{Ni}_3\text{Pb}_2\text{S}_2$  has the following structure (rhombohedral description):  $R\bar{3}m$ ;  $r=5.565$  kX,  $\alpha=60^\circ$ ;  $Z=1$ . Pb I at 0 0 0. Pb II at  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ . 3 Ni at  $\frac{1}{2} 0 0$ ;  $0 \frac{1}{2} 0$ ;  $0 0 \frac{1}{2}$ . 2 S at  $x x x$ ;  $\bar{x} \bar{x} \bar{x}$ ; with  $x=0.285$ .

Since the original description of parkerite by Scholtz (1936, p. 186) on scanty material from Waterfall Gorge, Insizwa, East Griqualand, South Africa, and the description of a structurally identical mineral from Sudbury, Ontario, by Michener & Peacock (1943), our attention has been recalled to this mineral by certain relevant spectrographic, thermal, and roentgenographic studies which have been made in South Africa, and by the discovery by Ramdohr (1950) of a closely related new mineral, shandite, at Trial Harbour, Tasmania. As the South African publications are not generally available, and Professor Ramdohr's paper on shandite is in press at the time of writing, a brief summary of the previous work will be needed for the present contribution.

Owing to limitations of material the first description of parkerite was rather tentative and incomplete. In particular, the suggested composition,  $\text{Ni}_2\text{S}_3$  or  $\text{NiS}_2$ , was misleading and subsequent occurrences of the mineral might not have been referred to parkerite except for the  $x$ -ray powder data supplied by Niggli in Scholtz' paper. Previous to 1940 Michener found an apparently new nickel bismuth sulphide in nickel ore from Sudbury, and subsequent detailed study by Michener & Peacock (1943) showed that this mineral is identical in all determinable crystallographic, physical, and chemical properties with artificial  $\text{Ni}_3\text{Bi}_2\text{S}_2$ , a

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compound previously prepared by Schenck & von der Forst (1939); practical identity of the  $x$ -ray powder pattern of the Sudbury mineral with that of the mineral from South Africa, and general compatibility of their observed properties, showed that the Canadian mineral is at least structurally identical with the South African mineral and decided the authors to refer the new occurrence to parkerite rather than to propose a new name.

Subsequently Scholtz re-investigated the composition of the Insizwa parkerite with the aid of the spectrograph. Two microsamples were obtained from a polished ore specimen and submitted to Dr. Strasheim for qualitative spectrochemical analysis. Naudé (1945) reported that the two samples gave identical spectra showing lines of Ni, Bi, and also Pb, and from this he inferred that Pb is an important constituent of the South African mineral. From this qualitative spectrographic work, perhaps supported by other evidence which we cannot find in print, Dr. Scholtz appears to have decided that the composition of the South African parkerite is close to  $\text{Ni}_3\text{Bi}_2\text{S}_2:\text{Ni}_3\text{Pb}_2\text{S}_2=6:4$ , or  $\text{Ni}_3\text{Bi}_{1.2}\text{Pb}_{0.8}\text{S}_2$  (du Preez, 1945; Cormack, 1948). This suggested that Pb, reported only as a chemical trace in Canadian parkerite, might actually be present in substantial amount.

Du Preez (1945) made a thermal study of a series of melts covering the whole range,  $\text{Ni}_3\text{Bi}_2\text{S}_2-\text{Ni}_3\text{Pb}_2\text{S}_2$ , which was called the "Parkerite series" with end-members "Bismuth-Parkerite, Bp" and "Lead-Parkerite, Lp." He found that Bp (mp  $686^\circ\text{C}$ .) forms a complete series of solid solutions with Lp (mp  $717^\circ\text{C}$ .) from pure Bp to practically  $\text{Bp}_{60}\text{Lp}_{40}$ , giving homogeneous products composed of large twinned crystals, like those of parkerite. The solid solution at  $\text{Bp}_{60}\text{Lp}_{40}$ , the supposed composition of South African parkerite, is distinguished by congruent melting at  $707^\circ\text{C}$ . Rapidly cooled melts from  $\text{Bp}_{60}\text{Lp}_{40}$  to  $\text{Bp}_{10}\text{Lp}_{90}$  are inhomogeneous, being composed of unmixed solid solutions and homogeneous twinned crystals of different composition, in various proportions. Pure Lp shows an unexplained deflection of the cooling curve at  $543^\circ\text{C}$ . and it will apparently hold less than 4 per cent Bp in solid solution at equilibrium.

Cormack (1948) made  $x$ -ray powder photographs of samples from du Preez' preparations, using unfiltered Cu-radiation and apparently strong exposures, and reporting the results by glancing angles and visual intensities. Cormack obtained a practically invariant parkerite pattern, substantially identical with those of Niggli and Michener & Peacock, from crystals ( $\alpha$ -phase) in the range  $\text{Ni}_3\text{Bi}_2\text{S}_2$  to  $\text{Ni}_3\text{Bi}_{0.7}\text{Pb}_{1.3}\text{S}_2$ . From samples in the range  $\text{Ni}_3\text{Bi}_{0.6}\text{Pb}_{1.4}\text{S}_2$  to  $\text{Ni}_3\text{Bi}_{0.2}\text{Pb}_{1.8}\text{S}_2$  he obtained a weakening pattern of the  $\alpha$ -phase with a strengthening pattern of

$Ni_3Pb_2S_2$  ( $\beta$ -phase), which is similar to the pattern of the  $\alpha$ -phase but distinct from it. Pure  $Ni_3Pb_2S_2$  of course gave the pattern of the  $\beta$ -phase alone. These results can be reconciled with du Preez' thermal work and they show that the composition of Bp-Lp solid solutions, Bp<sub>100</sub> to Bp<sub>50</sub>Lp<sub>50</sub>, cannot be determined by x-ray powder patterns. Cormack points out that Scholtz' supposition that his parkerite has the composition  $Ni_3Bi_{1.2}Pb_{0.8}S_2$  is not at variance with the powder data, and he repeats the suggestion that the composition of the Canadian material should be examined again for Pb.

#### PARKERITE

As pointed out by Cormack, there is an inconsistency in the chemical composition of the Sudbury parkerite reported by Michener & Peacock (1943), who gave Ni and Bi and traces of Cu and Sn by spectrographic analysis, while the chemical analysis gave the composition  $Ni_3Bi_2S_2$  with a trace of Pb. It was therefore decided to check the presence of Pb in our material and if possible to measure its proportion by quantitative spectrographic procedure.

The sample of parkerite used for quantitative spectrographic analysis was part of the material which had been prepared and used for the chemical analysis in Michener & Peacock (1943). This material still contained a few grains of sperrylite and other minerals which were removed as far as possible by hand.

For comparison the following series of  $Ni_3(Bi, Pb)_2S_2$  solid solutions were prepared by fusion of the elements in evacuated silica glass bulbs:  $Ni_3Bi_2S_2$ ,  $Ni_3Bi_{1.5}Pb_{0.5}S_2$ ,  $Ni_3BiPbS_2$ ,  $Ni_3Pb_2S_2$ . Subsequently, for closer comparison in the range  $Bi_2Pb_0 - Bi_{1.5}Pb_{0.5}$ , the following additional fusions were made:  $Ni_3Bi_{1.9}Pb_{0.1}S_2$ ,  $Ni_3Bi_{1.8}Pb_{0.2}S_2$ ,  $Ni_3Bi_{1.7}Pb_{0.3}S_2$ . In the range  $Ni_3Bi_2S_2 - Ni_3BiPbS_2$  the products show the excellent broad cleavage surfaces of parkerite unlike the product  $Ni_3Pb_2S_2$  which lacks this appearance.

To obtain a first approximation of the Pb content in our parkerite, ground samples of 10 mg. of parkerite and of the first four artificial preparations were arced for 60 seconds at 10 amps. in a 2 meter A.R.L. grating spectrograph. This treatment was sufficient to volatilize Bi and Pb completely, as shown by the fact that no Bi or Pb lines were obtained on re-arc-ing. By inspection of the spectrogram it was clear that the composition of parkerite lies between  $Ni_3Bi_2S_2$  and  $Ni_3Bi_{1.5}Pb_{0.5}S_2$ .

To fix the composition more closely the spectra from 10 mg. samples of the first two and the additional three fusion products and parkerite were recorded on one film, and the intensities of the Bi line ( $I_{Bi}$ ) at 2730.5 Å and the Pb line ( $I_{Pb}$ ) at 2663.2 Å were obtained from measurements

with a photometer, corrected for background. The ratio  $I_{Pb}/I_{Bi}$  for each sample was then plotted against the known Pb contents on log-log. paper giving a straight line which determined the Pb content of parkerite as 1.6 per cent.

An independent determination of Pb in parkerite was obtained by using 10 mg. of the same five materials with 5 mg. of Bi added to each; this reduced the variation of Bi in the samples. Using the Bi line at 2524.5 Å and the Pb line at 2663.2 Å, with the same procedure, the Pb content of parkerite was found to be 1.4 per cent (Figs. 1, 2).

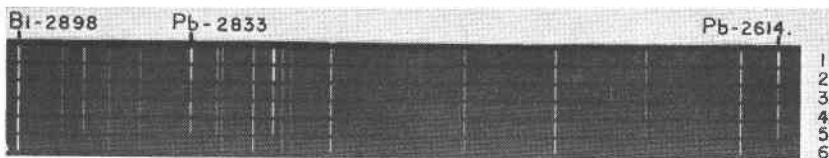


FIG. 1. Part of spectrograms of artificial  $Ni_3(Bi, Pb)_2S_2$  compounds and parkerite from Sudbury. 1— $Bi_{1.5}Pb_{0.5}$ ; 2— $Bi_{1.7}Pb_{0.3}$ ; 3—parkerite; 4— $Bi_{1.8}Pb_{0.2}$ ; 5— $Bi_{1.9}Pb_{0.1}$ ; 6— $Bi_2Pb_0$ . It can be seen that the Pb lines in 3 are weaker than in 5.

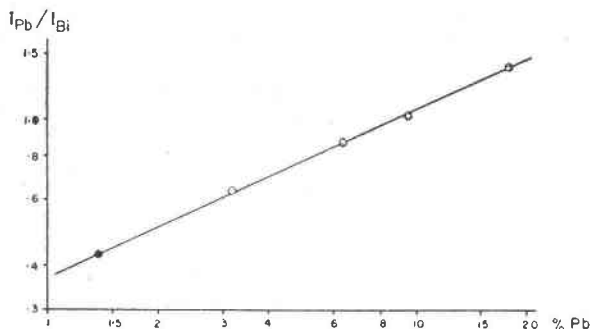


FIG. 2. Plot of spectrographic  $I_{Pb}/I_{Bi}$  against wt. percent Pb for artificial compounds (blank points) and parkerite (filled point).

The foregoing work shows that Pb is actually present in Sudbury parkerite to the extent of  $1.5 \pm 0.1$  per cent, in keeping with the previous chemical work, and showing that the previously reported spectrographic Sn was probably based on a misreading of Pb lines. The Canadian mineral is thus practically  $Ni_3Bi_2S_2$  and therefore, in a sense, it is not identical with the South African mineral, if we accept the supposed composition,  $Ni_3Bi_{1.2}Pb_{0.8}S_2$ , of the latter mineral. However, the tendency today is to identify a mineral species with an isostructural phase and, if necessary, to distinguish members of such a series as varieties with suitable adjectival qualifiers. Thus the natural equivalent of the isostructural  $\alpha$ -phase

extending from  $Ni_3Bi_2S_2$  to about  $Ni_3BiPbS_2$  would be named parkerite, and the Bi-rich and Pb-rich members could be described as bismuthian parkerite and plumbian parkerite respectively.

It should be emphasized, however, that the Pb content of the Insizwa mineral remains to be determined by quantitative means and that, therefore, the existence of a natural parkerite series is not yet proved. Actually there are some reasons for doubting the high Pb content attributed to the South African mineral. Both at Sudbury and at Insizwa, parkerite is intimately associated with galena; since nearly pure  $Ni_3Bi_2S_2$  formed in the former deposit we might expect the same in the latter. Again, the association of parkerite with galena inevitably raises the suspicion that microsamples extracted from polished sections of parkerite might be contaminated with PbS, in spite of careful manipulation. Finally, it is a curious fact that the  $x$ -ray powder patterns of parkerite from both localities and of pure artificial  $Ni_3Bi_2S_2$ , given by Niggli, Michener & Peacock, and Cormack, all run to  $\theta=69^\circ$  as the last legible line, whereas Cormack's pattern for artificial  $Ni_3Bi_{1.2}Pb_{0.8}S_2$ , the supposed composition of Insizwa parkerite, gives out at  $\theta=45.6^\circ$ , indicating the less perfect crystallinity of this solid solution. We propose, therefore, that the specific name parkerite be used for natural  $Ni_3(Bi, Pb)_2S_2$  in which as yet only a minor proportion of Pb (1.5 per cent) has been actually proved by a quantitative method. If the existence of a natural parkerite series should be clearly established, the name parkerite will still be appropriate in the range  $Ni_3Bi_2S_2-Ni_3BiPbS_2$ .

#### SHANDITE

In May, 1949, the senior author received from Professor P. Ramdohr, then stationed in Melbourne, a polished specimen of ore from Trial Harbour, Tasmania. The specimen is mainly serpentine in which Dr. Ramdohr had noted pentlandite, heazlewoodite, and other sulphides, and also a few minute grains of an ore mineral which he believed to correspond to the artificial compound  $Ni_3Pb_2S_2$ , hitherto unknown in nature. Dr. Ramdohr had located these grains on the polished surface with characteristic marks, and he asked if his presumption regarding their identity could be tested by  $x$ -ray powder photographs. Doubting his ability to obtain samples from such minute areas, the senior author sent the specimen to his skillful former student, Dr. R. M. Thompson, Vancouver, B. C., who kindly undertook the delicate task of excavating and  $x$ -raying samples from the grains in question. From two areas Dr. Thompson obtained identical  $x$ -ray powder photographs, and a list of observed intensities and spacings which was found to correspond to Cormack's data (1948) for pure artificial  $Ni_3Pb_2S_2$  and to differ distinctly from the

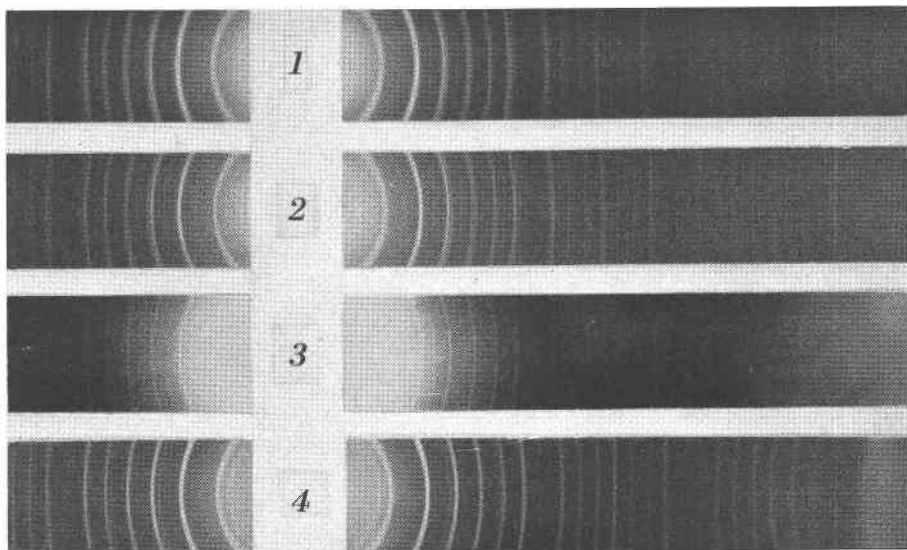


FIG. 3. X-ray powder patterns; Cu/Ni radiation; camera radius  $90/\pi$  mm.; contact prints, full size. 1—Artificial  $\text{Ni}_3\text{Bi}_2\text{S}_2$ ; 2—Parkerite, Sudbury; 3—Shandite, Trial Harbour, Tasmania (sample with impurities scraped from minute grains in polished section); 4—Artificial  $\text{Ni}_3\text{Pb}_2\text{S}_2$  (print somewhat stretched).

similar data for parkerite,  $\text{Ni}_3\text{Bi}_2\text{S}_2$  (Michener & Peacock, 1943) or members of the artificial series  $\text{Ni}_3(\text{Bi}, \text{Pb})_2\text{S}_2$  (Cormack, 1948). Thus it was proved that the mineral from Tasmania is indeed the natural form of  $\text{Ni}_3\text{Pb}_2\text{S}_2$ , and Dr. Ramdohr's remarkable prediction was confirmed (Fig. 3).

On receiving this result Dr. Ramdohr intimated in a private communication (Nov., 1949) that he proposed to name the new mineral *shandite*, after Professor S. J. Shand, the distinguished Scottish petrologist who had suggested to Dr. D. L. Scholtz the study of the Insizwa nickel ores which led to the discovery of parkerite. At the same time Dr. Ramdohr stated that his paper on shandite was nearly ready for publication; and therefore we venture to use the new name which should be in print by the time this work is published.<sup>1</sup> Our subsequent observations on  $\text{Ni}_3\text{Pb}_2\text{S}_2$  are confined to the artificial compound whose structural properties can be taken to supplement those of shandite, since the mineral is structurally identical with the laboratory compound.

Two lots of artificial shandite were prepared by fusing charges of 1 gm. and 2 gm. of the powdered elements in the proportions  $3\text{Ni}:2\text{Bi}:2\text{S}$

<sup>1</sup> Since this was written Dr. Ramdohr has sent us a copy of his MS on shandite with the information that the work is in press (Feb., 1950).

in evacuated silica glass bulbs of about 2 cc. capacity. The first of these was allowed to cool in air; the second was cooled overnight in a furnace. The compact metallic products are similar to galena in colour; when broken they show bright metallic lustre and a compact fine to medium grained aggregation of crystals with good cleavage. Unlike artificial parkerite which shows broad (001) cleavage plates traversed by (111) twin lamellae (orthorhombic indices), fragments of artificial shandite show discontinuous cleavage in four directions which give distinct reflections on the two-circle goniometer proving octahedral relationship.

Polished sections from these preparations are compact, cream-white, with noticeable reflection pleochroism and fairly strong anisotropism giving grey-blue and yellow-brown as maximum polarization colors. Crossed nicols reveal a mosaic of angular to irregular grains which are not in random arrangement but in several sets of optically parallel individuals which give simultaneous extinction sometimes over large areas. The Talmage hardness is C and the highest specific gravity by the Berne man balance is 8.72.

#### CRYSTAL STRUCTURE OF $Ni_3Pb_2S_2$

Table 1 compares the  $x$ -ray powder patterns of shandite and our artificial  $Ni_3Pb_2S_2$ . Except for some weak extra lines in the pattern of shandite, no doubt due to unavoidable contamination in sampling minute grains in a polished section, the glancing angles, spacings, and intensities are identical within the limits of observation. The pattern of shandite is markedly similar to that of parkerite in spacings and intensities, but it differs in having certain single lines in place of double lines in parkerite (Fig. 3). This is due to the fact that parkerite has a pseudo-cubic sub-structure with edges 3.97 and 4.02 kX (Peacock, 1947, p. 68); in shandite the corresponding sub-structure is, metrically, exactly cubic with the edge  $c' = 3.935$  kX. This cube-edge serves to index all but a few weak lines in  $Ni_3Pb_2S_2$ ; to index the pattern completely the double value,  $c = 7.87$  kX, is required. This gives indices which show the missing spectra of the  $F$ -lattice, and no others, and calculated spacings which agree with the values observed on natural and artificial material. The sharp shandite pattern shows no evidence of splitting of cubic lines, even in the sensitive back reflections, and therefore the lattice has strictly equal rectangular periods. With  $4[Ni_3Pb_2S_2]$  or  $Ni_{12}Pb_8S_8$  in the cube with edge  $c$  the calculated density is 8.86 as compared to the highest measured specific gravity 8.72. The cubelet with edge  $c'$  thus contains  $\frac{1}{2}[Ni_3Pb_2S_2]$ .

These results obtained from good powder photographs were verified by rotation and Weissenberg photographs on a fragment of artificial

TABLE 1. SHANDITE AND ARTIFICIAL  $\text{Ni}_3\text{Pb}_2\text{S}_2$ : X-RAY POWDER PATTERN  
 "Cubic",  $F$ ;  $a = 7.87$  kX

Shandite*			Artificial $\text{Ni}_3\text{Pb}_2\text{S}_2$ †			$(hkl)$	$d(\text{calc.})$
$I$	$\theta(\text{Cu})$	$d(\text{meas.})$	$I$	$\theta(\text{Cu})$	$d(\text{meas.})$		
1	6.2°	7.12	—	—	—	—	—
2	9.75	4.54	2	9.75°	4.54	(111)	4.544
8	11.25	3.94	7	11.2	3.96	(002)	3.935
$\frac{1}{2}$	12.05	3.68	—	—	—	—	—
$\frac{1}{2}$	12.9	3.44	—	—	—	—	—
$\frac{1}{2}$	14.3	3.11	—	—	—	—	—
10	16.05	2.78	10	16.0	2.79	(022)	2.782
1	17.85	2.51	—	—	—	—	—
1	18.9	2.37	2	18.85	2.38	(113)	2.373
7	19.8	2.27	8	19.8	2.27	(222)	2.272
6	22.95	1.971	6	23.0	1.969	(004)	1.968
$\frac{1}{2}$	23.65	1.916	—	—	—	—	—
$\frac{1}{2}$	25.05	1.816	2	25.25	1.803	(133)	1.805
5	25.9	1.760	5	25.9	1.760	(024)	1.760
$\frac{1}{2}$	27.45	1.668	—	—	—	—	—
7	28.5	1.611	7	28.55	1.609	(224)	1.606
—	—	—	$\frac{1}{2}$	30.7	1.506	{(115)}	1.515
4	33.55	1.391	4	33.55	1.391	{(333)}	1.391
3	35.9	1.311	3	35.95	1.309	{(044)}	1.312
3	38.2	1.243	3	38.15	1.244	{(006)}	1.244
5	40.3	1.189	5	40.35	1.187	{(244)}	1.186
1	42.6	1.136	2	42.65	1.135	(026)	1.244
1	44.9	1.089	2	44.9	1.089	(226)	1.186
3	47.0	1.051	4	46.95	1.052	(444)	1.136
$\frac{1}{2}$	48.7	1.023	$\frac{1}{2}$	48.65	1.024	(046)	1.091
$\frac{1}{2}$	51.5	0.982	2	51.45	0.983	(246)	1.052
2	53.6	0.955	3	53.65	0.954	{(137)}	1.025
1	56.0	0.927	3	56.1	0.926	{(355)}	1.025
1	58.4	0.903	3	58.35	0.903	(008)	0.984
2	61.0	0.879	3	60.85	0.880	{(028)}	0.954
$\frac{1}{2}$	63.6	0.858	3	63.6	0.858	{(446)}	0.927
$\frac{1}{2}$	66.1	0.841	$\frac{1}{2}$	66.2	0.840	(266)	0.903
2	72.6	0.806	2	72.95	0.804	(048)	0.880
—	—	—	1	78.0	0.786	(248)	0.859
						(466)	0.839
						{(448)}	0.803
						{(0.0.10)}	0.787
						{(068)}	0.787

\* Observations by R. M. Thompson (Vancouver, B.C.) on a sample from minute grains marked as shandite by P. Ramdohr in a polished section of ore from Trial Harbour, Tasmania.

† Intensities visually estimated by R. M. Thompson; spacings measured by J. McA.

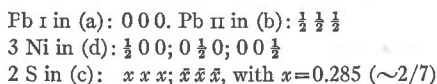


shandite showing interrupted octahedral cleavage. These also led to a simple cubic pseudo-cell with  $c' = 3.935$  kX and a face-centered cubic real cell with  $c = 2c' = 7.87$  kX. This real cell was indicated by a very weak first layer line in the rotation photograph about an axis of apparent 4-fold symmetry. There are no systematically missing spectra beyond those of the cubic  $F$ -lattice.

In view of the apparently normal cubic diffraction effects, the incompatible optical behavior was at first set aside and an attempt was made to find a cubic- $F$  structure for shandite. Since the structure of adjacent cubelets must be nearly alike the 8 Pb atoms are probably at the corners of the cubelets; but no reasonable arrangement of 12 Ni and 8 S could be found within the limitations of the  $F$ -lattice.

In keeping with the optical anisotropism tetragonal structures were then sought in a face-centered cell with  $a = c = 7.87$  kX or a body-centered cell with  $a' = c/\sqrt{2}$ . One plausible tetragonal structure was found with Pb atoms at the corners of the cubelets, Ni atoms distributed over the centers of their vertical faces, and S atoms paired along vertical 4-fold axes and about the centers of horizontal faces of the cubelets. However, certain interatomic distances for this structure and the calculated intensities were not satisfactory, and therefore the idea of a tetragonal structure was abandoned.

A face-centered rhombohedral structure with  $r' = c = 7.87$  kX,  $\alpha' = 90^\circ$ , containing  $4[Ni_3Pb_2S_2]$ , or a simple rhombohedral structure with  $r = c/\sqrt{2} = 5.565$  kX,  $\alpha = 60^\circ$ , containing  $Ni_3Pb_2S_2$ , next came into consideration; and a single structure was soon found that gave entirely satisfactory distances and calculated intensities and a good explanation of the optical behavior and cleavage appearance of the crystal. The structure has the symmetry of the centrosymmetrical space group  $R\bar{3}m$ , and the atoms in the  $60^\circ$  cell are placed as follows (rhombohedral coordinates):



The correctness of this structure is shown by the comparison of calculated and observed powder intensities in Table 2. For each cubic- $F$  structural form (with the number of equivalent sets of planes,  $n$ ), are given the equivalent rhombohedral ( $\alpha = 60^\circ$ ) and hexagonal structural form or forms (with the numbers of equivalent sets of planes,  $n$ ). The cubic indices, in all significantly different permutations having  $h \leq k \leq l$  (algebraically) are related to the rhombohedral indices with  $h \geq k \geq l$  by the transformations:

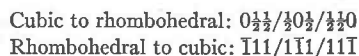


TABLE 2.  $\text{Ni}_3\text{Pb}_2\text{S}_2$  (SHANDITE): CALCULATED AND OBSERVED  
X-RAY POWDER INTENSITIES

Cubic <i>F</i>	<i>n</i>	Rhombohedral		Hexagonal	<i>I</i> (calc.)		<i>I</i> (obs.) M.A.P.* J.McA.†	
		<i>n</i>	<i>n</i>					
(111)	4	(111)	1	(0003)	0.73	0.96	1	0.3
		(100)	3	(10 $\bar{1}$ 1)	0.23			
(002)	3	(110)	3	(01 $\bar{1}$ 2)	5.48	5.48	4	3
(022)	6	(211)	3	(10 $\bar{1}$ 4)	4.71	10.00	10	10
		(10 $\bar{1}$ )	3	(1120)	5.29			
(113)	12	(221)	3	(01 $\bar{1}$ 5)	0.00	1.06	1	0.5
		(11 $\bar{1}$ )	3	(0221)	0.71			
		(210)	6	(1123)	0.35			
(222)	4	(222)	1	(0006)	1.68	6.07	6	6
		(200)	3	(2022)	4.39			
(004)	3	(220)	3	(0224)	3.99	3.99	5	5
(133)	12	(322)	3	(10 $\bar{1}$ 7)	0.12	0.61	$\frac{1}{2}$	0.5
		(311)	3	(2025)	0.42			
		(20 $\bar{1}$ )	6	(21 $\bar{3}$ 1)	0.03			
(024)	12	(321)	6	(11 $\bar{2}$ 6)	1.62	2.87	3	2
		(21 $\bar{1}$ )	6	(12 $\bar{3}$ 2)	1.25			
(244)	12	(332)	3	(01 $\bar{1}$ 8)	0.62	3.14	4	4
		(112)	3	(0330)	0.90			
		(310)	6	(21 $\bar{3}$ 4)	1.62			
{(115)}	12	(331)	3	(0227)	0.057	0.22	< $\frac{1}{2}$	0.1
		(22 $\bar{1}$ )	3	(0333)	0.041			
		(320)	6	(12 $\bar{3}$ 5)	0.000			
{(333)}	4	(333)	1	(0009)	0.078	0.22	< $\frac{1}{2}$	0.1
		(300)	3	(3033)	0.041			
(044)	6	(422)	3	(20 $\bar{2}$ 8)	1.10	2.48	3	3
		(20 $\bar{2}$ )	3	(2240)	1.38			
(135)	24	(432)	6	(1129)	0.000	0.20	—	—
		(31 $\bar{1}$ )	6	(2243)	0.104			
		(21 $\bar{2}$ )	6	(1341)	0.011			
		(421)	6	(2137)	0.080			
(006)	3	(330)	3	(0336)	0.311	1.52	2	2
{(244)}	12	(433)	3	(1.0. $\bar{1}$ . 10)	0.413			
		(411)	3	(3036)	0.311			
		(30 $\bar{1}$ )	6	(3142)	0.482			
(026)	12	(431)	6	(1238)	0.574	1.28	2	2
		(32 $\bar{1}$ )	6	(1344)	0.706			
(335)	12	(443)	3	(0.1. $\bar{1}$ . 11)	0.021	0.09	—	—
		(31 $\bar{1}$ )	3	(4041)	0.071			
		(410)	6	(3145)	0.000			
(226)	12	(442)	3	(0.2. $\bar{2}$ . 10)	0.634	2.42	3	2.5
		(222)	3	(0442)	0.538			
		(420)	6	(2246)	1.250			
(444)	4	(444)	1	(0.0.0.12)	0.164	0.85	1	1
		(400)	3	(4044)	0.681			
{(117)}	12	(441)	3	(0339)	0.024	0.24	—	—
		(33 $\bar{1}$ )	3	(0445)	0.084			
		(430)	6	(1347)	0.047			
{(155)}	12	(533)	3	(2.0. $\bar{2}$ . 11)	0.074	0.24	—	—
		(522)	3	(3039)	0.000			
		(302)	6	(3251)	0.006			

TABLE 2, *Continued*

Cubic <i>F</i>	<i>n</i>	Rhombohedral		Hexagonal	<i>I</i> (calc.)	<i>I</i> (obs.)		
		<i>n</i>	<i>n</i>			M.A.P.*	J.McA.†	
(046)	12	(532)	6	(2.1.3̄.10)	0.475	0.75	1	1
		(312̄)	6	(235̄2)	0.275			
(246)	24	(543)	6	(1.1.2̄.12)	0.191	1.59	2	2.5
		(213̄)	6	(145̄0)	0.502			
		(521)	6	(314̄8)	0.341			
		(411̄)	6	(325̄4)	0.557			
{(137)	24	(531)	6	(224̄9)	0.145	0.24	½	0.2
		(542)	6	(1.2.3̄.11)	0.025			
		(322̄)	6	(145̄3)	0.028			
{(355)	12	(421̄)	6	(235̄5)	0.000	0.09	—	—
		(544)	3	(1.0.1̄.13)	0.002			
		(511)	3	(404̄7)	0.017			
(008)	3	(440)	3	(415̄3)	0.028	0.44	1	0.5
(337)	12	(553)	3	(0.2.2̄.13)	0.048	0.09	—	—
		(223̄)	3	(055̄1)	0.005			
		(520)	6	(325̄7)	0.039			
{(028)	12	(541)	6	(1.3.4̄.10)	0.415	1.40	3	1.5
		(431̄)	6	(145̄6)	0.314			
{(446)	12	(554)	3	(0.1.1̄.14)	0.233	0.98	2	1.5
		(411̄)	3	(505̄2)	0.123			
		(510)	6	(415̄6)	0.314			
{(228)	12	(552)	3	(0.3.3̄.12)	0.126	0.98	2	1.5
		(330)	3	(033̄6)	0.160			
		(530)	6	(235̄8)	0.327			
{(066)	6	(633)	3	(3.0.3̄.12)	0.126	0.16	—	—
		(303̄)	3	(336̄0)	0.239			
{(157)	24	(643)	6	(2.1.3̄.13)	0.004	0.16	—	—
		(313̄)	6	(246̄1)	0.093			
		(632)	6	(3.1.4̄.11)	0.026			
		(412̄)	6	(336̄3)	0.025			
{(555)	4	(555)	1	(0.0.0.15)	0.015	0.20	—	—
		(500)	3	(505̄5)	0.000			
(266)	12	(644)	3	(2.0.2̄.14)	0.599	1.56	3	1.5
		(622)	3	(4.0.4̄.10)	0.556			
		(402)	6	(426̄2)	0.406			
(048)	12	(642)	6	(2.2.4̄.12)	0.819	1.94	3	1.5
		(422)	6	(246̄4)	1.124			
{(119)	12	(551)	3	(0.4.4̄.11)	0.026	0.20	—	—
		(441̄)	3	(055̄7)	0.021			
		(540)	6	(145̄9)	0.000			
{(357)	24	(654)	6	(1.1.2̄.15)	0.001	0.20	—	—
		(621)	6	(415̄9)	0.000			
		(511̄)	6	(426̄5)	0.154			
		(412̄)	6	(516̄1)	0.002			
(248)	24	(521̄)	6	(336̄6)	0.380	1.29	3	1.5
		(653)	6	(1.2.3̄.14)	0.566			
		(323̄)	6	(156̄2)	0.296			
		(631)	6	(3.2.5̄.10)	0.050			

\* By inspection.

† By visual comparison with a standard film of Al.

The resulting hexagonal indices then have  $hk*l$  all positive, which is required. The intensity for each structural form was most conveniently computed from the rhombohedral indices, with the usual formula:

$$I = kn \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \left\{ \sum f_0 \cos 2\pi(hx + ky + lz) \right\}^2$$

where  $k$  is a constant chosen to reduce the intensities for convenient comparison with the observed values,  $n$  is the number of equivalent sets of planes, and  $f_0$  are scattering factors taken from the *International Tables for the Determination of Crystal Structures*, vol. 2. The sum of the calculated intensities of all rhombohedral forms contributing to a single "cubic" powder ring is thus directly comparable with two independent sets of readings on a good powder film. The qualitative, even quantitative, agreement in Table 2 is satisfactory. The observed intensities in Table 1 show qualitative agreement with the calculated values.

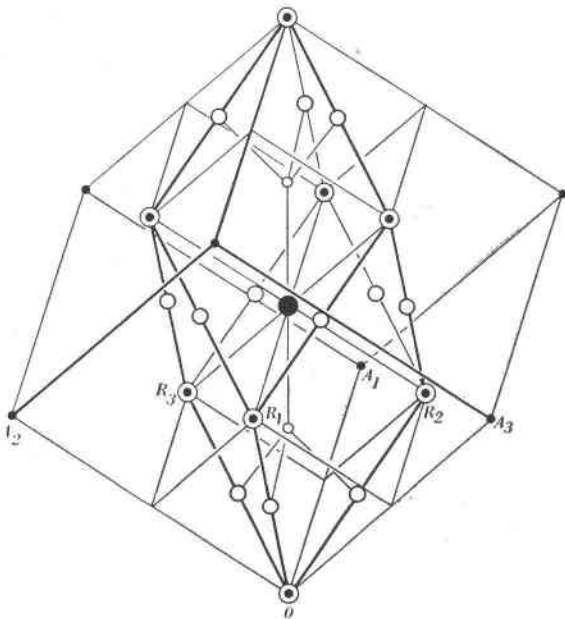


FIG. 4.  $\text{Ni}_3\text{Pb}_2\text{S}_2$  (shandite): Atomic arrangement in the primitive ( $60^\circ$ ) rhombohedral cell,  $OR_1, OR_2, OR_3$ , in relation to the face-centered ( $90^\circ$ ) rhombohedral (cubic) cell,  $OA_1, OA_2, OA_3$ , and two of the eight contained cubelets. Large circles at  $F$ -lattice points;  $\text{PbII}$ ; large filled circle,  $\text{PbII}$ ; medium circles,  $\text{Ni}$ ; small circles  $\text{S}$ .

As shown in Fig. 4, which gives the structure of  $\text{Ni}_3\text{Pb}_2\text{S}_2$  in one  $60^\circ$  cell in relation to the face-centered  $90^\circ$  cell—the large cube, which is best seen with the edge  $OA_2$  vertical— $\text{PbII}$  is at the origin and face-centers of

the large cube,  $Pb_{II}$  is at the body-centre, 3 Ni are at non-opposite face-centers of a cubelet, and 2 S are on a body diagonal, resting between 3 Ni and  $Pb_{II}$ .

The atomic positions in the face-centered  $90^\circ$  rhombohedron (or cube) with identical points  $000$ ;  $0\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}0$ ; are:

$$\begin{aligned} 4 \text{ Pb I: } & 000; 4 \text{ Pb II: } \frac{1}{2}\frac{1}{2}\frac{1}{2} \\ 12 \text{ Ni: } & 0\frac{1}{4}\frac{1}{4}; \frac{1}{4}0\frac{1}{4}; \frac{1}{4}\frac{1}{4}0; \\ 8 \text{ S: } & x x x; \bar{x}\bar{x}\bar{x}. \end{aligned}$$

The entire structure in the  $90^\circ$  cell is shown in Fig. 5. 4  $Pb_{I}$  and 4  $Pb_{II}$  are in NaCl arrangement and the 12 Ni occupy half the 24 face-centers of the 8 cubelets; it is this arrangement of Pb and Ni atoms which presumably determines the cubic form of the large cell.  $Pb_{I}$  is surrounded

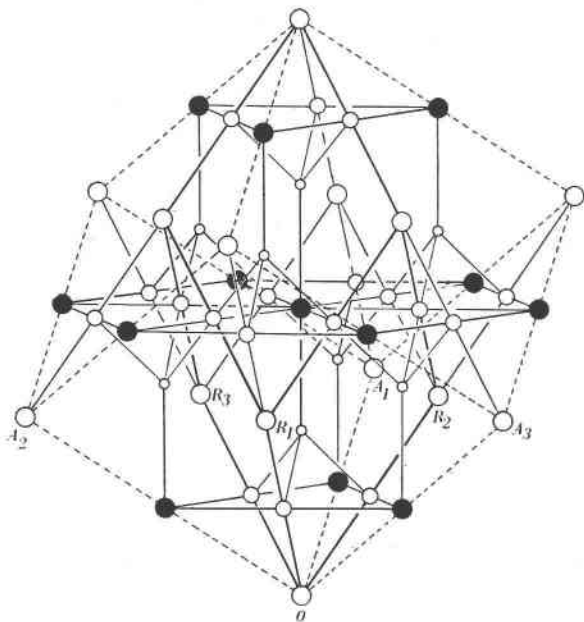


FIG. 5.  $Ni_3Pb_2S_2$  (shandite): Atomic arrangement in the face-centered ( $90^\circ$ ) rhombohedral cell. Cell edges and scheme of atoms as in Fig. 4. The unbroken lines show only the shortest atomic connections.

by 6 Ni at the corners of two equilateral triangles, one above and one below;  $Pb_{II}$  is at the center of a hexagonal bipyramid made by 6 Ni and 2 S. S is surrounded by 3 Ni at the corners of an equilateral triangle, above or below, and on the opposite side by  $Pb_{II}$ . Since the S-parameter could hardly be determined by the intensities, it has been chosen to give

the S—Ni distance 2.28 kX, as in  $\text{Ni}_3\text{S}_2$  (heazlewoodite) (Peacock, 1947). The shortest interatomic distances in this structure are: Ni—Pb=2.78 kX, Ni—S=2.28 kX, Pb—S=2.93 kX. Comparable distances are Ni—S=2.3 in NiS (millerite); Pb—S=2.96 in PbS (galena). A Ni—Pb distance was not found.

The rhombohedral structure of  $\text{Ni}_3\text{Pb}_2\text{S}_2$  is in keeping with the optical anisotropism of the compound and it explains the peculiar mosaic texture and the apparent cubic symmetry and octahedral cleavage of single fragments. With a metrically cubic lattice we would expect the crystal to form complementary twins on all the elements of symmetry of the cube which are not elements of symmetry of the structure. These are the cube faces, the 4-fold axes, etc., which can altogether give rise to four orientations in which the singular 3-fold axis of the structure is brought into the four directions of the body-diagonals of the cube while the twinned complex is still pervaded by the undeviated face-centered cubic lattice. In twinning of this sort (twinning by merohedry of Friedel) the twinned parts will fit on any composition surface and thus they could give rise to the observed angular to irregular mosaic with several groups of optically parallel grains. A fragment of such a twinned complex large enough for single crystal reflection and  $x$ -ray measurements would therefore show cubic symmetry by twinning. The interrupted octahedral cleavage of such a fragment is therefore most likely the result of a single cleavage, namely (111) (basal rhombohedral) repeated by twinning to give the four directions of the octahedron; and the cubic appearance of the "single" crystal  $x$ -ray photographs is no doubt due to the same cause.

Finally, the structure of  $\text{Ni}_3\text{Pb}_2\text{S}_2$  (shandite) shows again how unsatisfactory it is to define the crystal systems by the metrical relations of their lattice elements or axes. With equal rectangular cell edges shandite cannot be placed in the cubic system, in view of the symmetry of the structure and optical anisotropism; and even the stipulation that cubic crystals must have equal rectangular cell edges *at all temperatures*, fails in this case and is generally impracticable. The face-centered lattice of shandite very probably retains its cubic form from room temperature up to the deflection noted by du Preez at 543° C., where, by analogy with other crystals, the structure may invert to a truly cubic disordered arrangement. But, in any case, it is impossible to measure cell dimensions at all temperatures, and therefore it may often be impossible to assign a crystal to its metrical crystal system. Actually, working crystallographers have always assigned crystals to their systems on the basis of symmetry, accepting the systems in effect as groups of crystal classes. The crystal systems have lattices with certain typical metrical relations; but by specialization of lengths and angles the lattice in any symmetry system

may occasionally assume the metrical relations typical of any higher symmetry system, even over a range of temperature.

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