Canadian Mineralogist
Vol. 13, pp. 418-419 (1975)

NEW DATA ON WAKABAYASHILITE*

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INTRODUCTION

As part of the continuing program in this laboratory of the study of arsenic sulphosalts, it was decided to investigate the crystal structure of wakabayashilite. Currently-available information on this mineral is sufficient only for species recognition (Kato *et al.* 1970; Sadanaga & Bunno 1974); this preliminary report is intended to provide a better characterization of the species.

EXPERIMENTAL

Well-formed, transparent crystals were selected from a nest of golden yellow wakabayashilite needles covering an area about 1×1 cm on a specimen of massive realgar from the White Caps mine, Manhattan, Nevada, belonging to the collection of W. W. Pinch of Rochester, New York.

The specific gravity was determined for each of five large crystals, using a Berman balance with toluene as the flotation agent. The average value obtained was 3.98(2), in reasonable agreement with the previously-reported value of 3.96. A crystal mounted on a two-circle optical goniometer gave good signals at intervals of 60° ± 5′, indicating that the cell was dimensionally hexagonal or pseudo-hexagonal.

Weissenberg and precession photographs showed a pronounced hexagonal sub-cell with $6/mmm$ symmetry, having the extinction conditions hhl, $l \neq 2n$ and $00l$, $l \neq 2n$. A monoclinic supercell, with $a_m = c_m = 2a_h$, $b_m = c_h$, is also clearly visible on the photographs; however, in the super-cell only the second extinction condition obtains. There was no sign of a doubling of the monoclinic b axis on long-exposure rotation photographs. In view of the slightly differing monoclinic (pseudo-hexagonal) cell dimensions reported by Kato *et al.*, cell dimensions were carefully checked using a double-radius Weissenberg camera with a silicon powder standard (a = 5.4305Å). No difference could be detected between the monoclinic a and c (hexagonal a) dimensions.

The hexagonal nature of the sub-cell was confirmed by diffractometer measurements in which all hexagonal-equivalent reflections, in a triply-redundant data set, were equivalent within 3% of their average. Both intensity statistics and E-statistics favour a centric structure for the sub-cell, with $P6_3/mmc$ as the most probable space group.

Crystal data for wakabayashilite are listed in Table 1, and the powder pattern is given in Table 2.

DISCUSSION

The short (6.48Å) c dimension of the structure precludes full occupation of either of the two 4-fold positions or the 24-fold general position of $P6_3/mmc$, leaving only 2-, 6- or 12-fold special positions available to the heavy atoms. Given the "inner" analysis of Kato *et al.*, $Sb_{1.95}As_{19.92}S_{34.71}$, if the sub-cell is not to be severely disordered, it is likely that its ideal composition is $Sb_2As_{20}S_{36}$, with a discrete 2-fold antimony site.

The crystals are highly flexible and elastic, and bend at the slightest touch. Such deformation appears to induce the formation of the super-cell. Visible differences in the intensities

TABLE 1. CRYSTAL DATA FOR WAKABAYASHILITE

	sub-cell	super-cell
a	14.564(3)Å	29.128Å
b	14.564(3)	6.480
c	6.480(4)	29.128
β		120°
Space group	$P6_3/mmc$	$P2_1/m$
D_m	3.98(2) g/cm^3	
D_c	4.04 g/cm^3	
Ideal formula	$Sb_2As_{20}S_{36}$	
Z	1	4
μ_L(CuKα)	403 cm^{-1}	
μR	0.85	

*Contribution No. 279. — Part 85 on sulphides and sulphosalts.

TABLE 2. POWDER PATTERN OF WAKABAYASHILITE

Present study				Kato *et al.*	
I_{est}	d_{obs}*	d_{calc}	*hkl***	*I*	d_{obs}
5	12.57	12.61	100		
100	6.28	6.31	200	100	6.33
25	5.77	5.76	101		
70	4.78	4.77	210	50	4.78
5	4.520	4.519	201		
5	4.204	4.204	300		
5	4.038	4.039	(-702)†		
30	3.834	3.840	211		
80	3.488	3.498	310	50	3.50
40	3.239	3.240	002	20	3.24
5 b	3.150	3.153	400, 102		
40	3.078	3.078	311, (-902)	25	3.08
5	2.980	2.970	(-718)		
10	2.963	2.960	112		
20	2.883	2.882	202		
10	2.836	2.835	401		
30	2.753	2.752	410		
10	2.638	2.642	321		
25	2.565	2.566	302		
35	2.535	2.533	411	20	2.55
40	2.423	2.427	330, 222		
30	2.239	2.237	421		
25	2.139	2.138	511		
20	2.071	2.073	430		
20	2.020	2.020	520		
8 b	1.939	1.943	332		
30	1.843	1.844	611		
20	1.818	1.820	440		
		1.736	531		
8 b	1.734	1.731	323		
8 b	1.712	1.714	522, 413		
15	1.670	1.671	710		
8 b	1.616	1.615	540, 004		
40	1.590	1.589	630, 442		
10	1.439	1.439	811, 613		
8	1.322	1.322	650, 713		

* 114.6 mm camera, Ni-filtered Cu$K\alpha$ radiation.
** Indexed on the hexagonal sub-cell a = 14.564, c = 6.480Å.
† Indices in brackets refer to the monoclinic super-cell.

of the weak super-structure reflections and diffuse streaks exist on either side of the hexagonal mirror planes of the sub-cell, clearly demonstrating the monoclinic nature of the super-cell. It was observed that, although the positions of the super-structure reflectons were constant for different crystals, the intensities of these reflections were not. Two crystals were found which gave a minimum of diffuse streaking on zero-level Weissenberg films. One of these was reserved for data collection, and the other was deliberately deformed by repeated flexing of the crystal. A subsequent zero-level photograph of the deformed crystal showed a much stronger and more widespread pattern of diffuse streaks, as well as increased intensity values for several of the super-structure reflections. These reflections correspond in *d*-value to the extra (non-hexagonal) reflections given in the powder pattern (Table 2). Since they also appear in the powder pattern, these super-cell reflections must be even further enhanced by the grinding of the specimen. An explanation of this variation of intensity in terms of the movement of atoms in the cell must await the full determination of at least the hexagonal substructure.

ACKNOWLEDGEMENT

The investigation was supported by Schweiberischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (project no. 2.516.71) and by Stiftung Entwicklungsfonds Seltene Metalle.

REFERENCES

KATO, A., SAKURAI, K. I. & OHSUMI, K. (1970): *Introduction to Japanese Minerals.* Geol. Surv. Japan, pp. 92-93.

SADANAGA, R. & BUNNO, M. (1974): The Wakabayashi mineral collection. *Univ. Museum, Univ. Tokyo Bull.* 7, p. 73 and Plate I.

Manuscript received August 1975.

PUBLICATIONS RECEIVED

COPPER DEPOSITS; J. H. Tatsch, 339 pages. Tatsch Associates, Sudbury, Massachusetts 01776. $72.00 U.S.

POLITICS, MINERALS, AND SURVIVAL; edited by Ralph W. Marsden, 86 pages, soft cover. University of Wisconsin Press, Madison, Wisconsin 53701. $2.45 U.S.

READING THE ROCKS (The Story of the Geological Survey of Canada 1842-1972); M. Zaslow, 620 pages. MacMillan of Canada, 70 Bond Street, Toronto, Ontario M5B 1X3. $25.00 Canadian.

SEMI-CONDUCTING ORE MINERALS; R. T. Shuey, 415 pages. Elsevier Excerpta Medica North-Holland, Jan van Galenstraat 335, Amsterdam, Netherlands. $22.95 U.S.

THE FACIES OF REGIONAL METAMORPHISM AT HIGH PRESSURES; N. L. Dobretsov, V. S. Sobolev, N. V. Sobolev & V. V. Khlestov; translated by D. A. Brown. Australian National University Press, Canberra, A.C.T. 2600, Australia. Available from International Scholarly Book Services Inc., P.O. Box 4347, Portland, Oregon 97208. $14.80 U.S.