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Preparation, Properties and Crystal Structure of Barium Vanadium Sulfide, BaVS$_3$*

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Barium vanadium sulfide, BaVS$_3$, has been prepared and single crystals have been grown from a barium chloride flux. The crystal structure of BaVS$_3$ at room temperature has been determined by single-crystal analysis and the space group is $P6_3/mmc$ with two formula units per unit cell. The hexagonal cell dimensions are $a = 6{\cdot}724 \pm 0{\cdot}005$ Å and $c = 5{\cdot}610 \pm 0{\cdot}005$ Å. The calculated density is 4·30 g.cm^{-3} and the observed density is 4·22 g.cm^{-3}. The structure has been refined by least-squares techniques to a final R value on F of 7·5% for 192 independent reflections above background. The structure is based on hexagonal close-packed BaS$_3$ layers with the vanadium cations occupying one quarter of the octahedral voids between these layers. These are all the voids that are bounded exclusively by anions. The vanadium cations form chains parallel to the c axis with a V–V distance of $2{\cdot}805 \pm 0{\cdot}002$ Å. Low temperature powder X-ray studies indicate that a crystallographic distortion begins to occur near 185°K and this distortion gradually increases as the temperature is decreased. At liquid nitrogen temperature the distortion is considerable, but its exact nature is unknown. A plot of resistivity as a function of temperature indicates a change in the slope at approximately 130°K. This change is associated with a transition from the metallic to the semiconducting state. The electrical properties of BaVS$_3$, in the metallic state, are discussed in terms of direct interactions between the vanadium cations.

Introduction

Katz & Ward (1964) have recently described the structures of a number of mixed metal oxides in terms of the stacking sequence of essentially close-packed metal-oxygen layers. The concept of structure in terms of stacking sequences permits the correlation of a large number of structure types. In addition, it is possible to utilize these ideas in order to predict the existence of new compounds.

Compounds of the type ABX$_3$ where A is a large cation, B a small cation, and X is an anion, can be described as an essentially close-packed array of A and X ions, provided A and X are approximately the same size. In such an array, one quarter of the octahedral voids are bounded exclusively by the anions; these are the octahedra occupied by the B cations. The well known perovskite-type structure may be described in terms of cubic close-packing of the AX$_3$ layers. If the stacking sequence of the close-packed layers is hexagonal, then a different structure-type results. In addition, other structure-types can be described in terms of different sequences of hexagonal and cubic layers. The structure of compounds with a common packing sequence has usually been classified according to the crystal structures of minerals or specific compounds, *e.g.* perovskite, spinel, nickel arsenide, *etc.* This may at times lead to confusion because many such compounds often show marked differences in their crystallographic properties; a common packing sequence does not necessarily imply a common crystal structure. In this study it is preferred to designate the compounds according to the packing sequence rather than by association with the structure of a particular class of minerals or compounds.

In ABX$_3$ compounds with a cubic close-packed arrangement of ions, the octahedra occupied by B cations share corners; in the hexagonal close-packed structure these octahedra share faces and form continuous chains parallel to the c axis of the crystal. The ternary transition metal sulfides and selenides BaTiS$_3$ (Hahn & Mutschke, 1956; Clearfield, 1963; Aslanov & Kovba, 1964), BaTiSe$_3$ (Aslanov, 1964), SrTiS$_3$ (Hahn &

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Mutschke, 1956), $BaTaS_3$ (Aslanov & Kovba, 1964), $BaTaSe_3$ (Aslanov, 1964), $BaZrSe_3$ (Aslanov, 1964), appear to crystallize with the hexagonal close-packed type structure. The room temperature form of $BaVS_3$, which has not previously been reported, can be classified with this group of compounds. This structure is also similar to that of $CsNiCl_3$ (Tishchenko, 1955), in which the nickel cations occupy one quarter of the octahedral voids between close-packed $CsCl_3$ layers. In addition $BaNiO_3$ (Lander, 1951) has been reported, on the basis of powder work, to have a similar structure. The stoichiometry of $BaNiO_3$, however, has been questioned (Gushee, Katz & Ward, 1957). In the room temperature form of $BaVS_3$ the vanadium cations, which occupy one quarter of the face shared octahedra, form continuous chains. If the V–V distance is sufficiently small, then there may be enough overlap of the transition metal *d*-orbitals to result in the formation of conduction bands. This has been observed for other ternary vanadium chalcogenides (Bouchard, Robinson & Wold, 1966). Since the *d*-orbitals of vanadium in the compound $BaVS_3$ contain only one electron, the conduction bands would only be partially filled and metallic conduction should result.

Previous studies of V^{3+} and V^{4+} oxides (Perrakis, 1927; Hoschek & Klemm, 1939; Rüdorff, Walter & Stadler, 1958; Morin, 1959; Warekois, 1960; Goodman, 1962; Goodenough, 1963; Feinleib & Paul, 1967) indicate that crystallographic transitions occur in these compounds which may result in a change from semiconducting to metallic behavior. This transition results from the formation of covalent V–V bonds with the trapping of conduction electrons (Goodenough, 1965). It was therefore decided to investigate the electrical and crystallographic properties of $BaVS_3$ at low temperatures in order to ascertain the nature of the V–V bonding in this compound.

Experimental

Preparation

$BaVS_3$ was prepared by heating an intimately ground mixture of barium carbonate and vanadium pentoxide ('Specpure' Johnson, Matthey & Co., Ltd.) at 500°C for 12 hours and then at 900°C for 24 hours in a hydrogen sulfide atmosphere.

Crystal growth

Single crystals of $BaVS_3$ were grown using barium chloride as a flux. A mixture of the sulfide and flux was placed in an evacuated silica tube and then sealed inside a second silica tube. This procedure prevented any exposure of the melt to air, since the inner tube tended to devitrify and crack. The double-tubed sample was heated to 1050°C and held at that temperature for 12–24 hours. The furnace was then programmed to cool from 1050°C to 800°C at 3°/hour and then to room temperature at 50°/hour. The melt was extracted with cold water, filtered and washed with acetone. The larger crystals were separated from the treated melt by passing the mixture through a series of standard sieves. The largest crystals grown by this technique were 0·5 to 3 mm long. They were gold-colored and grew primarily in the habit of first order hexagonal prisms $\{10\bar{1}0\}$, although some crystals formed as small hexagonal platelets $\{0001\}$.

Analyses

Both the polycrystalline and single crystal forms of $BaVS_3$ were analyzed. Barium was determined by a standard gravimetric sulfate procedure after the sample was dissolved in hot 6*N* hydrochloric acid. Vanadium was determined volumetrically by titration with standardized ferrous ammonium sulfate solution. Sulfur in the polycrystalline sample was determined by oxidizing the sample in a stream of oxygen at 500°C and measuring the gain in weight of the sample. The products of the oxidation are barium sulfate and vanadium pentoxide, as verified by X-ray diffraction. The weight gain upon oxidation was related to the amount of sulfur initially present. The single crystals were analyzed for barium, vanadium and chlorine. The sulfur content was determined by difference. The amount of chloride present in the single crystals was determined

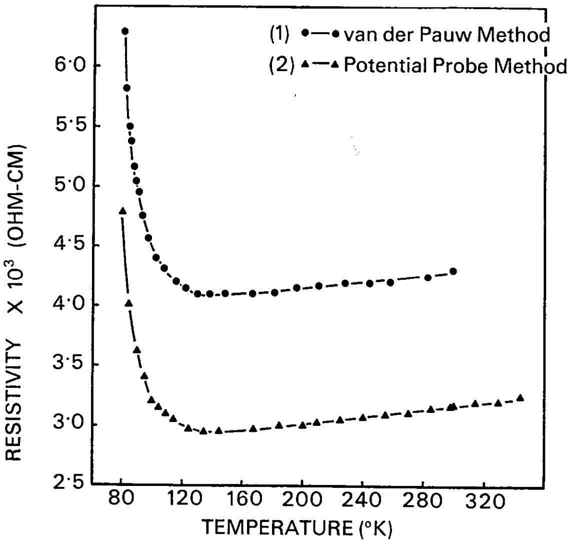

Fig. 1. Resistivity *vs.* temperature for $BaVS_3$.

Table 1. *Analytical results*

	% Ba		% V		% S		% Cl
	found	calc.	found	calc.	found	calc.	found
Polycrystalline sample	48·25	48·28	17·83	17·91	33·88	33·81	—
Single crystals	48·04	48·28	17·88	17·91	33·63	33·81	0·45

by the Volhard method. The analytical results are presented in Table 1.

Physical measurements

Electrical resitivity as a function of temperature was determined on sintered bars from 80°K to 350°K. ($BaVS_3$ begins to lose sulfur at approximately 370°K under vacuum). For these measurements the samples were pressed at 20000 p.s.i. and sintered in a hydrogen sufide atmosphere at 900°C. Electrical resistivity as a function of temperature was determined by means of both the van der Pauw (1958) and conventional potential-probe techniques. For both methods, spring-loaded contacts were used and the results obtained are plotted as curves 1 and 2 in Fig. 1. The shape of the curves and the approximate transition point was duplicated on several different preparations of $BaVS_3$. In this study a compound is classified as metallic if the resistivity has a positive temperature coefficient and also has a low Seebeck coefficient.

Collection and reduction of room temperature X-ray data

Powder samples were examined by X-ray diffraction methods with the use of a high intensity copper source [λ(Cu $K\alpha_1$)1·5405 Å]. The diffracted X-rays were monochromatized (AMR–202 focusing monochromator) and detected by a Norelco scintillation counter. Powder diffraction data of $BaVS_3$ at 25° were indexed on the basis of a hexagonal cell with $a=6.714+0{\cdot}005$, $c=5{\cdot}610\pm0.005$ Å. In addition, lattice dimensions at 25° were determined from single-crystal rotation and Weissenberg photographs calibrated with sodium chloride. For $BaVS_3$, $a=6{\cdot}724\pm0{\cdot}005$ and $c=5{\cdot}610\pm0{\cdot}005$ Å [λ(Mo $K\alpha_1$)0·70926 Å]. The pycnometrically measured density was $d_m=4{\cdot}22\pm0{\cdot}05$ g.cm^{-3} which indicated a cell containing two formula units. The calculated density was $d_c=4{\cdot}30$ g.cm^{-3}. The reported errors for both the powder and single-crystal cell parameters represent the average deviations in the observed cell constants.

The Laue symmetry for $BaVS_3$ was found to be $6/mmm$. Systematic extinctions, determined from zero- and upper-layer Weissenberg and precession photographs, occurred only for $hh2hl$: $l=2n+1$. In addition, structural absences $h-k=3n$ for $l=2n+1$ were observed. These absences are consistent with the space groups $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$. Piezoelectric and pyroelectric measurements were not made since metallic crystals do not show these effects (Cady, 1929).

A single crystal of $BaVS_3$, in the form of a thin hexagonal platelet (approximately $0{\cdot}1\times0{\cdot}02$ mm), was mounted about its b axis. Multiple-film equi-inclination Weissenberg photographs were taken with Zr-filtered Mo $K\alpha$ radiation in order to obtain intensity data. A total of 703 reflections were measured visually by comparison with a standard intensity scale. These data were scaled and averaged to give a total of 192 independent reflections. The inter-film and inter-layer scaling was carried out by the usual scaling algorithms (Hamilton, Rollett & Sparks, 1965). The intensity data were corrected for spot-shape and Lorentz–polarization effects. No absorption or extinction corrections were applied. Before the averaging of equivalent reflections was made, failure to consider absorption caused an estimated maximum of 20% error in the F_{obs} for some of the reflections.

Solution and refinement of the structure

An inspection of the three-dimensional Patterson function, calculated by the use of the NCR–8 Fourier program of Ahmed, Hall, Pippy & Saunderson (1966), indicated that the vanadium, barium and sulfur atoms occupy the positions 2(*a*), 2(*b*) and 6(*c*) in space group $P6_3mc$ and 2(*a*), 2(*d*) and 6(*h*) in both $P\bar{6}2c$ and $P6_3/mmc$ (*International Tables for X-ray Crystallography*, 1962). The approximate positional parameters were determined to be (0,0,0) for V, $(\frac{1}{3},\frac{2}{3},\frac{3}{4})$ for Ba, and $(x,2x,\frac{1}{4})$ with $x=\frac{1}{6}$ for S. Although all three space groups were possible, it was decided initially to refine the structure in the centrosymmetric $P6_3/mmc$. A full-matrix least-squares refinement was carried out with the use of the Busing, Martin & Levy (1962) *ORFLS program* modified to make real and imaginary anomalous dispersion corrections. The atomic scattering factors for S^{2-} were taken from *International Tables for X-ray Crystallography* (1962), and those for Ba^{2+} and V^{4+} were the values given by Thomas & Umeda (1957). The necessary parameters used for the anomalous dispersion were those given by Dauben & Templeton (1962). Weights were assigned to each reflection according to the scheme of Cruickshank & Pilling (1961), *i.e.* $w=(A+BF+CF^2)^{-1}$, with $A=2\,F_{\min}$, $B=1{\cdot}0$, $C=2/F_{\max}$.

The function $\Sigma\, w(|F_o|-|F_c|)^2$ was minimized where F_o and F_c are the observed and calculated structure amplitudes and w is the weight defined above. The unobserved reflections were assigned zero intensity and

Table 2. *Calculated and observed structure factors for* $BaVS_3$

K	L	OBS	CALC
H=0			
0	2	136	127
0	4	125	123
0	6	53	56
0	8	50	45
H=1			
0	0	0	0
0	1	65	63
0	2	64	62
0	3	45	50
0	4	0	2
0	5	32	32
0	6	27	26
0	7	20	20
1	0	118	134
1	2	34	35
1	4	61	64
1	6	14	17
1	8	25	24
H=2			
0	0	53	50
0	1	138	133
0	2	108	96
0	3	69	58
0	4	28	29
0	5	66	67
0	6	41	42
0	7	34	41
1	0	0	4
1	1	50	53
1	2	50	54
1	3	41	42
1	4	0	4
1	5	28	28
1	6	25	24
1	7	21	18
2	0	140	145
2	2	81	88
2	4	41	47
2	6	48	46
2	8	40	34
H=3			
0	0	92	87
0	2	30	30
0	4	50	55
0	6	18	16
1	0	0	3
1	1	40	46
1	2	40	44
1	3	35	37
1	4	0	3
1	5	27	25
1	6	23	21
2	0	0	4
2	1	37	40
2	2	33	36
2	3	35	33
2	4	0	3
2	5	26	23
2	6	20	18
2	7	10	15
3	0	54	54
3	2	23	22
3	4	34	33
3	6	10	12
H=4			
0	0	37	36
0	1	95	93
0	2	60	68
0	3	72	78
0	4	26	25
0	5	55	56
0	6	34	34
0	7	32	35
1	0	61	62
1	2	27	24
1	4	39	42
1	6	17	13
2	0	34	30
2	1	76	75
2	2	48	54
2	3	54	64
2	4	27	22
2	5	44	46
2	6	29	28
2	7	30	29
2	8	13	8
3	0	0	6
3	1	26	26
3	2	26	26
3	3	23	22
3	4	6	4
3	5	19	17
3	6	18	14
4	0	76	74
4	2	48	52
4	4	49	54
4	6	33	28
4	8	25	23
H=5			
0	0	0	6
0	1	31	33
0	2	31	36
0	3	28	28
0	4	5	5
0	5	22	20
0	6	15	17
1	0	0	5
1	1	28	30
1	2	26	25
1	3	25	25
1	4	0	4
1	5	22	15
1	6	20	18
2	0	41	41
2	2	25	17
2	4	25	30
2	6	9	11
2	8	0	4
3	1	24	[illegible]
3	2	19	15
3	3	22	15
3	4	[illegible]	[illegible]
3	5	15	15
4	0	0	2
4	1	25	19
4	2	14	15
4	3	21	16
5	0	23	22
5	2	10	12
H=6			
0	0	[illegible]	56
0	2	59	61
0	4	59	65
0	6	33	33
0	8	[illegible]	27
1	0	0	3
1	1	25	25
1	2	20	21
1	3	21	21
1	4	0	3
1	5	19	16
2	0	26	22
2	1	50	52
2	2	35	35
2	3	40	44
2	4	22	16
2	5	32	33
2	6	21	20
2	7	23	21
3	0	29	27
3	2	10	13
3	4	20	21
4	0	20	16
4	1	34	37
4	2	24	25
4	3	33	37
4	4	0	12
4	5	24	24
4	6	20	14
6	0	37	41
6	2	34	26
6	4	27	26
H=7			
0	0	0	3
0	1	24	23
0	2	18	14
0	3	21	14
0	4	0	7
0	5	16	15
0	6	0	11
1	0	30	31
1	2	21	16
1	4	23	21
1	6	9	7
2	0	0	5
2	1	18	15
2	2	17	16
2	3	18	14
H=8			
0	0	25	19
0	1	43	44
0	2	28	20
0	3	35	37
0	4	16	14
0	5	28	28
0	6	23	17
0	7	22	18
1	0	0	4
1	1	22	15
1	2	12	14
1	3	18	13
2	0	36	43
2	2	32	32
2	4	27	32
2	6	22	18
4	0	12	10
4	1	25	23
4	2	15	15
4	3	25	20
H=9			
0	0	17	20

0 INDICATES UNOBSERVED REFLECTIONS

Table 3. *Positional and thermal parameters**†

	x	y	z	β_{11}	β_{22}	β_{33}
S	0·1656 (6)	0·3312 (6)	$\frac{1}{4}$	63 (9)	66 (9)	125 (12)
V	0	0	0	141 (10)	141 (10)	118 (17)
Ba	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	87 (4)	87 (4)	114 (7)

* The standard deviations are shown in parenthesis and refer to the last decimal position of the respective values.

† The temperature factor expression used was $\exp[-10^{-4}(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. Constraints placed on the β_{ij}'s are: for sulfur $\beta_{11}=2\beta_{12}$, $\beta_{23}=\beta_{13}=0$, and for vanadium and barium $\beta_{11}=\beta_{22}=2\beta_{12}$, $\beta_{23}=\beta_{13}=0$.

given zero weight in the refinement. For the refinement procedure, one overall scale factor was used.

Three cycles of isotropic least-squares refinement led to the following R indices:

$$R=\frac{\Sigma\,||F_o|-|F_c||}{\Sigma\,|F_o|}=0{\cdot}095\,,$$

$$wR=\left[\frac{\Sigma\,w(|F_o|-|F_c|)^2}{\Sigma\,w|F_o|^2}\right]^{1/2}=0{\cdot}107\,.$$

The refinement was continued in the centrosymmetric space group with three cycles of anisotropic calculations. The final values of R and wR for the observed data were 0·075 and 0·083 respectively. In addition, the final error of fit was 1·298. These results indicate a moderate decrease in wR that seems to justify the anisotropic refinement. The final positional and thermal parameters of this refinement are given in Table 3. Interatomic distances, bond angles and standard deviations were calculated by the use of the Busing, Martin & Levy (1964) *ORFFE* program and are shown in Table 4. The final structure amplitudes are given in Table 3.

Table 4. *Selected distances and bond angles**

Atoms	Distance (Å)	Atoms (central atom is vertex)	Angle (°)
S'—V'	2·385 (3)	S'–V'—S''	91·07 (15)
S'—Ba''	3·362 (3)	S'–V'—S^{vi}	88·93 (8)
S''–Ba''	3·418 (3)	S'–V'—S^{iv}	180·00 (8)
S'—S''	3·404 (2)	V'–Ba''–V''	39·73 (4)
V'–V''	2·805 (2)	S'–Ba''–V''	35·30 (3)
S'—S^{vi}	3·340 (2)		
V'–Ba''	4·128 (3)		
Ba'–Ba''	4·790 (3)		

Root-mean-square radial thermal displacements of atoms (Å)

S	0·206
V	0·260
Ba	0·220

* Errors in cell parameters are included in the standard deviations.

The above results indicate that a reasonable refinement was obtained in the centrosymmetric $P6_3/mmc$ space group. In the absence of any stereochemical evidence which would show that the choice is incorrect, the centrosymmetric group is assumed.

Low temperature X-ray study

Powder samples of $BaVS_3$ were mixed with collodion and amyl acetate and spread on an aluminum-backed Pyrex slide with a copper-constantan thermocouple mounted between the aluminum and pyrex. The samples were then examined using monochromatized (AMR-202 focusing monochromator) high intensity copper radiation [λ(Cu $K\alpha$)1·5405 Å] with a Norelco diffractometer. The radiation was detected with a Norelco scintillation counter. A temperature of approximately 77°K was reached by blowing liquid nitrogen directly on to the sample. To obtain temperatures between that of liquid nitrogen and room temperatures an apparatus similar to that described by Post, Schwartz, & Fankuchen (1951) was used.

Results and discussion

Analyses of the product obtained from various crystal growth experiments indicated that less than 0·5% chlorine from the flux was present in the samples. The small amount of chlorine present in the crystals should not affect the crystallographic results reported. However, since electrical properties are affected by impurity content, resistivity and Seebeck measurements were not made on the small crystals but on well-characterized sintered bars.

A representation of the room temperature structure of $BaVS_3$ is shown in Fig. 2 and indicates the parallel chains of vanadium cations. There are also columns of unoccupied octahedra, with barium cations at two of their opposite corners, which share edges with the vanadium occupied octahedra shown in the Figure. The

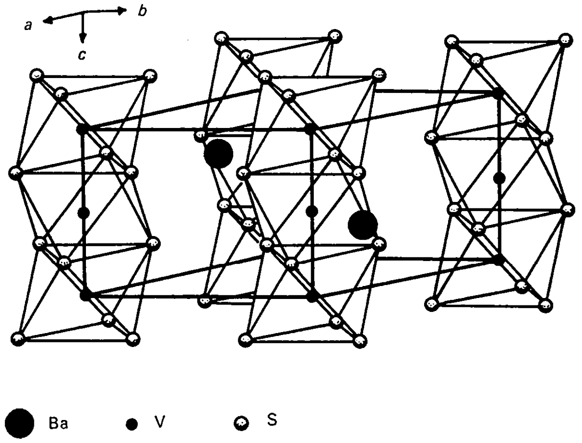

Fig. 2. Structure of $BaVS_3$ showing chains of face-sharing sulfur octahedra. The hexagonal unit cell is outlined with bold lines.

unoccupied octahedra are not shown for the sake of simplicity. Fig. 3 shows the packing sequence of the nearly close-packed BaS_3 layers perpendicular to the c axis; the vanadium cations occupy one quarter of the octahedral voids between the layers. It can be seen from Fig. 4 that within the BaS_3 layers the S–S distances are $3{\cdot}340 \pm 0{\cdot}002$ Å while the distance between sulfurs in adjacent layers is $3{\cdot}404 \pm 0{\cdot}002$ Å. The S–V–S angle for sulfur atoms in adjacent layers is $91{\cdot}07 \pm 0{\cdot}15°$ and $88{\cdot}93 \pm 0{\cdot}08°$ for sulfur atoms in the same layer. The Ba–S distance (not shown in Fig. 4) within the layers is $3{\cdot}362 \pm 0{\cdot}003$ Å. The errors on the distances and angles are standard deviations. In a perfect close-packed structure Ba–S and S–S distances should be the same. However, the Ba–S and S–S distances within the layers are shorter than the corresponding distances between adjacent layers.

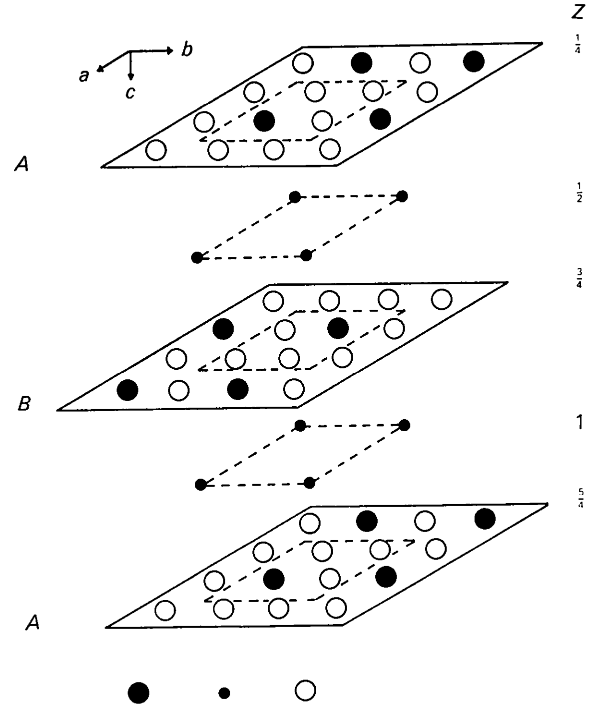

Fig. 3. Schematic diagram of close-packed layer structure of $BaVS_3$. Dashed lines indicate outline of unit cell.

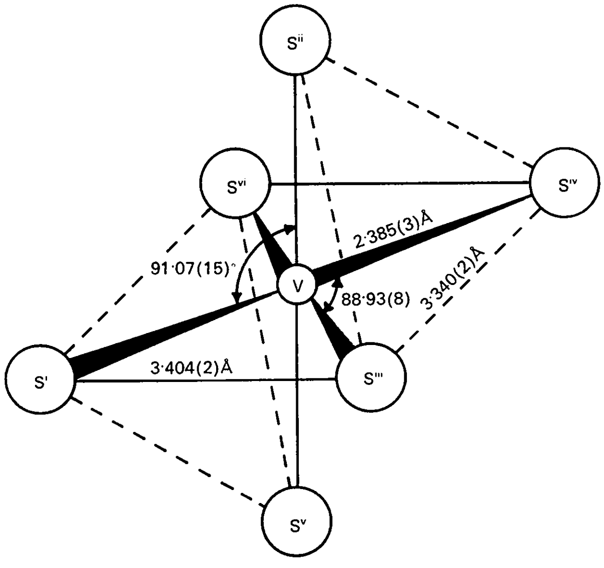

Fig. 4. Vanadium occupied sulfur octahedron with bond distances and angles. Dashed lines indicate the planes of close-packed layers. Errors are noted in parentheses and represent standard deviations.

An exploratory diffraction pattern was recorded at 77 °K up to $2\theta = 80°$. It was observed that the overall diffraction pattern at 77 °K showed a considerable change when compared with the room temperature pattern. Numerous splittings and great changes in the intensities of the hexagonal lines were observed. When the sample was warmed to room temperature its X-ray pattern was identical to the original hexagonal pattern.

In order to determine the temperature at which the structure changes begin to occur X-ray diffraction patterns were recorded at several temperatures between 298 °K and 77 °K from $2\theta = 30°$ to $2\theta = 37°$. Between 2θ values of 30° to 37°, the observed splittings were most pronounced. The temperature for each X-ray scan was maintained to within ± 2°. A diagram of the relative intensities of the diffraction peaks *vs.* 2θ for $T = 298°$, 183°, and 77 °K is presented in Fig. 5. A crystallographic change on cooling is first noticed at approximately 183 °K as determined from the first observable splitting of the 200 and 201 diffraction peaks of the hexagonal structure. The extent of the splitting of these peaks is shown in Fig. 5. It appears from these low temperature observations that the structural change is still incomplete at 77 °K. The diffraction pattern at this temperature could be indexed tentatively on an orthorhombic cell with $a = 11{\cdot}55$, $b = 6{\cdot}52$, $c = 5{\cdot}54$ Å. The following relationships exist between the hexagonal and orthorhombic cells: $a_0 \simeq \sqrt{3}\, a_h$; $b_0 \simeq a_h$; $c_0 \simeq c_h$. Such transitions are quite common for ABX_3 type compounds.

From Fig. 1 it can be seen that there is a resistivity minimum at approximately 130 °K. Above this temperature, the resistivity increases with increasing temperature, indicating metallic behavior. Below 130 °K there is a sharp increase in the resistivity with decreasing temperature. Thus the crystallographic change observed below 185° K is undoubtedly associated with the significant change in the resistivity data.

The Seebeck coefficient of $BaVS_3$ at room temperature has the rather low value of $-54\mu V\,°C^{-1}$. The values of the resistivity at room temperature and 80 °K were between 10^{-3} and 10^{-2} ohm-cm, whereas the resistivity measured at 5 °K was 10^{10} ohm-cm. This represents a change in the resistivity of approximately twelve orders of magnitude between 80 °K and 5 °K.

The metallic behavior of hexagonal $BaVS_3$ can be explained by examination of the structure of $BaVS_3$ shown in Fig. 2. It can be seen that the vanadium atoms form chains parallel to the c axis. Goodenough (1963) has proposed that direct interaction between transition metal atoms can occur by the overlap of d-orbitals, provided the two metal atoms are within a critical distance, R_c, of each other. Goodenough has formulated an expression for the critical distance, R_c, needed for direct interaction between metal atoms in an anion lattice. The expression for R_c for $3d$ transition metal oxides is:

$$R_c^{3d}(\text{oxides}) = [3{\cdot}05 - 0{\cdot}03\ (Z - Z_{\text{Ti}})\ - 0{\cdot}04J\ (J+1)]\ \text{Å},$$

where Z_{Ti} and Z are, respectively, the atomic numbers of titanium and of the transition metal cation in question, and J is the total angular momentum quantum number of the transition metal cation. For sulfides (Goodenough, 1967) the above expression requires a correction of $+0{\cdot}5$ Å. Hence for $BaVS_3$ it is anticipated that R_c for V^{4+}–V^{4+} interaction is approximately 3·45 Å.

In the structure of the room temperature form of $BaVS_3$ shown in Fig. 2, the distance between successive vanadium atoms through the faces of the shared octahedra is $\frac{1}{2}(c) = \frac{1}{2}(5{\cdot}610) = 2{\cdot}805$ Å. (The V–V distance in vanadium metal is 2·61 Å.) Thus the metal–metal distance along the c axis is clearly less than $R_c = 3{\cdot}45$ Å and metallic conduction should be observed. The observed metallic behavior of hexagonal $BaVS_3$ is consistent with the concepts proposed by Goodenough.

The change in electrical behavior is related to a crystallographic transition in which the hexagonal structure is distorted. The exact nature of the distortion is unknown but it undoubtedly affects the V–V chains which are parallel to the c axis in the hexagonal structure. Any type of distortion in these chains would interfere with the delocalization of the electrons and would explain the marked increase in the resistivity of the sample below 130°K.

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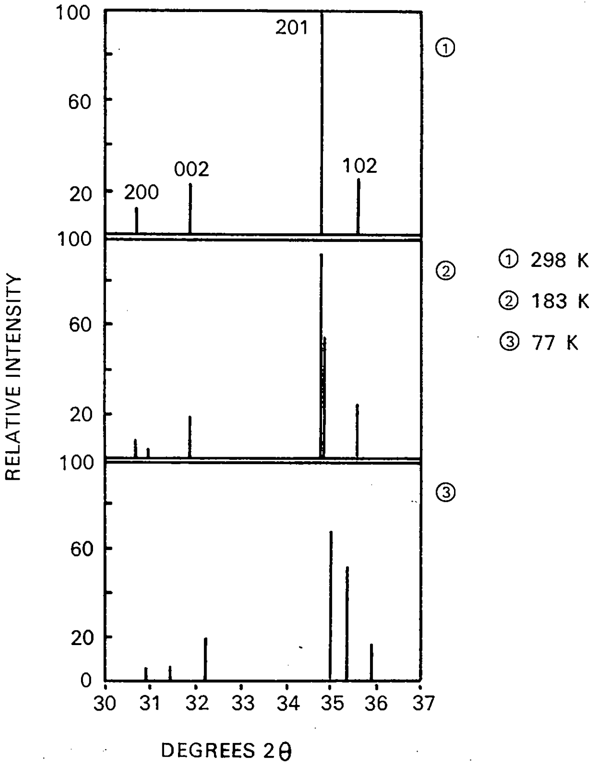

Fig. 5. Schematic diagram of relative intensities *vs.* 2θ for $T = 298°$, 183° and 77°K.

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The Structure of Some Alkaline-Earth Metal Uranates

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The structures of $CaUO_4$, $SrUO_4$ (orthorhombic), $BaUO_4$, Ca_2UO_5, Sr_2UO_5, Ca_3UO_6, and Sr_3UO_6 have been, where necessary, further determined and refined from neutron powder diffraction data. Least-squares parameters were obtained by fitting a calculated profile to the observed data. The standard deviations in the atomic positions varied with the number of independent structure parameters from 0·0007 Å for $CaUO_4$ to 0·029 Å for Sr_3UO_6.

Introduction

The crystal structures of $CaUO_4$ (Zachariasen, 1948) and $BaUO_4$ (Samson & Sillén, 1947) were determined previously with the use of both single-crystal and powder X-ray techniques. $SrUO_4$ (orthorhombic) was found to be isomorphous with $BaUO_4$ (Ippolitova, Simanov, Kovba, Polunina & Bereznikova, 1959). The rhombohedral form of $SrUO_4$ (Zachariasen, 1948) was found to be formed only in the absence of oxygen (Ippolitova *et al.*, 1959; Cordfunke & Loopstra, 1967). This phase is probably oxygen-deficient and has therefore been excluded from the present investigation.

Ca_2UO_5 and isostructural Sr_2UO_5 were solved by X-ray powder methods, but only as regards the metal positions (Sawyer, 1963). Ca_3UO_6 and Sr_3UO_6, which also are isostructural, were determined from X-ray and neutron diffraction powder data (Rietveld, 1966).

The present investigation was undertaken to determine the oxygen positions in Ca_2UO_5 and Sr_2UO_5 and to obtain better oxygen coordinates in the other compounds by using neutron diffraction data and the profile refinement technique (Rietveld, 1967, 1968).

Experimental

All compounds were prepared by heating stoichiometric mixtures of UO_3 and the alkaline earth metal carbonates, or nitrates, at 1000°C until X-ray powder diagrams showed the product to react no further. The final products contained only a few traces of impurities except Ca_2UO_5 where several per cent of $CaUO_4$ and Ca_3UO_6 were still present even after heating for weeks.

Neutron powder diagrams were obtained under the conditions listed in Table 1. The impurity lines in the diagram of Ca_2UO_5 were corrected for by subtracting properly scaled diagrams of $CaUO_4$ and Ca_3UO_6 obtained under identical conditions.

Table 1. *Experimental details*

α_1 is the angular divergence of the collimator between the reactor and the monochromator, α_3 that of the collimator in front of the BF_3 detector; λ is the wavelength used and $(\sin\theta_m)/\lambda$ the range of observation.

Compound	α_1	α_3	λ	$(\sin\theta_m)/\lambda$
$CaUO_4$	30′	30′	2·576 Å	0·350
$SrUO_4$	10	10	2·566	0·350
$BaUO_4$	10	10	2·562	0·350
Ca_2UO_5	10	10	2·565	0·348
Sr_2UO_5	10	10	2·565	0·333
Ca_3UO_6	10	10	2·565	0·353
Sr_3UO_6	5·5	10	1·103	0·373

X-ray powder intensities were collected on a Philips diffractometer with Cu $K\alpha$ radiation. Unit-cell data for all compounds are shown in Table 2.

Structure determination of Sr_2UO_5 and Ca_2UO_5

From the previous X-ray work (Sawyer, 1963), the metal atoms in Sr_2UO_5 had been found to occupy the positions given in Table 3. Packing considerations led to initial parameters of the oxygen atoms. These were used to construct four structure models which differed from each other only with regard to the sign of the Sr y parameters. The Sr coordinates of all four models were then refined by a least-squares method (Rietveld,