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Structural and Magnetic Properties of "One-Dimensional" Barium Vanadium Triselenide*†

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$BaVSe_3$ has been synthesized and its crystal structure determined at 293(2)°K. The structure was solved in the hexagonal space group $P6_3/mmc$ (D_{6h}^4), with $a = 6.9990(11)$ and $c = 5.8621(13)$ Å. Scans (2Θ) of a polycrystalline sample revealed that $BaVSe_3$ undergoes a transition to an orthorhombic unit cell ($b' \simeq 3^{1/2}a, a' \simeq a, c' \simeq c$) at 303(5)°K. Magnetic susceptibility measurements between 4 and 300°K indicate that $BaVSe_3$ is paramagnetic down to 41(1)°K, where magnetic ordering occurs, with a magnetic moment in the ordered phase of 0.2 μ_B per vanadium atom. The orthorhombic lattice distortion may be caused by the "freezing in" of "soft" vibrational modes.

Introduction

Gardner and co-workers (*1*) first reported the structure and conductivity of the one-dimensional conductor barium vanadium trisulfide. In their study, the crystal structure at 298°K of $BaVS_3$ is hexagonal ($P6_3/mmc$), and undergoes an orthorhombic distortion between 298 and 180°K. In the hexagonal phase, the vanadium–vanadium interchain distance is 6.724(5) Å, while the intrachain distance is only 2.805(5) Å. (The V–V distance in vanadium metal is 2.61 Å.) In addition, Goodenough (*2*) has proposed a semiempirical expression for the maximum distance at which direct interaction between transition metal atoms can occur via overlap of the *d* orbitals. For $BaVS_3$ this critical distance (*3*) is 3.45 Å. On this basis, one expects a one-dimensional partially filled band (vanadium is formally V^{4+}) and therefore metallic conduction.

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The resistivity exhibited a "metallic" temperature dependence (i.e., a slight decrease with decreasing temperature) down to 130°K, at which time a sharp rise in resistivity with decreasing temperature was observed. Gardner *et al.* (*1*) attributed this electronic behavior to the delocalization of vanadium valence electrons in a one-dimensional band composed of vanadium *d* orbitals. The rise in resistivity was attributed to a destruction of *d*-orbital overlap by the lattice distortion.

Powder X-ray measurements, resistivity, and magnetic susceptibility studies of $BaVS_3$ by Takano *et al.* (*4*) showed a more complex situation. In these experiments a sharp rise in resistivity with decreasing temperature was observed at 70°K, contrary to the 130°K value found by Gardner *et al.* (*1*). From magnetic susceptibility measurements, an apparent antiferromagnetic ordering was observed at 70°K, and a lattice distortion was observed at 258°K. The sharp rise in resistivity was attributed to the onset of magnetic order, not to a lattice distortion.

Further work by Massenet and coworkers (*5*) on $BaVS_{3-x}(0 \leq x \leq 0.12)$ largely confirmed the results reported by Takano and revealed surprising magnetic behavior. The magnetic, electronic, and crystallographic properties of $BaVS_3$ were found to be highly sensitive to sulfur content.

The apparent coupling of the electronic and magnetic transitions and their independence of the lattice distortion, combined with the sensitivity of these properties to sulfur content, indicates that the model of a one-dimensional partially filled band composed of vanadium *d* orbitals is not completely adequate to describe the magnetic and electronic properties of $BaVS_3$.

In order to ascertain the influence of the ligands on these properties, experiments with $BaVSe_3$ were begun. In this paper we report the synthesis, crystal structure, and magnetic susceptibility of $BaVSe_3$.

Synthesis and Compositional Analysis

Two samples of $BaVSe_3$ (hereafter called I and II) were each prepared in the following manner. Stoichiometric amounts of barium, vanadium, and selenium were placed in an evacuated quartz tube. The inside of the tube was coated with a layer of carbon to retard barium and vanadium attack on the quartz. The reactants were placed in the tube under an argon atmosphere and the tube was evacuated, sealed, and placed in a furnace.

One end of the tube (with the reactants) was heated for 24 hr while the other end was left outside the furnace. The selenium condensed on the cold end of the tube, which was then gradually pushed into the furnace until all the selenium was reacted. (The temperatures of the ends of the tube were at 650 and 450°C.) The entire tube was heated at 700°C for 24 hr, then at 800°C for 1 week, cooled gradually (~10°C/hr) to 650°C, and cooled overnight to room temperature.

In both cases the result was a dull gray sintered mass on the surface of which grew dark needle-shaped crystals (the largest of which was 2 or 3 mm long and 0.5 mm in diameter). A single crystal from I was used for the single-crystal X-ray studies. X-Ray powder measurements were carried out on powdered samples made by grinding the sintered mass of I.

Variation of the atomic multipliers in the single-crystal X-ray structure refinement gave a nearly stoichiometric composition of $BaVSe_{2.96\pm0.02}$. However, chemical analysis of powdered samples from the sintered mass of I gave a nonstoichiometric composition of $Ba_{0.7\pm0.01}VSe_{2.9\pm0.01}$. Barium content was determined by thermogravimetric analysis of $BaSO_4$, vanadium content by titration with EDTA. Selenium content was determined by absence. Extra lines in the Debye–Sherrer film pattern of this sample (absent in the Gandolphi film pattern of a single crystal from I) indicated that at least one vanadium selenide phase was present in the sintered mass of I (though not in the single crystals).

A second powder sample was made by grinding single crystals of II. Barium content was determined by flame emission, vanadium content by extraction with ferrous ammonium sulfate; Se content was calculated by the difference. The results gave a nearly stoichiometric composition: $Ba_{0.9\pm0.1}V_{1.1\pm0.2}Se_{3.1\pm0.5}$. The relatively large uncertainties are due to the small size of the sample. *No* extra lines were observed in the Debye–Sherrer film pattern.

Magnetic susceptibility measurements carried out on powdered samples of I and II gave similar results, but the results from the powdered sample of II are discussed here.

X-Ray Analysis

Precession and Weissenberg results at 293(2)°K showed $BaVSe_3$ to be hexagonal with systematic absences hhl; $l = 2n + 1$. Single-crystal data were collected at 293(2)°K, using a Syntex $P2_1$ four-circle diffractometer with Mo$K\alpha$ radiation. Complete descriptions of the Syntex $P2_1$ crystal alignment and data collection routines have appeared previously (*6, 7*). Monochromatic radiation was obtained by using the 002 reflection of a graphite single crystal. The single crystal of $BaVSe_3$ was shaped like a hexagonal prism, roughly 0.02 mm in diameter and 0.12 mm in length. Pertinent experimental data are given in Table I.

The intensities of 692 reflections consisting of four unique data sets ($0 \leq \pm h \leq 8$, $0 \leq \pm k \leq h$, $0 \leq +l \leq 8$; $0 \leq \pm k \leq 8$, $0 \leq \pm h \leq k$, $0 \leq +l \leq 8$) were measured. Lorentz, polarization, and absorption corrections[1] were applied to the data. Systematic absences were collected and agreed with the camera results. The systematic absences were then deleted and the intensities of equivalent reflections were averaged to 164 unique reflections. The close agreement of intensities of inversion-related reflections indicated that the space group was centrosymmetric. The structure was refined in the space group $P6_3/mmc$ by full-matrix least-squares using a local version of ORFLS[1]. The function $\sum w||F_{\text{obs}}|^2 - |F_{\text{calc}}|^2|^2$ was minimized. (F is the structure factor and w the weight assigned to the reflection.) The weight of each reflection was set equal to $[\sigma(|F_{\text{obs}}|^2)]^{-1/2}$, where σ is the standard deviation of the intensity of the reflection. Calculation of this quantity is described elsewhere (*7*). Scattering factors for neutral barium, vanadium, and selenium were taken from the computation (*8*) of Cromer and Waber.

TABLE I

RELEVANT EXPERIMENTAL DATA

Space group: $P6_3/mmc$
Cell constants: $a = 6.9990(11)$ Å, $c = 5.8621(13)$ Å
Cell volume: 248.68(10) Å^3
Calculated density: 5.68 g cm^{-3}
Data collection
  Number of asymmetric units per unit cell: 2
  Radiation: Mo$K\alpha$ ($\lambda = 0.71073$)
  Temperature: 293(2)°K
  Absorption coefficient: 335.200 cm^{-1}
  Max 2Θ: 60°
  Scan width: $[2.4° + \Delta(\alpha_1 - \alpha_2)°]$
  Scan speed: variable, 0.98–29.30° min^{-1}
  Scan type: Θ–2Θ coupled
Crystal
  c-axis mounted
  Volume $= 4.70 \times 10^{-5}$ mm^3
  Max. trans. factor = 0.55
  Min. trans. factor = 0.38
Isotropic extinction factor = 0.05(2)
Numbers of independent reflections above σ: 150
Number of independent reflections: 164
$R(F^2)$ for all reflections above $\sigma = 0.039$
$R(F^2)$ for all reflections = 0.040
$wR(F^2) = 0.052$

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[1] The absorption correction was made using a local version of ORABS, a computer program written by W. R. Busing and H. A. Levy. ORFLS and ORFEE are also computer programs written by W. R. Busing and H. A. Levy.

During the refinement, several constraints were imposed. The positional parameters of barium and vanadium were fixed at $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$ and $(0, 0, 0)$, respectively (special positions "*d*" and "*a*" of the space group). The selenium was placed in the special position "*h*"; $(x, 2x, \frac{1}{4})$. Anisotropic thermal factors were fitted to all atoms using the expression: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. The constraints placed on the thermal parameters were (*9*) for the selenium, $\beta_{22}=2\beta_{12}, \beta_{23}=\beta_{13}=0$; for the barium and vanadium, $\beta_{11}=\beta_{22}=2\beta_{12}, \beta_{23}=\beta_{13}=0$. A correction was made for isotropic extinction after the method (*10*) of Coppens and Hamilton. Bond distances and angles were calculated using ORFEE.[1] Final values for positional and thermal parameters are given in Table II and the bond distances and angles in Table III.

The final value of $R(F^2) = (\sum \| F_{\text{obs}}|^2 - |F_{\text{calc}}|^2|)/\sum |F_{\text{obs}}|^2$ keeping all atom multipliers constant was 0.039 for the 150 reflections with intensities greater than one standard deviation and 0.040 for all reflections. Variation of the selenium atom multiplier gave a final $R(F^2)$ value of 0.039 for all reflections. The final value for the atom multiplier showed that the single crystal was nearly stoichiometric with a composition of $BaVSe_{2.96\pm0.02}$. Allowing both the barium and selenium atom multipliers to vary gave no definitive results and no improvement in the $R(F^2)$ value. A listing of F^2 (observed) and F^2 (calculated) is provided as supplementary material.[2]

A detailed examination of the crystal structure of $BaVSe_3$ shows it to be analogous to the sulfide. The structure consists of hexagonally close-packed $BaSe_3$ layers perpendicular to the *c*-axis with vanadium cations occupying one-fourth of the octahedral voids between layers (Fig. 1a). The Ba–Se distance is 3.4996(12) Å within a layer and 3.5479(9) Å between layers. The corresponding Se–Se distances are 3.5364(23) and 3.5721(15) Å, respectively. As in $BaVS_3$, the interlayer distances (*1*) are longer than the corresponding intralayer distances. In a perfect hexagonal close-packed structure the corresponding interlayer and intralayer distances would be equal. The one-dimensional nature of the structure is shown in Fig. 1b. The chains of vanadium atoms run parallel to the *c*-axis and are surrounded by face-sharing selenium

TABLE II

BOND DISTANCES AND ANGLES

Bond distances (Å)		Bond angles (°)	
V–V	2.9310 (7)		
V–Se	2.5133 (8)	Se(1)–V–Se(1)	89.43(3)
Se(1)–Se(1)	3.5364(23)	Se(1)–V–Se(2)	90.57(3)
Se(1)–Se(2)	3.5721(15)	Se(1)–Ba(1)–Se(1)	120.00(0)
Se(1)–Ba(1)	3.4996(12)	Se(1a)–V–Se(2a)	180.00(4)
Se(2)–Ba(1)	3.5479(9)	Se(1a)–Ba(1)–V	36.78(1)
Ba(1)–Ba(2)	4.9920(1)		
V–Ba	4.2984(1)		

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[2] See NAPS document No. 03524 for 1 page of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering, however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada postage is $3.00 for a photocopy and $1.50 for a fiche.

TABLE III

FINAL POSITIONAL AND THERMAL PARAMETERS

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}
Ba	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	0.0115(3)	—	0.0094(3)
V	0	0	0	0.033(1)	—	0.014(1)
Se	0.1684(1)	0.3369	0.25	0.0110(3)	0.0076(4)	0.0166(3)

RMS THERMAL DISPLACEMENTS (Å^2)

Atom	U_{11}	U_{22}	U_{33}
Ba	0.021	—	0.011
V	0.061	—	0.024
Se	0.020	0.014	0.029

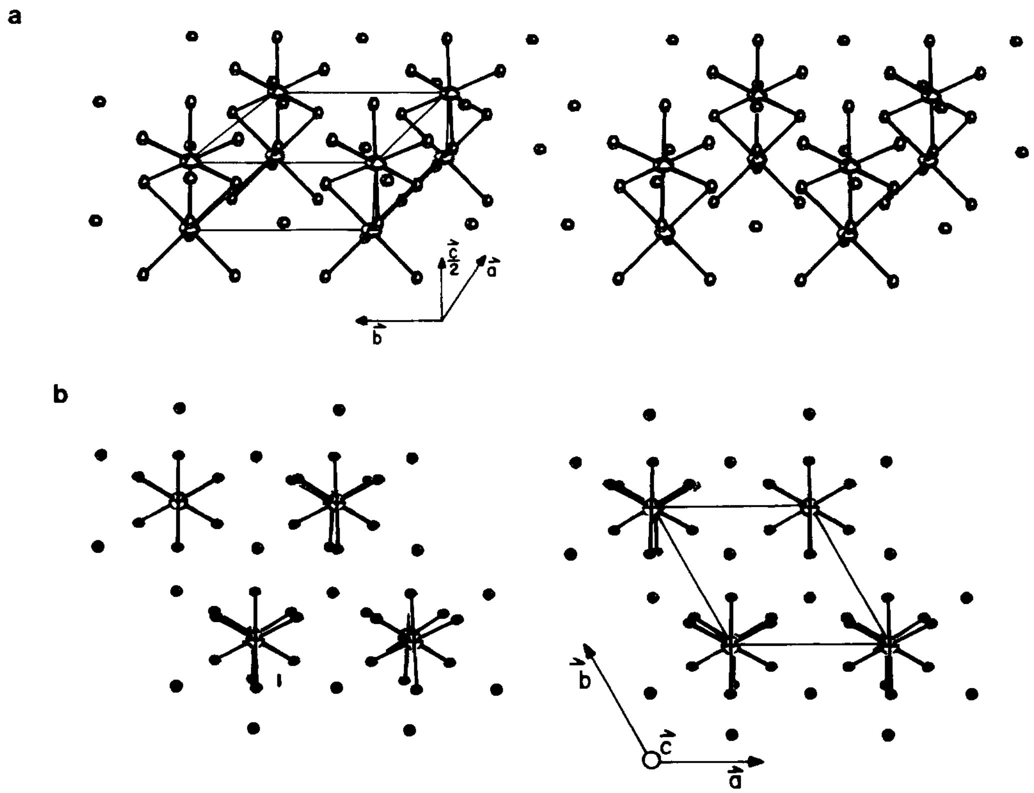

FIG. 1(a) Stereo view of BaVSe$_3$, showing chains of vanadium atoms surrounded by selenium face-sharing octahedra. Large thermal motions are displayed by the vanadium atoms $\perp c$ and by the selenium atoms $\| c$. (b) Stereo view of unit cell of BaVSe$_3$ looking down the c-axis. The barium and selenium atoms form hexagonal layers. The vanadium atoms fill one-quarter of the octahedral voids between layers.

octahedra. The intrachain V–V distance is 2.9310(7) while the interchain distance is 6.9990(11) Å. As in the sulfide these octahedra have a small trigonal distortion along the *c*-axis (Fig. 2). The Se–V–Se angle for seleniums in adjacent layers is 90.57(3)°. For seleniums within a layer the angle is 89.43(3)°. (The corresponding angles in the sulfide (*1*) are 91.07(15) and 88.93(8)°.)

The thermal motions of the atoms are shown in Figs. 1 and 2. While the selenium atoms display an anisotropic motion with the major component parallel to the *c*-axis, the vanadium atoms display very large thermal motion perpendicular to the *c*-axis. Somewhat similar results were obtained for the sulfide (*1*).

Powder diffraction measurements on $BaVSe_3$ (the ground sintered material of I) were determined between 150 and 310°K. In order to compare the lattice distortion to $BaVS_3$, measurements were done on a standard powder diffractometer (Cu*Kα* radiation) using a liquid-nitrogen-filled cryostat with a beryllium window. The temperature was controlled and monitored by a platinum-resistance thermocouple. $BaVSe_3$ did indeed undergo a distortion which was indexed to the orthorhombic unit cell $b' \simeq 3^{1/2}_{a_{hex}}$, $a' \simeq a_{hex}$, and $c' \simeq c_{hex}$. As was the case with $BaVS_3$ (*5*), the distortion was most easily observed by monitoring the splitting of the 220 reflection (hexagonal indices). As Fig. 3 shows, the splitting began between 298(1) and 308(1)°K. No hysteresis was observed.

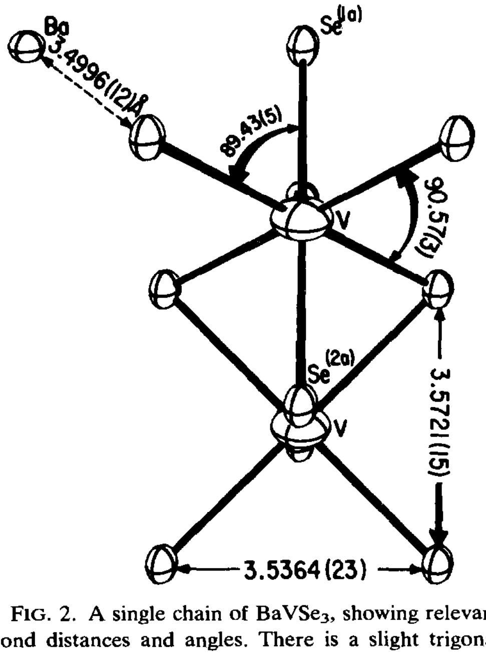

FIG. 2. A single chain of $BaVSe_3$, showing relevant bond distances and angles. There is a slight trigonal distortion of the selenium octahedra. The V–V intrachain distance (not shown) is 2.9310(7) Å

The single-crystal study was carried out at 293(2)°K. However, a hexagonal cell was observed. The distortion may have been present at this temperature but not resolvable by the instrument. The 2Θ intensity profile scans of the 201, 200, and 002 reflections show that the full width at half maximum is roughly twice as large for the first two reflections as for the 002 reflection, but that peak splittings were not resolved. The powder data (Fig. 3) show that at 293°K the splitting of the 002 peak is only 0.2(1)° in 2Θ. This is much less than the resolution of the 2Θ scans of the single-crystal diffractometer (~1.0°, (FWHM)].

That the single crystal might have a slightly different transition temperature than the powder is not unlikely, since the two seem to be of slightly different composition, and the transition temperature in $BaVS_3$ was shown (*5*) to be sensitive to stoichiometry. The differences may also be due to the existence of carbon or other impurities in the powder.

Magnetic Susceptibility

Magnetic susceptibility measurements were determined on a powdered sample of $BaVSe_3$ (made by grinding the single crystals of batch II) between 280 and 4.2°K on a Faraday microbalance. Susceptibility $(= \partial M / \partial H)$ was determined by measuring magnetization (*m*) as a function of applied field (*H*) between 0.5 and 15 kOe.

As the graph of inverse molar susceptibility (χ^{-1}) against temperature shows (Fig.

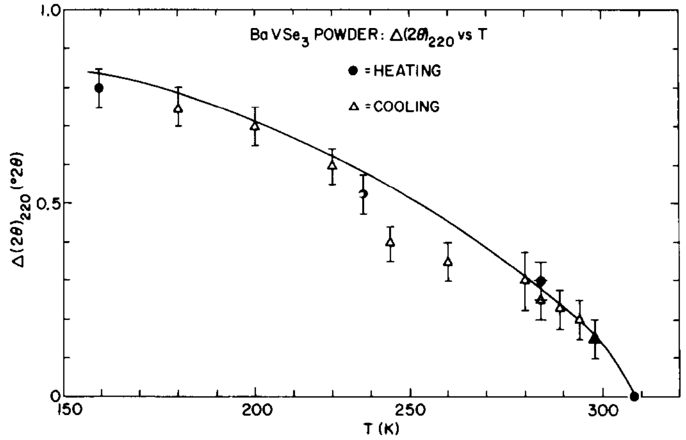

FIG. 3. Temperature dependence of splitting of the 220 peak of the hexagonal phase in BaVSe$_3$ powder. The distortion appears to be incomplete at 150 K. Solid line is a guide for the eye.

4), the magnetic behavior of BaVSe$_3$ is similar to that of sulfur-deficient BaVS$_3$. In both compounds there is a critical temperature below which some type of magnetic ordering with a small net ferromagnetic moment (~0.2 μ_B/V atom) occurs.

An effective moment of ~1.5 μ_B/V atom is obtained for the susceptibility data (Fig. 4) between 50 and 150°K. This is less than the spin-only value of 1.73 expected for a linear chain. Effective moments lower than the spin-only value are also observed for BaVS$_3$ (*5*). Due to experimental uncertainties, it is not possible to determine the magnitude of any temperature-independent contribution to the susceptibility. In the ordered region, the field dependence of the magnetization was fitted to an approach-to-saturation equation of the form $M(H) = M_0(1-a/H^{1/2})+\chi H$ to yield the spontaneous magnetization M_0, which was then plotted against $T^{3/2}$ to yield an extrapolated value at 0°K of $M_0(0) = 0.2\ \mu_B$. The result is very similar to the value obtained (*5*) for the sulfur-deficient sulfide at 4.2°K. The susceptibility values measured above 150°K are uncertain due primarily to the small sample size and possible systematic errors in the sample holder correction. Further work is necessary to determine more precisely the paramagnetic susceptibility.

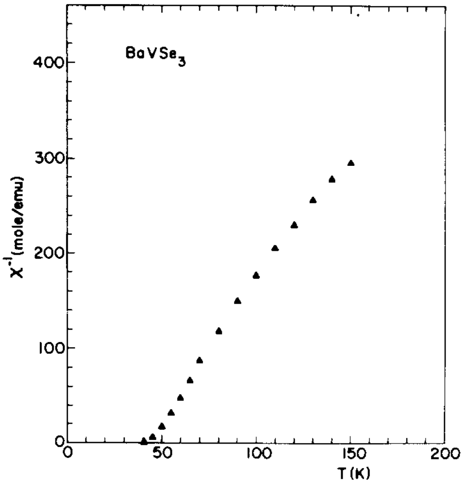

FIG. 4. Plot of the inverse molar susceptibility of BaVSe$_3$ against temperature. The ordering temperature is 41 ± 1 K. Standard deviation of values are between 1 and 2%.

The major difference between the magnetic behavior of the selenide and that of the sulfide is the ordering temperature. Sulfur-deficient BaVS$_3$ was found (*5*) to order at 16(1)°K. The critical temperature for the selenide, determined by plotting M^2 against H/M and finding the temperature at which a zero intercept was obtained, is 41(1)°K.

The thermal motions of the atoms (Figs. 1 and 2) suggest a driving mechanism for the lattice distortion. Takano (*4*) and colleagues reported the systematic absences of the orthorhombic phase powder pattern of $BaVS_3$ to be those of the space group $C222_1(D_2^5)$. The low-temperature powder pattern for $BaVSe_3$ also shows these absences. The transition from the hexagonal space group symmetry to this space group symmetry can be accomplished by slight movements of the E_{2u} mode of V($\|a$) and Se or S($\|c$) and the E_{2g} mode of Ba($\|b$) and Se or S($\perp c$) (*4*). The relatively large components of thermal motion (see Table III) of the vanadium atoms perpendicular to *c* and of the selenium and sulfur atoms (similar results were obtained by Gardner (*1*) for $BaVS_3$) parallel to *c* suggest the "freezing in" at low temperatures of a "soft" vibrational mode. However, the large ellipsoids might be due to possible static disorder.

The magnetic ordering observed in $BaVSe_3$ is similar to that observed in samples of $BaVS_3$ annealed in the absence of sulfur (*5*), in that the magnetic moment in the ordered phase is $\sim 0.2\ \mu_B$/vanadium atom and the effective moment in the paramagnetic phase is less than the spin-only value. A study of the dependence of the magnetization (and other physical properties) of $BaVSe_3$ with Se content would be most interesting.

Conclusion

$BaVSe_3$ is isostructural with $BaVS_3$ and exhibits magnetic ordering at 41 K with a magnetic moment of $0.2\ \mu_B$/vanadium atom, and an effective moment of $1.5\ \mu_B$/vanadium atom in the paramagnetic phase. Analysis of the thermal motions of the atoms suggests that the lattice distortion is due to either the "freezing in" of a "soft" vibrational mode, or static disorder in the high-temperature structure.

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