SHORT COMMUNICATION

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1979). B35, 2473–2475

Influence of annealing on the lattice constants of $BaVS_3$.

By J. Kelber,* J. D. Jorgensen and M. H. Mueller, *Argonne National Laboratory,*† *Argonne, IL* 60439, *USA*, O. Massenet, *CNRS, GTP,* 166*X*, 38042 *Grenoble CEDEX, France* and G. Stucky,‡ *Department of Chemistry, University of Illinois, Urbana, IL* 61801, *USA*

(*Received* 22 *January* 1979; *accepted* 18 *June* 1979)

Abstract

$BaVS_3$, hexagonal, $P6_3/mmc$, $Z = 2$, $D_{calc} = 4{\cdot}30$ Mg m^{-3}. Lattice constants for nonferromagnetic and ferromagnetic $BaVS_3$ (as well as BaS content) were determined by profile analysis of time-of-flight neutron diffraction data. Nonferromagnetic sample: $a = 6{\cdot}7160\,(4)$, $c = 5{\cdot}6168\,(6)$ Å, BaS impurity $< 1{\cdot}0$ at.%. Ferromagnetic sample: $a = 6{\cdot}7142\,(6)$, $c = 5{\cdot}6209\,(8)$ Å, BaS impurity = 6(2) at.%.

Introduction

The room-temperature crystal structure of $BaVS_3$ was reported by Gardner, Vlasse & Wold (1969). $BaVS_3$ was found to be hexagonal ($P6_3/mmc$). The structure consists of chains of face-sharing VS_6 octahedra running parallel to the *c* axis with Ba ions separating the chains. A lattice distortion to orthorhombic symmetry was observed at lower temperature. Because of the short V–V intrachain distance (in the hexagonal phase), one-dimensional metallic interaction is expected (Goodenough, 1963).

Magnetization, resistivity and X-ray diffraction measurements performed by Massenet, Buder, Since, Schlenker, Mercier, Kelber & Stucky (1978) showed that the physical properties of $BaVS_3$ can be altered by annealing the material in the presence or absence of sulfur. $BaVS_3$ annealed in the absence of sulfur is ferromagnetic [$T_c = 16(1)$ K, magnetic moment in the ordered phase of ~0·2 Bohr magnetons (μ_B) per vanadium atom], with anomalies in the resistivity near 16 K, 70 K and 150 K, and the commencement of an orthorhombic lattice distortion at 150 K. In the same study, it was found that annealing powdered $BaVS_3$ in the presence of sulfur gradually changed the physical properties up to a limit beyond which further annealing with sulfur caused no observable changes in the sample or in its physical properties. At this point the material, which chemical analysis indicated was stoichiometric, displayed magnetic, electronic and crystallographic properties identical to those observed by Takano, Kosugi, Nakanishi, Shimada, Wada & Kiozumi (1977) for samples reported to be stoichiometric; namely nonferromagnetic behavior with a broad maximum in the susceptibility near 70 K, a rapid rise in the resistivity with decreasing temperature beginning near 70 K, and a lattice-distortion temperature of 250 K.

An important question is whether the observed changes in the physical properties of $BaVS_3$ are due simply to the inclusion (or reaction) of bulk impurities during the annealing process

$$[e.g.\, BaVS_3 \xrightleftharpoons[+S]{-S} (1-x)BaVS_3 + xBaS + xVS]$$

or are a result of changes in the lattice structure of $BaVS_3$. If the difference in properties is due to the presence of bulk impurities in the powder samples then the lattice constants of ferromagnetic and nonferromagnetic $BaVS_3$ should be the same. More fundamental changes (*e.g.* changes in Ba, V or S site occupancy) should be reflected in a change in the room-temperature lattice constants of $BaVS_3$ upon annealing. Massenet *et al.* (1978), using Debye–Scherrer X-ray measurements, did not observe any such variation in the lattice constants. We report here the variation of the room-temperature lattice constants of $BaVS_3$ upon annealing in the presence of sulfur as determined by profile analysis of time-of-flight (TOF) neutron diffraction data.

A powder sample of $BaVS_3$ was prepared by the method of Gardner *et al.* (1969). Magnetic-susceptibility measurements show this sample to be ferromagnetic [$T_c = 16{\cdot}5\,(5)$ K, ordered-phase magnetic moment $\simeq 0{\cdot}2$ μ_B/vanadium]. Debye–Scherrer X-ray measurements (Cu $K\alpha$) indicate a lattice-distortion temperature of 213 (5) K and a BaS impurity. Some of the ferromagnetic material was annealed with ~4% sulfur by weight in the manner detailed by Massenet *et al.* (1978). Magnetic-susceptibility measurements show this sample to be non-ferromagnetic (with a maximum in the susceptibility near 70 K). A lattice distortion was observed at 247 (2) K by Debye–Scherrer measurements. A single faint impurity line, assigned to the BaS 200 reflection, was observed in the X-ray measurements. Details of the magnetic properties of both samples will be published elsewhere. A least-squares fit of the X-ray diffraction lines showed that the difference in the lattice constants of the two

---

* CEA Grad-Lab Fellow; permanent address: Department of Chemistry, University of Illinois, Urbana, IL 61801, USA.

† Work supported by the US Department of Energy.

‡ Work supported by the National Science Foundation (Grant No. NSF/DMR 772 3999).

phases was no greater than experimental error (Table 1), in agreement with earlier results (Massenet *et al.*, 1978). To obtain greater precision, profile refinement of neutron powder data was carried out.

Neutron data were collected on the H8 TOF neutron diffractometer at the Argonne CP-5 research reactor. The samples were packed in thin-walled vanadium tubes $\frac{1}{4}''$ (6·4 mm) in diameter. Time-focused neutron detectors were located at a fixed scattering angle of $2\theta = 90°$. The instrumental resolution is $\Delta d/d$ (FWHM) = 0·01 at d = 1·0 Å. Data were collected for about 24 h on each sample at room temperature. Complete descriptions of the Argonne TOF facility have appeared elsewhere (Worlton, Jorgensen, Beyerlein & Decker, 1976; Jorgensen, 1978).

Lattice parameters and atomic positions were determined for both samples by a nonlinear least-squares refinement of the neutron data (Worlton *et al.*, 1976). During the refinement, the space-group symmetry and atomic coordinates of the previous structural study (Gardner *et al.*, 1969) (Table 2) were used. The sulfur positional parameter [special position $(x,2x,\frac{1}{4})$], the lattice constants, the isotropic temperature factors for Ba and S, and the lattice constants of BaS and scale factors of BaS and $BaVS_3$ were varied independently during the refinement.

The calculated profiles for each sample (Figs. 1 and 2) included 82 independent reflections of $BaVS_3$ and 12 of BaS. For the nonferromagnetic material, variation of the BaS scale factor led to a value less than its standard deviation, and no improvement in the agreement factor. During the final refinement for this sample the BaS scale factor was fixed at zero. The difference pattern ($I_{obs} - I_{calc}$) for the nonstoichiometric (ferromagnetic) sample (Fig. 2) shows the presence of a third phase, the exact nature of which could not be determined. Regions where this phase made large contributions to the total intensity were ignored during the refinement.

No corrections to the data were made for absorption or extinction. The excellent agreement between observed and calculated intensities at long wavelengths (Figs. 1 and 2) shows that extinction is insignificant for both samples.

Table 1. *Results of neutron profile refinement*

For expressions for $\chi^2_{reduced}$ and statistical errors, see Worlton *et al.* (1976). For expressions for agreement factors, see text.

	Nonferromagnetic	Ferromagnetic
a (Å)	6·7160 (4)	6·7142 (6)
c (Å)	5·6168 (6)	5·6209 (8)
Unit-cell volume (Å)	219·40 (4)	219·44 (4)
Mol% BaS	<1	6·2 (6)
$\chi^2_{reduced}$	2·25	2·62
$R_{profile}$	0·017	0·015
R_{sample}	0·14	0·17
X-ray film measurements		
a (Å)	6·716 (3)	6·716 (3)
c (Å)	5·617 (3)	5·624 (3)

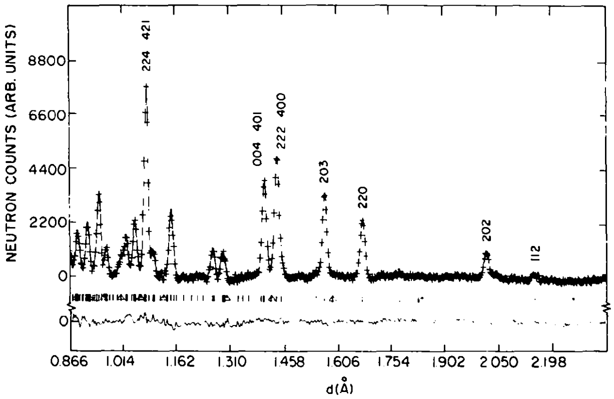

Fig. 1. Calculated and observed intensities for nonferromagnetic material (sample I). Triangles mark calculated positions for BaS peaks with a = 6·386 Å. Lower trace is $I_{obs} - I_{calc}$.

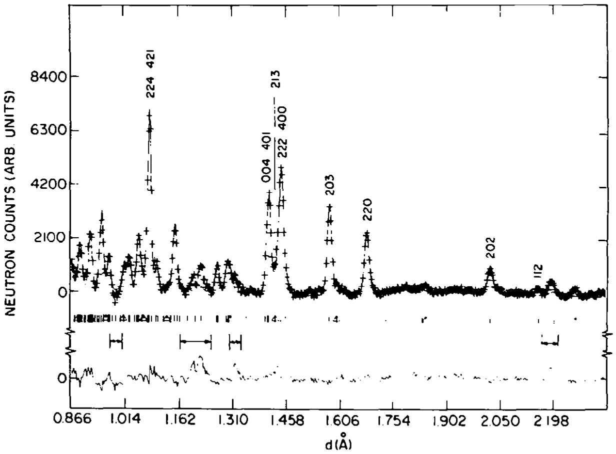

Fig. 2. Calculated and observed intensities, sample (II). Triangles mark peak positions in calculated profile due to BaS [a = 6·381 (3) Å]. Lower trace: $I_{obs} - I_{calc}$, bracketed regions ignored during refinement.

Table 2. $BaVS_3$ *atomic coordinates and thermal parameters from profile refinement*

Expression for thermal parameters (B_o) is $b = b_o \exp(-B_o \sin^2\theta/\lambda^2)$, where b_o is the scattering length of an element. The first number in a pair refers to the nonferromagnetic sample.

	x	y	z	B_o (Å^2)	Thermal displacement (Å)
Ba	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	0·6 (2), 0·8 (2)	0·09 (3), 0·10 (3)
V	0	0	0	0·5	0·08
S	0·167 (1), 0·166 (1)	0·333 (2), 0·332 (2)	$\frac{1}{4}$	0·2 (3), 0·4 (4)	0·05 (8), 0·07 (7)

Table 3. $BaVS_3$ *profile refinement; bond distances* (Å) *and angles* (°)

Atoms with the same superscript belong to the same asymmetric unit and have the same *z* coordinate. Atoms with different superscripts are separated by one half the unit-cell length along the *c* axis.

	S^{III} Nonferromagnetic	S^{IV} Ferromagnetic
V–V	2·8084 (3)	2·8105 (4)
V–S	2·40 (1)	2·39 (1)
S^{I}–S^{I}	3·36 (2)	3·34 (2)
S^{I}–S^{II}	3·43 (2)	3·42 (2)
Ba–V	4·1239 (5)	4·1232 (7)
Ba^{I}–S^{I}	3·36 (2)	3·36 (2)
Ba^{I}–S^{II}	3·41 (2)	3·42 (2)
Ba^{I}–Ba^{II}	4·7887 (6)	4·7880 (8)
Bond angles (central atom is vertex atom)		
S^{I}–V^{I}–S^{I}	88·9 (6)	88·7 (6)
S^{II}–V–S^{I}	91·1 (6)	91·3 (6)
V^{I}–Ba–V^{II}	39·815 (8)	39·853 (8)

Attempts to fit the atoms in $BaVS_3$ with anisotropic temperature factors during the refinement led to no improvement in the goodness of fit and unphysical values for the temperature factors. Allowing the sulfur occupancy factor to vary did not significantly improve on the refinement and led to final values for both samples near 1·0 (stoichiometric). Preferred orientation is not a problem, since this should lead to systematically poor agreement for the most intense *hk*0 and *hkl* reflections. Figs. 1 and 2 show that this is not the case. A possible explanation is that the resolution of the data at high Q ($= 2\pi/d$) is inadequate.

The results of the refinement for each sample are presented in Table 1. The expressions for the χ^2 factor and the expressions for the uncertainties for the parameters are given by Worlton *et al.* (1976). $R_{\text{profile}} = \sum_l |Y_l - Y(\lambda_l)|/\sum_l Y_i$, where Y_l and $Y(\lambda_l)$ are the observed and calculated intensities, respectively, at wavelength λ_l. R_{sample} is the same as R_{profile} except that $y_l =$ (total observed intensity − calculated background intensity). R_{sample} is thus similar to the R factor discussed by Rietveld (1969). The atomic coordinates and thermal parameters are given in Table 2 and calculated bond distances and angles in Table 3.

Discussion

For both samples, the lattice parameters did not change significantly for different refinement conditions. For the nonstoichiometric material, refinement values with no regions of the profile excluded and with the BaS scale factor fixed at zero were: $R_{\text{profile}} = 0{\cdot}02$, $R_{\text{sample}} = 0{\cdot}27$, $a = 6{\cdot}7127$ (8), $c = 5{\cdot}622$ (1) Å. Corresponding values for the final refinement (Table 1) show that including BaS peaks and ignoring regions where other impurity peaks were visible led to an improvement in the agreement factors but very little change (less than twice the statistical uncertainty) in the lattice parameters. For both samples, the lattice constants were insensitive to changes in the values of the thermal parameters.

The neutron data show that while significant amounts of foreign phases were present in the ferromagnetic sample, annealing the sample in the presence of sulfur did cause a roughly 0·03% expansion of the unit cell along the *a* axis and a 0·07% contraction along the *c* axis. This is evidence that ferromagnetic and nonferromagnetic $BaVS_3$ are chemically different.

The results do not rule out the presence of a magnetic substitutional impurity in the $BaVS_3$ lattice. The observation of different lattice constants for ferromagnetic and nonferromagnetic $BaVS_3$, together with the recently reported preparation of single crystals of each type of $BaVS_3$ (Massenet *et al.*, 1979), shows that the observed variation in physical properties upon annealing is not caused by bulk impurities such as BaS present in the powder samples.

The 'bumpiness' of the background for the nonferromagnetic sample profile (Fig. 1) may indicate the presence of an amorphous component (*e.g.* free sulfur). A repetition of this experiment on the high-resolution powder diffractometer at the Argonne pulsed neutron source (IPNS-I) is contemplated. The higher resolution at small *d* spacings will hopefully lead to better values for the thermal parameters and sulfur occupation parameters, thus yielding more detailed information on the variation of structure with stoichiometry in the $BaVS_3$ system.

One of the authors (JK) would like to thank the Center for Educational Affairs for financial support during his stay at Argonne.

References

Gardner, R. A., Vlasse, M. & Wold, A. (1969). *Acta Cryst.* B**25**, 781–786.

Goodenough, J. B. (1963). *Magnetism and the Chemical Bond*, pp. 17–48, 294–295. New York: Interscience.

Jorgensen, J. D. (1978). *J. Appl. Phys.* **49**, 5473.

Massenet, O., Buder, R., Since, J., Schlenker, C., Mercier, J., Kelber, J. & Stucky, G. (1978). *Mater. Res. Bull.* **13**, 187–195.

Massenet, O., Since, J. T., Mercier, J., Avignon, M., Buder, R., Nguyen, V. D. & Kelber, J. (1979). *J. Phys. Chem. Solids.* To be published.

Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

Takano, M., Kosugi, H., Nakanishi, N., Shimada, M., Wada, T. & Kiozumi, M. (1977). *J. Phys. Soc. Jpn*, **43**, 1101–1103.

Worlton, T. G., Jorgensen, J. D., Beyerlein, R. A. & Decker, D. L. (1976). *Nucl. Instrum. Methods*, **137**, 331–337.