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# Magnetization and Neutron Study of $BaVS_3$[1]

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Magnetization and neutron diffraction measurements have been made on both stoichiometric and nonstoichiometric $BaVS_3$. The crystal structure is characterized by linear chains of $V^{4+}$ atoms, so that cooperative phenomena are constrained to one dimension by the crystal structure. Both materials exhibit Curie–Weiss behavior between 100 and 400 K. The stoichiometric sample shows a cusp in the susceptibility near 70 K but the neutron experiments show that if the material orders antiferromagnetically the ordered moment is less than 0.5 $\mu_B$. The nonstoichiometric sample orders ferromagnetically at 16.5 ± 0.5 K with an ordered magnetic moment of 0.2 $\mu_B$/V atom. The results are discussed in the context of present models for this pseudo-one-dimensional material.

## Introduction

Pseudo-one-dimensional materials have been much studied in recent years, both as physical approximations of theoretically tractable magnetic lattices and as possible prototypes of high-temperature superconductors. The structural and electronic properties of $BaVS_3$ were first reported by Gardner and co-workers (*1*). In their study, $BaVS_3$ was found to be hexagonal ($P6_3/mmc$) at room temperature, with a distortion to orthorhombic symmetry beginning near 250 K. The vanadium intrachain and interchain distances [2.805 and 6.724 Å, respectively (*1*)] are such that one expects metallic interaction (*2*) along the *c*-axis through the formation of partially filled one-dimensional bands of vanadium $3d_{z^2}$ orbitals (the *z*-axis being taken parallel to the crystallographic *c*-axis).

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Resistivity and susceptibility measurements by Takano *et al.* (*3*) showed the resistivity to be temperature independent down to about 70 K, at which point both a sharp rise in resistivity and a broad maximum in the magnetic susceptibility were observed. Since the lattice distortion began near 250 K, it appeared that the electronic transition was coupled to the magnetic transition and not the structural distortion.

These results were confirmed by Massenet and co-workers (*4*), who also found that the electronic, magnetic, and structural properties varied with sulfur content. In particular, nonstoichiometric $BaVS_3$ is characterized by approximately Curie–Weiss paramagnetism at high temperatures, a ferromagnetic Curie temperature of about 17 K, and an anomalously low saturation moment in the ordered phase [0.2 to 0.4 Bohr magnetons ($\mu_B$) per vanadium atom]. At high temperature, stoichiometric $BaVS_3$ also exhibits Curie–Weiss paramagnetism but has a broad maximum in the susceptibility near 70 K ($T_{max}$), with no further anomaly below 70 K.

To better understand the magnetic properties of $BaVS_3$, and especially the influence of annealing in the presence of sulfur, we have carried out magnetic susceptibility and neutron diffraction measurements on two samples within the $BaVS_3$ system. The results of these measurements are reported in this paper and their significance concerning the electronic and magnetic measurements is discussed.

## Sample Synthesis and Characterization

A powdered sample of $BaVS_3$ was prepared according to the method of Gardner *et al.* (*1*). Preliminary magnetic susceptibility measurements on this sample (II) showed it to be nonstoichiometric $BaVS_3$. Stoichiometric $BaVS_3$ powder (sample I) was prepared by annealing some of II with 4% sulfur by weight in the manner described previously (*4*). This sample displaye magnetic behavior characteristic of stoichiometric $BaVS_3$ (*4*).

X-Ray Debye–Scherrer film measurements ($CuK\alpha$ radiation, room temperature of II displayed extra lines attributed to th (111), (200), and (222) reflections of Ba Powder patterns of I revealed (in addition t the $BaVS_3$ pattern) only a barely visibl (200) line, indicating a lower impurit content. These results were confirmed b profile refinement of room temperatur time-of-flight neutron diffraction measurements, which showed that II contains about atom% BaS and a small amount of anothe (presumably vanadium sulfide) phase whic could not be identified. Sample I contain less than 1% BaS and no observable amoun of vanadium sulfide. The two $BaVS_3$ phase also have slightly different lattice constant The details of the X-ray and time-of-fligh neutron measurements will be reporte elsewhere.

## Magnetization Results

The magnetization $\sigma$ (emu/g) of bot samples was measured as a function of applied magnetic field up to ~15 kOe over th temperature range 4.2 to 470 K on a Farada balance system previously described (*5*). Th samples were cooled to 4.2 K in the maximum applied field. Corrections were mad for demagnetizing effects to yield the interna field *H*. A slight field dependence of th susceptibility, as defined by $\chi = \sigma/H$, wa observed in the paramagnetic regime ove the entire temperature range for bot samples; the data were fit to an expression o the form

$$\sigma = \sigma_0 + \chi H. \qquad (1$$

The $\sigma_0$ term, which was essentiall temperature independent, probably reflect the presence of a ferromagnetic impurit and its magnitude corresponds, for exampl to one part in $10^4$ of pure iron in the sample

The estimated uncertainty in $\chi$ is about $\pm 4 \times 10^{-6}$ emu/mole, i.e., a maximum uncertainty of ±1%. Most vanadium sulfide phases (present as possible impurities) have small, weakly temperature-dependent, susceptibilities (*6*). The exception, $V_5S_8$, orders antiferromagnetically at 30 K (*6*). A small amount of $V_5S_8$ as an impurity cannot account for the magnetic transition observed in the present samples, especially since the impurity level is largest for the sample that orders ferromagnetically. Corrections to the susceptibility are at most of the order of 1% for any of the vanadium sulfide impurities and have been neglected. Sample I (stoichiometric) is paramagnetic down to 74 K where a maximum in the susceptibility is observed (Fig. 1). A small change in slope occurs near 200 K, and the data between 80 and 470 K did not give a good fit to a single modified Curie–Weiss expression:

$$\chi = \chi_0 + C/(T - \theta). \qquad (2)$$

Least-squares analysis of the data in the different temperature regions in terms of Eq. (2) yields the results shown in Table I. Below 30 K, the experimental isotherms deviate from the linear behavior indicated by Eq. (1) (Fig. 2). This result suggests the presence of ferromagnetic interactions in this sample below 20 K. However, without examining this effect as a function of stoichiometry, further analysis is unjustified. The susceptibilities plotted in Fig. 1 below 30 K represent the values obtained at the maximum field.

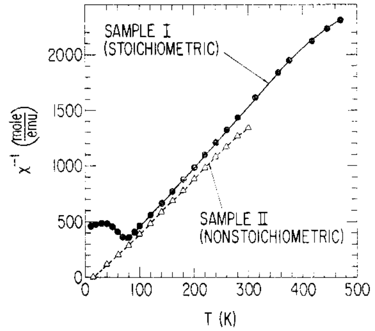

FIG. 1. Inverse magnetic susceptibility vs temperature for both samples. Solid lines are guides for the eye. Estimated accuracy of data is ±1%.

The susceptibility of sample II was also determined by means of Eq. (1) between 30 and 300 K and the results are shown in Fig. 1. The temperature dependence of the susceptibility was again least-squares fit to Eq. (2) and the results are given in Table I. The parameters obtained for both samples are in good agreement with previous work (*4*). Below 30 K the curvature in the $\sigma$ vs $H$ isotherms of sample II was characteristic of the approach to a ferromagnetic transition. Accordingly, the data were plotted in the form (*7*) $\sigma^2$ vs $H/\sigma$ (Fig. 3) to determine the Curie temperature $T_c$ ($= 16.5 \pm 0.5$ K). There is a substantial field dependence of the magnetization at 4 K despite the fact that the powder samples were field-cooled. The

TABLE I

LEAST-SQUARES FIT OF MAGNETIC SUSCEPTIBILITY DATA TO MODIFIED CURIE–WEISS LAW [$\chi = \chi_0 + C/(T - \theta)$]

| Sample (K) | $C$ (emu/mole-K) | $\theta$ (K) | $\chi_0$ (emu/mole) | $\mu_{\mathrm{eff}}$ ($\mu_B$/V) |
|---|---|---|---|---|
| I | | | | |
| 200–470 | 0.134(6) | 54(5) | $0.10(1) \times 10^{-3}$ | 1.04 |
| 80–200 | 0.23(1) | 3(3) | — | 1.36 |
| II | | | | |
| 80–300 | 0.194 | 24.8(4) | $0.3(1) \times 10^{-4}$ | 1.25 |

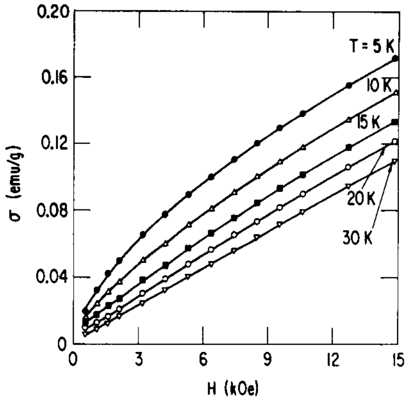

FIG. 2. Magnetic isotherms for stoichiometric $BaVS_3$ at low temperature. Low field behavior suggests ferromagnetic interaction below ~20 K.

maximum measured magnetization at 15 kOe and 4 K, 3.36 emu/g, corresponds to a moment of 0.16 $\mu_B$/V atom.

## Neutron Diffraction Results

Neutron diffraction measurements were carried out on a fixed-wavelength powder diffractometer at the Argonne CP-5 research reactor. A monochromatic beam (wavelength = 1.61 Å) was achieved using the (111) reflection of a Ge single crystal. The samples (each about 7 g) were contained in thin-walled vanadium tubes mounted in a cryostat. Intensity was measured as a function of scattering angle ($2\theta$) at various temperatures. Measurements were carried out at 80 and 8 K on I and at 260, 80, and 8 K on II.

The 80 K powder pattern for I was that calculated (*1*) for hexagonal $BaVS_3$ (the resolution of the instrument is such that the low-temperature pattern was indexable on the hexagonal unit cell). The 8 K spectrum (Fig. 4) is identical to the 80 K spectrum. The lower part of the figure shows the difference pattern $I$(8 K)–$I$(80 K), in which no additional scattering is seen.

Similar results were obtained for sample II. The 260 K pattern is that calculated for hexagonal $BaVS_3$ with some BaS impurity peaks. The 80 K pattern shows some peak broadening but is indexable on the hexagonal unit cell. The 8 K pattern shows no additional scattering.

The integrated intensities are summarized in Table II. As this table and Fig. 4 show, the neutron results are negative in that no new peaks or additional magnetic scattering are seen from either sample at low temperature Although the vanadium incoherent background is obviously large in these scans, we have attempted to address the question of the sensitivity of these measurements by calculating the expected magnetic intensities from a number of models consistent with the magnetization data. The ferromagnetic model refers to a moment of 0.2 $\mu_B$ per vanadium atom and the intensities are too small to be detected at the nuclear positions (For all models, the first number of a pair is the intensity calculated for spins aligned parallel to the *c*-axis, the second for spins aligned perpendicular to the *c*-axis.)

The second model (ferrimagnetism) assumes ferromagnetic sheets of V atoms stacked along the *c*-axis such that alternating sheets have moments +1.0 $\mu_B$/V atom and −0.6 $\mu_B$/V atom. This model predicts observable intensity at the (101) position and

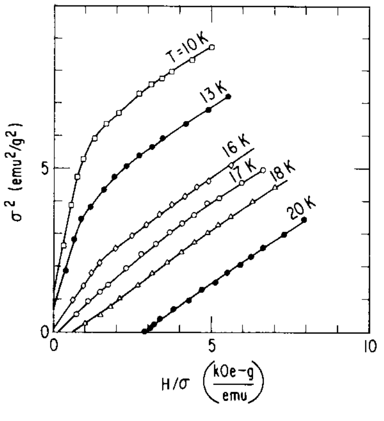

FIG. 3. Plot of $\sigma^2$ vs $H/\sigma$ for nonstoichiometric $BaVS_3$ at various temperatures to determine $T$ (= 16.5 ± 0.5 K).

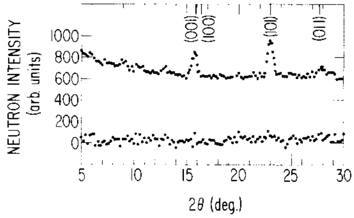

FIG. 4. Neutron data of stoichiometric BaVS$_3$ at 80 K (average of two scans). Lower trace is the intensity at 8 K−intensity at 80 K. (Indices based on hexagonal unit cell.)

can be eliminated. Thus, for the nonstoichiometric sample (II) our results are consistent with the magnetization measurements, which indicate a ferromagnetic component of 0.2 $\mu_B$/V atom.

For the stoichiometric sample (I), previous work (*4*) has led to the suggestion of short-range antiferromagnetic correlations at low temperature. Since we do not observe any new peaks, the only possible approach is to test the data against simple models of antiferromagnetic order. AF1 (see Table II) is a nearest-neighbor configuration in which each spin is surrounded by oppositely aligned nearest neighbors. The intensities in Table II correspond to 1 $\mu_B$ ($d^1$ configuration), and such a model predicts a strong new reflection at $2\theta = 21.5°$ ($\frac{1}{2}\frac{1}{2}1$). We estimate that the observed moment per vanadium would have to be less than ~0.5 $\mu_B$ for this model to be applicable. AF2 is a model with the same symmetry as the ferrimagnetic model, but with both sublattices having a magnetization of 1.0 $\mu_B$/V atom. As with AF1, the maximum moment per vanadium existing in such an antiferromagnetic arrangement must be less than ~0.5 $\mu_B$.

For sample I we cannot exclude the possibility of a complex magnetic ordering arrangement. The cusp at ~70 K in the magnetization experiments, together with evidence from Mössbauer spectra (*4*), suggest complex antiferromagnetic interactions, probably of a short-range nature. Such short-range order is predicted (*8, 9*) and observed (*10, 11*) in one-dimensional magnetic systems.

As Table II shows, the observed intensities of the (100) and (101) reflections of both samples are rather higher (at all tempera-

TABLE II

NEUTRON DATA[a]

| | | $I_{obs}$ | | | | $I_{calc}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Sample II | | Sample I | | | | | | |
| *h k l* | $2\theta$ | 80 K | 8 K | 80 K | 8 K | Nucl. | Ferro. | Ferri. | AF2 | AF1 |
| 1 0 0 | 15.9 | 5.1(7) | 5.5(7) | 4.6(5) | 4.4(5) | 3.8 | 0.3, 0.2 | 0.3, 0.2 | — | |
| 0 0 1 | 16.5 | — | <0.8 | — | 0 | — | — | 0, 1.8 | 0, 2.9 | — |
| $\frac{1}{2}$ $\frac{1}{2}$ 1 | 21.5 | <0.8 | <0.8 | <0.8 | <0.8 | 0 | — | — | — | 3.0, 5.9 |
| 1 0 1 | 23.0 | 6.9(7) | 6.6(7) | 6.8(5) | 6.9(7) | 5.0 | — | 1.9, 3.1 | 3.0, 4.9 | |
| 1 1 0 | 27.7 | 1.6(6) | 1.5(7) | 1.5(7) | 1.6(6) | 1.3 | 0.1, <0.1 | 0.1, <0.1 | — | — |
| 1 1 1 | 32.4 | — | — | — | — | 0 | — | 1.0, 0.9 | 1.6, 1.4 | — |
| 2 0 0 | 32.1 | 52(1) | 52(1) | 54(1) | Not Measured | 24.0 | <0.1, <0.1 | <0.1, <0.1 | — | — |
| 0 0 2 | 33.3 | | | | | 28.0 | 0, <0.1 | 0, <0.1 | — | — |
| 3 $\frac{1}{2}$ 1 | 33.4 | — | — | — | — | 0 | — | — | — | 3.2, 2.6 |
| 2 0 1 | 36.3 | 98(1) | 97(1) | 95(1) | Not measured | 100 | — | 0.8, 0.7 | 1.3, 1.0 | — |

[a] Comparison of observed intensities with those calculated for various spin orderings (see text). In the calculated models (see text) the first column refers to the spins parallel to *c*, the second to $\boldsymbol{\mu} \perp \mathbf{c}$.

tures) than the calculated intensities. This is consistent with both samples being somewhat deficient in Ba and S, with a larger deficiency in sample II. The X-ray results would seem to support this, but the statistics of the neutron measurements are too poor to be conclusive.

## Discussion

The magnetic properties of nonstoichiometric BaVS$_3$ are difficult to account for by assuming that the vanadium 3$d$ electrons are localized at V$^{4+}$ ions. The paramagnetic effective moment determined from the value of $C$ in Table I, 1.25 $\mu_B$ per vanadium, is well below the spin-only value, $g[S(S+1)]^{1/2} =$ 1.73, and implies a $g$ value of 1.4. It is then hard to account for the ferromagnetic moment of 0.2 $\mu_B$/V atom in the ordered phase, since the neutron diffraction results rule out ferrimagnetism.

The low values of the magnetic moments in both phases suggest that an itinerant model will be needed to explain the magnetic properties of this material. However, the observation of an ESR signal (*4*) in nonstoichiometric ferromagnetic BaVS$_3$ indicates the presence of localized electrons, at least in this material. Moreover, the observed average $g$ value $(=\frac{1}{3}g_\parallel+\frac{2}{3}g_\perp)$ is ~1.9 and this is not characteristic of a $d^1$ ion in an octahedral environment (*12*). This suggests that the ferromagnetic interaction observed in the nonstoichiometric sample arises from an interaction between itinerant vanadium 3$d$ electrons and localized electrons, perhaps trapped at sulfur vacancies.

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