

# $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>: A Strontium Vanadyl(IV) Arsenate with a Tunnel Structure

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A new polymorph of strontium vanadium(IV) arsenate,  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>, has been synthesized hydrothermally at 450°C in a quartz glass tube and characterized by single-crystal X-ray diffraction and magnetic susceptibility measurements. It crystallizes in the orthorhombic space group  $P2_12_12_1$ . Crystal data:  $a = 4.9269(5)$  Å,  $b = 12.565(1)$  Å,  $c = 12.739(1)$  Å,  $V = 788.7(1)$  Å<sup>3</sup>,  $Z = 4$ . The intensity data were collected using a CCD area detector system and MoK $\alpha$  radiation. Final  $R = 0.0381$  and  $R_w = 0.0423$  for 1315 unique reflections with  $I > 3\sigma(I)$ . The three-dimensional framework [V<sub>2</sub>As<sub>2</sub>O<sub>10</sub>]<sub>z</sub> is characterized by the assemblage of infinite chains of *cis*-corner-sharing VO<sub>6</sub> octahedra running along the *a*-axis which are linked by monoarsenate groups along [010] and [001]. One-dimensional tunnels are formed along the chain direction where strontium cations are located. Magnetic susceptibility data confirm the presence of V<sup>4+</sup> in the compound. The structure is discussed and compared with the other polymorph,  $\alpha$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>. © 1996

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## INTRODUCTION

We have been applying hydrothermal techniques to the synthesis of new phases in the transition metal arsenate system and reported several new structural types in the A–M–As–O system (1–7), where *A* includes alkali metal, alkaline-earth metal, or organic cations, and *M* = V, Fe, Co, Ni, or Mo. The hydrothermal method is useful for the synthesis of low-temperature phases and is particularly suited for crystal growth. Recently we prepared two alkaline-earth vanadium arsenates, Sr(VOAsO<sub>4</sub>)<sub>2</sub> (now labeled as the  $\alpha$ -phase) and Ba(VOAsO<sub>4</sub>)<sub>2</sub> (4), hydrothermally at 230°C. The two compounds are isostructural and are the first compounds containing discrete dimers of edge-sharing V<sup>IV</sup>O<sub>6</sub> octahedra. The phosphate analogue of  $\alpha$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> has not been reported. Interestingly, the barium vanadyl phosphate Ba(VOPO<sub>4</sub>)<sub>2</sub> (8) adopts a rather different structure, which consists of V<sub>2</sub>O<sub>10</sub> units built up from one VO<sub>6</sub> octahedron and one VO<sub>5</sub> pyramid sharing

a corner. In an attempt to discover new phases in the alkaline-earth vanadium arsenate systems, we obtained a new polymorph of Sr(VOAsO<sub>4</sub>)<sub>2</sub> under a more vigorous hydrothermal condition. In this paper, we report the synthesis, crystal structure, and magnetic susceptibility of  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>.

## EXPERIMENTAL

### Synthesis

Reagent-grade chemicals were used as received. Dark blue crystals of  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> were obtained as a major phase through hydrothermal reactions. The experiment was based on the method of Rabenau (9) for the hydrothermal synthesis of chalcogenides. A mixture of Sr(OH)<sub>2</sub>·8H<sub>2</sub>O (0.1539 g), VO<sub>2</sub> (0.0961 g), and 5 M H<sub>3</sub>AsO<sub>4</sub> (1.3 mL) molar ratio Sr:V:As = 1:2:11.2) was sealed in a quartz glass tube (i.d. = 0.8 cm and o.d. = 1.0 cm) with 49.2% filling. The pressure inside the glass ampoule was balanced by adding an appropriate amount of water in the autoclave. The autoclave was maintained at 450°C and autogenous pressure for 2 d before cooling to room temperature over a period of 15 h. The product was filtered off, washed with water, rinsed with ethanol, and dried at ambient temperature. Visual microscopic inspection showed that in addition to the dark blue crystals, a small amount of unknown yellow crystalline materials also crystallized from the reaction. A single-crystal X-ray diffraction study showed the dark blue crystals to be the new compound  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>. Large crystals with better quality (vide infra) of the compound could be obtained under high-temperature/high-pressure hydrothermal conditions. A mixture of Sr(OH)<sub>2</sub>·8H<sub>2</sub>O (0.1727 g), VO<sub>2</sub> (0.0415 g), and 3 M H<sub>3</sub>AsO<sub>4</sub> (0.29 mL) (molar ratio Sr:V:As = 1.3:1:1.74) were sealed in a gold ampoule contained in a Leco Tem-Pres autoclave and heated to 550°C for 8 h at 38,000 psi, where the pressure was provided by water pumped by a compressed air driven intensifier. The autoclave was then cooled at 5°C/h to 250°C and quenched by removing the autoclave from the furnace. The product

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contained a few dark blue crystals of  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> plus unknown green powders as a major phase. Optimized synthetic conditions for obtaining pure phase of  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> have not been found. Attempts to synthesize the same orthorhombic phase as  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> for Ba(VOAsO<sub>4</sub>)<sub>2</sub> under similar reaction conditions always yielded the known tetragonal Ba(VOAsO<sub>4</sub>)<sub>2</sub>.

### Magnetic Measurements

The distinct color and morphology of  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> crystals allowed for hand sorting of enough pure sample for magnetic measurements. Variable-temperature magnetic susceptibility  $\chi(T)$  data were obtained from 4 to 300 K in a magnetic field of 3 kG after zero-field cooling using a Quantum Design SQUID magnetometer on 31.2 mg of a powder sample of manually selected crystals. Diamagnetic contributions for Sr<sup>2+</sup>, V<sup>4+</sup>, As<sup>5+</sup>, and O<sup>2-</sup> were estimated according to Selwood (10), which were subtracted from the experimental susceptibility data to obtain the molar susceptibilities of the compound.

### Single-Crystal X-Ray Diffraction

Many of them had to be examined using  $\omega$ -scan profile analysis before a satisfactory one was obtained. The crystals synthesized in quartz glass tubes were all twinned to various extent. Finally a dark blue columnar crystal of dimensions 0.10 × 0.14 × 0.25 mm, obtained from high-temperature/high pressure hydrothermal reactions, was chosen for indexing and intensity data collection on a Siemens-Smart CCD diffractometer equipped with a normal focus, 3 KW sealed tube X-ray source (MoK $\alpha$  radiation,

**TABLE 2**  
Atomic Coordinates and Thermal Parameters ( $\text{\AA}^2 \times 100$ )  
for  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>

Atom	x	y	z	$U_{eq}^a$
Sr	0.75493(23)	0.99489(7)	0.26770(7)	2.53(3)
As(1)	0.23737(19)	0.23888(7)	0.78117(7)	1.67(3)
As(2)	0.54182(19)	0.46729(8)	0.49819(7)	1.69(3)
V(1)	0.7214(3)	0.2419(1)	0.5992(1)	1.68(5)
V(2)	1.0010(3)	0.6507(1)	0.4928(1)	1.67(5)
O(1)	0.5142(14)	0.1865(6)	0.7226(5)	2.2(2)
O(2)	0.0238(15)	0.2977(6)	0.6953(5)	2.2(2)
O(3)	0.1052(13)	0.1362(5)	0.8486(5)	1.9(2)
O(4)	0.3273(14)	0.3476(5)	0.8533(6)	2.1(2)
O(5)	0.8266(13)	0.5185(6)	0.4490(5)	2.2(2)
O(6)	0.3240(13)	0.5577(5)	0.5451(5)	1.9(2)
O(7)	0.5920(14)	0.3937(6)	0.6092(5)	1.9(2)
O(8)	0.4091(14)	0.3992(6)	0.3965(5)	2.0(2)
O(9)	0.4887(12)	0.2139(6)	0.5107(5)	2.3(2)
O(10)	0.7511(15)	0.7314(5)	0.4676(5)	2.3(2)

<sup>a</sup>  $U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

$\lambda = 0.71073 \text{ \AA}$ ). Intensity data were collected in 1200 frames with increasing  $\omega$  (0.3° per frame). Orientation matrix and unit cell dimensions were determined by a least-squares fit of 1266 reflections having  $15 < 2\theta < 40^\circ$ . Of the 3775 reflections collected ( $2\theta_{max} = 53.65^\circ$ ), 1490 were

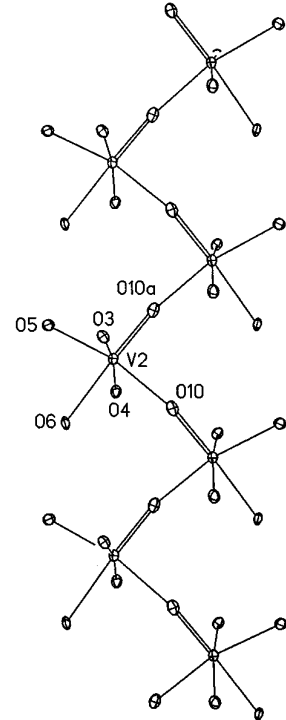
**TABLE 1**  
Crystal Data for  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>

Formula	SrV <sub>2</sub> As <sub>2</sub> O <sub>10</sub>
Color, habit	Dark blue, columnar
Space group	$P2_12_12_1$ (No. 19)
$M_r$ (g)	499.3
$a$ ( $\text{\AA}$ )	4.9269(5)
$b$ ( $\text{\AA}$ )	12.565(1)
$c$ ( $\text{\AA}$ )	12.739(1)
$V$ ( $\text{\AA}^3$ )	788.7(1)
$Z$	4
$T$ (K)	297
$\lambda$ ( $\text{\AA}$ )	0.71073
$D_c$ (g cm <sup>-3</sup> )	4.221
$\mu(\text{MoK}\alpha)$ (cm <sup>-1</sup> )	174.3
$R^a$	0.0381
$R_w^b$	0.0423
GOF	0.97

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]}{w} \quad w = 1/[\sigma^2(F_o) + 0.0019826 F_o^2]$$

with  $\sigma^2(F_o)$  from counting statistics.



**FIG. 1.** The screw-like chains  $[\text{VO}_4\text{O}_2]_\infty$  in  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>. The backbone of the infinite chain contains alternatively short V=O and long V—O bonds.

TABLE 3  
Selected Bond Lengths (Å) and Bond-Valence Sums ( $\Sigma s$ )  
for  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>

Sr–O(1)	2.611(7)	Sr–O(2)	2.880(7)
Sr–O(3)	2.631(7)	Sr–O(4)	2.534(7)
Sr–O(6)	2.498(6)	Sr–O(7)	2.679(7)
Sr–O(8)	2.545(7)		
$\Sigma s[\text{Sr–O}] = 1.86$			
As(1)–O(1)	1.689(7)	As(1)–O(2)	1.678(7)
As(1)–O(3)	1.681(7)	As(1)–O(4)	1.705(7)
$\Sigma s[\text{As(1)–O}] = 4.95$			
As(2)–O(5)	1.666(7)	As(2)–O(6)	1.673(7)
As(2)–O(7)	1.707(7)	As(2)–O(8)	1.684(7)
$\Sigma s[\text{As(2)–O}] = 5.03$			
V(1)–O(1)	2.000(7)	V(1)–O(2)	2.061(7)
V(1)–O(7)	2.015(7)	V(1)–O(8)	2.001(7)
V(1)–O(9)	1.646(7)	V(1)–O(9)	2.000(7)
$\Sigma s[\text{V(1)–O}] = 4.13$			
V(2)–O(3)	2.095(7)	V(2)–O(4)	1.968(7)
V(2)–O(5)	1.952(7)	V(2)–O(6)	2.084(7)
V(2)–O(10)	1.627(7)	V(2)–O(10)	1.992(7)
$\Sigma s[\text{V(2)–O}] = 4.22$			

unique ( $R_{\text{int}} = 0.052$ ) and 1315 were considered observed ( $I > 3.0 \sigma(I)$ ) after Lorentz polarization and empirical absorption corrections. The parameters for absorption correction were estimated from 3709 reflections using the SHELXTL-Plus program package (11). The transmission factors ranged from 0.315 to 0.984. On the basis of intensity statistics, systematic absences and successful phase solution and refinement of the structure, the space group was determined to be  $P2_12_12_1$ . Direct methods were used to locate Sr, As, V, and several O atoms with the remaining oxygen atoms being found from successive difference maps. The structure was refined by full-matrix least squares based on  $F$  values. All atoms were refined with anisotropic thermal parameters. The total number of refined variables were 138. On the final Fourier difference map, the largest residual electron density peak (hole) was 1.1 ( $-1.5$ )  $e\text{\AA}^{-3}$ . Final  $R(F_o)$  and  $R_w(F_o)$  values were 0.0381 and 0.0423, respectively. Calculations were performed on a DEC VAX 4000/90 computer system using SHELXTL-Plus programs. Neutral-atom scattering factors and corrections for anomalous dispersion were from Ref. (12). Anisotropic thermal parameters, bond lengths and angles, and structure factor tables are deposited as supplementary materials.

## RESULTS AND DISCUSSIONS

The crystallographic data are listed in Table 1. Final atomic coordinates and thermal parameters are listed in

Table 2. Selected bond distances and bond-valence sums are given in Table 3. All atoms are located at general positions. The V and As atoms are six- and four-coordinated, respectively. The coordination number of  $\text{Sr}^{2+}$ , determined on the basis of the maximum gap in the Sr–O distances ranked in increasing order, is seven. The maximum cation–anion distance,  $L_{\text{max}}$ , according to Donnay and Allmann, was also considered (13). The eighth Sr–O bond length is 3.45 Å. Bond-length and bond-valence calculations (14) show that the V and As atoms are tetravalent and pentavalent, respectively. Bond-valence sums for most oxygen atoms are also in good agreement with their formal oxidation state.

$\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> adopts a new structural type. It is characterized by screw-like  $[\text{VO}_4\text{O}_{2/2}]_{\infty}$  chains which are composed of *cis*-corner-sharing VO<sub>6</sub> octahedra along the *a*-axis (Fig. 1). The backbone of the chains are formed of alternately short and long V–O bonds. Infinite chains containing alternately short V=O ( $\sim 1.6$  Å) and long V–O ( $\sim 2.1$ – $2.4$  Å) are also observed in structures of VO (H<sub>2</sub>AsO<sub>4</sub>)<sub>2</sub> and NaVOAsO<sub>4</sub>. But rather than *cis*-corner sharing, the VO<sub>6</sub> octahedra in these formulation analogues are *trans*-corner-shared in the chains. In  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>, the two crystallographically independent vanadium sites,

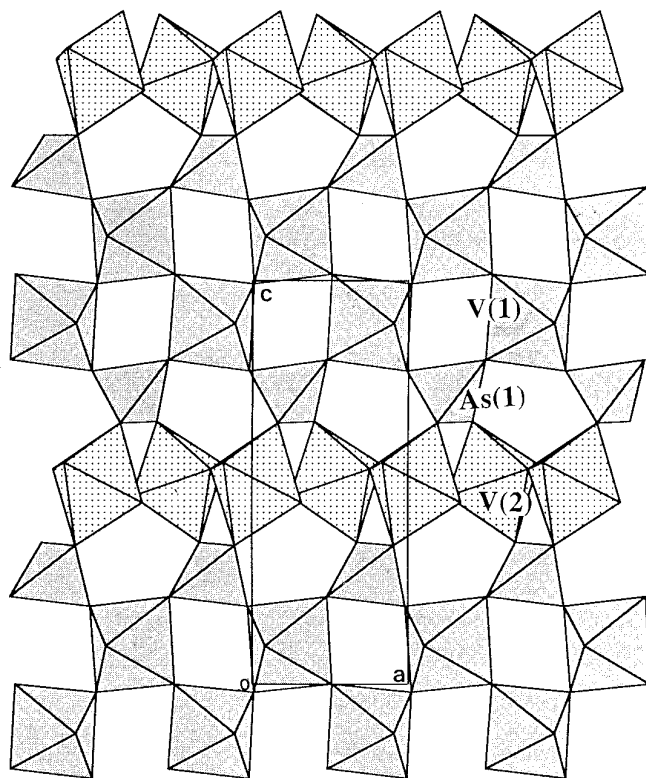


FIG. 2. The polyhedral sheets formed by infinite chains and tetrahedra of AsO<sub>4</sub> parallel to the (001) planes. In these representations the corners of octahedra and tetrahedra are O atoms and the V and As atoms are at the center of each octahedron and tetrahedron, respectively.

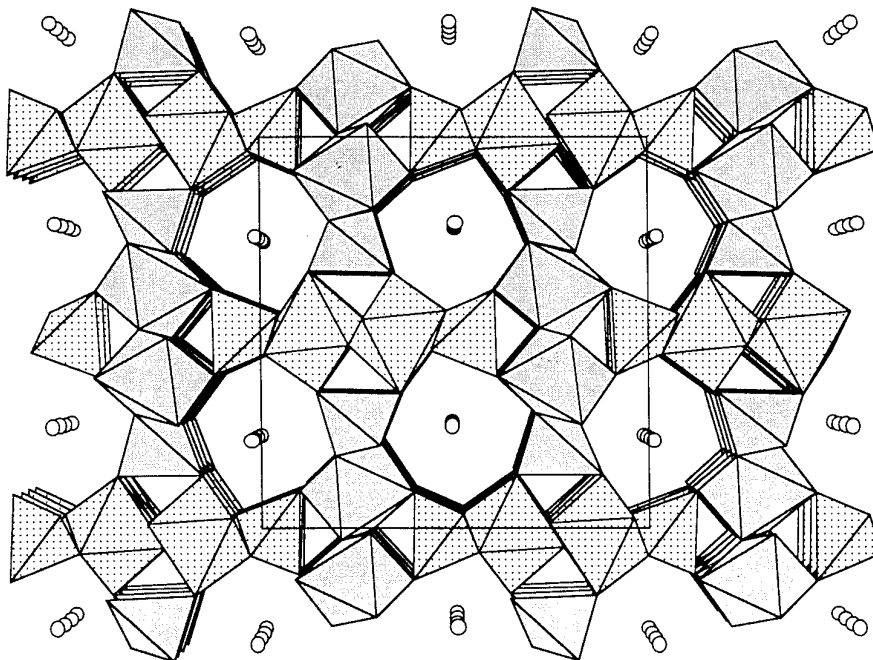


FIG. 3. A perspective view of the  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> structure along [100] showing straight tunnels. Open circles are Sr atoms.

V(1) and V(2), present two unique chains,  $[V(1)O_4O_{2/2}]_\infty$  and  $[V(2)O_4O_{2/2}]_\infty$ , running into the same direction. They are similar in conformation and are linked to each other via AsO<sub>4</sub> tetrahedra to form sheets parallel to (010) planes or (001) planes (Fig. 2). The two unique arsenate groups, As(1)O<sub>4</sub> and As(2)O<sub>4</sub>, are also similar in polyhedral linkage. Each AsO<sub>4</sub> group shares two corners with two adjacent VO<sub>6</sub> octahedra (related by 2<sub>1</sub> symmetry) within a chain and the other two corners with two VO<sub>6</sub> octahedra (related by a translation of **a**) in a neighboring chain. Each V(1)O<sub>6</sub> (V(2)O<sub>6</sub>) octahedron shares a pair of *cis* corners with two octahedra within the chain and another pair of *cis* corners (*trans* to the previous pair) with two As(1)O<sub>4</sub> (As(2)O<sub>4</sub>) tetrahedra, and the remaining two corners (*trans* to each other) with two As(2)O<sub>4</sub> (As(1)O<sub>4</sub>) tetrahedra. These arrangements fulfill the 2<sub>1</sub> symmetry in both *b*- and *c*-axis directions. The polyhedral sheets shown in Fig. 2 are further connected by As(2)O<sub>4</sub> (As(1)O<sub>4</sub>) tetrahedra in [001] ([010]) to give the three-dimensional framework in which straight tunnels are formed (Fig. 3). The opening of the tunnel is an eight-membered ring formed by the edges of four VO<sub>6</sub> octahedra and four AsO<sub>4</sub> tetrahedra. The diameter of the ring is approximately 5 Å.

The two polymorphs of Sr(VOAsO<sub>4</sub>)<sub>2</sub> have considerably different structures. The  $\alpha$ -phase consists of no infinite chains but discrete dimers of edge-sharing VO<sub>6</sub> octahedra. Octahedral distortion, estimated by using the equation  $\Delta = 1/6 \Sigma [(R_i - \bar{R})/\bar{R}]^2$  where  $R_i$  = an individual bond length and  $\bar{R}$  = an average bond length (15), is greater in the dimer than in the infinite chain ( $\Delta \times 10^4$ : 91 vs  $\sim$ 57).

In addition, the distance between two V centers in the dimer is shorter than the shortest V  $\cdots$  V distance in the screw-like chain (3.34 vs 3.53 Å) due to edge-sharing. The coordination of V in both structures is characteristic of vanadyl groups, i.e., one very short V = O bond length ( $\sim$ 1.6 Å) which is about 0.4 Å shorter than the four equatorial V–O bonds. However, the sixth V–O bond which is *trans* to V=O is considerably longer in the dimer than in the screwy chain (2.21 vs 2.00 Å). The V–O bond lengths *trans* to the V=O group is usually longer than 2.2 Å in the  $[VO_4O_{2/2}]_\infty$  chains which are formed of *trans*-corner-sharing V<sup>IV</sup>O<sub>6</sub> octahedra.

The bonding between the strontium cation and the framework are noted in the two polymorphs. Half of the cations are loosely bound in the  $\alpha$ -phase whereas all of the Sr cations are tightly bound in the tunnels in the  $\beta$ -phase. Corresponding bond-valence sums and thermal parameters of the Sr atoms<sup>2</sup> suggest that the  $\alpha$  framework is better than the  $\beta$  framework to accommodate the larger Ba<sup>2+</sup> cation in the tunnel. This can be taken into account for the failure in our attempts to synthesize the orthorhombic phase for Ba(VOAsO<sub>4</sub>)<sub>2</sub> as mentioned in the Experimental section.

Magnetic susceptibilities were measured to confirm the presence of V<sup>4+</sup> ( $d^1$ ) in  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>. In contrast to the  $\alpha$ -phase, the plot of  $\chi_M$  vs  $T$  for  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> clearly

<sup>2</sup> The bond-valence sums and  $U_{eq}$  values for the two unique Sr atoms in  $\alpha$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub> are 1.84 v.u. and 0.017 Å<sup>2</sup> for Sr(1) and 1.40 v.u. and 0.059 Å<sup>2</sup> for Sr(2).

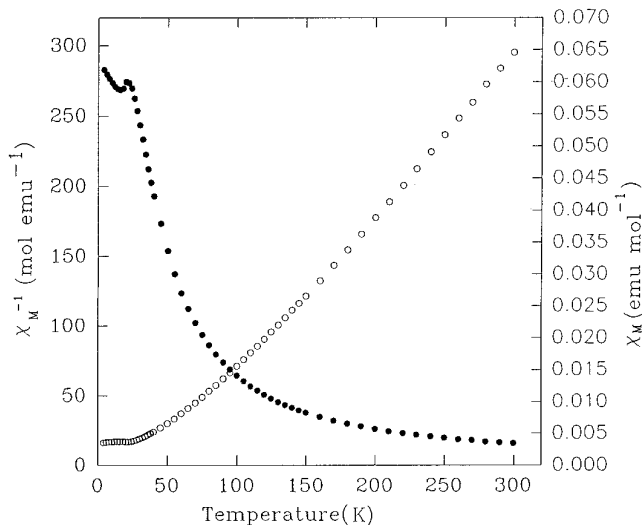


FIG. 4. Magnetic susceptibility ( $\chi_M$ , open circles) and inverse magnetic susceptibility ( $1/\chi_M$ , solid circles) plotted as a function of temperature for a powder sample of  $\beta$ -Sr(VOAsO<sub>4</sub>)<sub>2</sub>.

shows an antiferromagnetic phase change at about 20 K (Fig. 4). But the fact that the susceptibility continues to rise at lower temperature indicates that it is not a straightforward antiferromagnet. The data above 140 K can be described by the Curie-Weiss equation:  $\chi_M = C/(T - \theta)$  with  $C = 0.8633 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  and  $\theta = -52.8 \text{ K}$ . The magnetic moment for the paramagnetic region is  $\mu_{\text{eff}} = 1.86 \text{ B.M.}$ , slightly larger than the spin-only value of  $d^1$ , 1.73.

In conclusion, we have synthesized a new polymorph

of Sr(VOAsO<sub>4</sub>)<sub>2</sub> by a hydrothermal method. The use of different pressure and temperature conditions can aid the search for new phases. The structure of this new polymorph is characterized by infinite screw-like chains formed of *cis*-corner-sharing V<sup>IV</sup>O<sub>6</sub> octahedra. Further investigation of the *M-V-As-O* system (*M* = alkaline-earth metals) system is in progress.

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