

BRIEF COMMUNICATIONS

Crystal Structure and Magnetic Properties of Orthorhombic Sr_2VO_4 with Tetrahedral Vanadium(IV)

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A new crystalline modification of Sr_2VO_4 , isostructural with Sr_2CrO_4 , has been prepared by both low and high temperature methods. The space group appears to be $Pna2_1$ with $a = 14.092(4)$ Å, $b = 5.806(2)$ Å, and $c = 10.106(3)$ Å. Atomic positions have been refined by the Rietveld method from powder neutron and X-ray diffraction data. The structure is a supercell of the K_2SO_4 -type and thus appears to be the first example of an oxide containing VO_4^{-4} polyhedra. This phase is apparently a high temperature modification stable above about 1100°C. Orthorhombic Sr_2VO_4 can also be prepared at low temperature (about 500°C) by reduction of $\text{Sr}_2\text{VO}_4\text{Cl}$ with Na metal. Surprisingly, the magnetic susceptibility shows a broad maximum at 60 K and the data can be understood very well on a $S = \frac{1}{2}$ dimer model. These results are compared with similar ones for electronically related Cu(II) salts. © 1991 Academic Press, Inc.

1. Introduction

Tetragonal Sr_2VO_4 with the K_2NiF_4 -type structure has been reported and characterized recently (1, 2). Other materials with related structure types have also been reported such as $\text{Sr}_{1.5}\text{La}_{1.5}\text{V}_2\text{O}_7$ (3) and $\text{Sr}_4\text{V}_3\text{O}_{10-x}$ (3, 4). As a result of attempts in this laboratory to prepare Sr_2VO_4 by low temperature methods, a new orthorhombic modification which is isostructural with Sr_2CrO_4 , a supercell of the K_2SO_4 -type, was discovered. This work describes the preparation and structural characterization of the new phase along with magnetic susceptibility data and an interpretation of the surprising results.

II. Experimental

Sample Preparation

Orthorhombic Sr_2VO_4 can be prepared by two basic methods, a high temperature ceramic firing and a low temperature sodium reduction. Stoichiometric quantities of SrVO_3 and SrO were well ground in a dry-box, pelleted, and sealed into a half-inch diameter molybdenum crucible under 0.5 atm prepurified argon by welding. The pellet was heated at 1100(50)°C for a total of 30 hr with one intermediate regrinding. A radiation thermometer (300C, IRCON Inc.) was used to measure the temperature. The same orthorhombic phase of Sr_2VO_4 could also be formed by H_2 reduction of a stoichio-

metric mixture of $\text{Sr}_3\text{V}_2\text{O}_8$ and SrO at 1300°C for 10 hr. $\text{Sr}_3\text{V}_2\text{O}_8$ was prepared by firing SrCO_3 and V_2O_5 together at 1000°C for 10 hr. The oxidation state of V in Sr_2VO_4 was determined by thermogravimetric analysis (Netzsch STA 409). The sample was heated to 900°C in O_2 flow and the weight gain observed was 2.75(2)%. The theoretical value is 2.76%.

Another method of preparing orthorhombic Sr_2VO_4 is by sodium reduction of Sr_2VO_4X , where $X = \text{Cl}$ or Br . Starting materials were either sealed directly in quartz tubing under high vacuum or a molybdenum tube welded under 0.5 atm prepurified argon gas. When Sr_2VO_4X and Na metal were fired at 500°C for 40 hr, the products are orthorhombic Sr_2VO_4 and NaX . Quartz tube preparations showed evidence of side reactions with the tube. If the heating temperature is between 600 and 900°C , however, the products are tetragonal K_2NiF_4 -type Sr_2VO_4 and NaX .

X-Ray and Neutron Diffraction

X-ray powder data were obtained using a Guinier camera (IRDAB XDC700) with $\text{CuK}\alpha_1$ radiation and a Si standard. Data suitable for profile refinement were collected in the range $14^\circ < 2\theta < 91^\circ$ using a Nicolet I2 diffractometer with $\text{CuK}\alpha$ radiation, entrance beam sller collimator, exit beam monochromator, and a scintillation counter. The step width was $0.03^\circ 2\theta$ and a step time of 16 sec was used.

Neutron diffraction data were obtained at the McMaster Nuclear Reactor using 1.3907-\AA neutrons obtained by reflection from a Cu [200] monochromator. Details of the data collection and refinement methods have been described previously (5).

Magnetic Susceptibility

Susceptibility data were collected using a Quantum Design Squid magnetometer in the

temperature range 5 to 300 K at an applied magnetic field of 0.2 T.

III. Results and Discussion

Crystal Structure

Orthorhombic Sr_2VO_4 was identified as isostructural with Sr_2CrO_4 by comparison of unit cell constants in angstroms obtained from the X-ray Guinier camera data. They were $a = 14.075(3)$, $b = 5.8058(7)$, $c = 10.100(2)$ for Sr_2VO_4 and $a = 14.182(1)$, $b = 5.788(3)$, $c = 10.100(2)$ for Sr_2CrO_4 (6). The Guinier data are summarised in Table I.

Positional parameters for all atoms were refined independently from both X-ray and neutron powder data in space group $Pna2_1$. Efforts to describe the structure in the higher symmetry space group $Pnam$ were not successful. Because of the large number of positional parameters, 41 in all, an overall temperature factor was refined in both cases. Of course the neutron data contain little information regarding the vanadium positions while the X-ray data are only weakly influenced by the oxygen atoms.

In both cases a version of the Rietveld profile refinement method was used. The procedure for the neutron data has been described previously (5). Neutron scattering lengths (fm) used were 7.02, -0.382 , and 5.805 for Sr, V, and O, respectively (7). The X-ray data were refined using LHPM1 of Hill and Howard (8) which is a modified version of DBW 3.2 due to Wiles and Young (9). A pseudo-Voigt profile shape function including a Reitveld asymmetry correction was used. Two impurity reflections not overlapping the Sr_2VO_4 peaks were excluded from the refinement. Such reflections were not prominent in the neutron data.

The neutron data were refined first using the positions from Sr_2CrO_4 as a trial model and the results are shown in Table II and in Fig. 1. This structure was used in turn to begin the X-ray data refinement, the results

TABLE I
BRAGG PEAK POSITIONS FOR Sr_2VO_4 DERIVED FROM
GUINIER FILM AND X-RAY DIFFRACTION DATA

$a = 14.075(3) \text{ \AA}, b = 5.8058(7) \text{ \AA}, c = 10.100(2) \text{ \AA}$											
h	k	l	D_{cal}	D_{obs}	I	h	k	l	D_{cal}	D_{obs}	I
2	0	1	5.774	5.777	2	6	1	1	2.126	2.126	5
0	0	2	5.050	5.056	3	2	2	3	2.099	2.098	6
0	1	1	5.033	5.038	6	4	0	4	2.052	2.052	9
1	1	1	4.740	4.745	1	4	2	2	2.047	2.047	25
2	1	1	4.094	4.096	1	3	2	3	1.991	1.990	3
1	1	2	3.678	3.679	5	2	0	5	1.942	1.941	11
3	1	0	3.649	3.652	1	0	1	5	1.908	1.907	4
3	1	1	3.432	3.434	4	1	3	1	1.884	1.883	1
2	1	2	3.351	3.352	23	5	2	2	1.876	1.875	4
4	0	1	3.323	3.324	6	4	2	3	1.865	1.865	19
2	0	3	3.037	3.038	11	6	1	3	1.827	1.826	1
4	1	0	3.009	3.009	34	6	2	1	1.796	1.796	4
0	1	3	2.912	2.913	100	1	3	2	1.792	1.792	4
0	2	0	2.903	2.901	50	3	1	5	1.767	1.768	1
4	0	2	2.887	2.889	26	3	3	1	1.762	1.762	4
4	1	1	2.884	2.885	76	4	0	5	1.752	1.753	5
1	1	3	2.852	2.852	2	2	3	2	1.750	1.751	5
1	2	0	2.843	2.843	11	523,801			1.733	1.733	10
1	2	1	2.737	2.737	3	6	2	2	1.716	1.716	2
2	1	3	2.691	2.693	3	4	3	0	1.696	1.696	3
2	2	1	2.594	2.594	3	3	3	2	1.686	1.687	3
4	1	2	2.585	2.585	8	006,810			1.683	1.683	7
5	1	0	2.533	2.533	4	033,415			1.678	1.678	16
0	2	2	2.517	2.515	3	4	2	4	1.675	1.675	6
3	1	3	2.474	2.475	2	4	3	1	1.672	1.673	6
5	1	1	2.457	2.456	5	1	3	3	1.666	1.667	11
4	0	3	2.433	2.432	24	811,802			1.661	1.661	16
3	2	1	2.398	2.396	4	6	1	4	1.648	1.649	11
2	0	4	2.377	2.377	7	1	2	5	1.657	1.646	2
2	2	2	2.370	2.369	7	2	2	5	1.614	1.615	5
601,114			2.285	2.286	18	4	3	2	1.608	1.608	2
4	2	0	2.239	2.241	2	8	1	2	1.597	1.597	4
3	2	2	2.218	2.217	11	5	3	0	1.595	1.595	1
2	1	4	2.200	2.200	6	216,531			1.576	1.576	12
4	2	1	2.186	2.186	6	7	2	2	1.571	1.571	2
1	2	3	2.172	2.173	5	8	0	3	1.559	1.560	3
6	0	2	2.128	2.128	7	6	0	5	1.531	1.531	2

of which are also included in Table II. In both cases in addition to the position and thermal parameters a scale factor, and zero point, unit cell, and peak shape parameters were also refined.

A perusal of Table II shows modest agreement between the two refinements with only a few parameters differing by more than 3σ (standard deviation). The vanadium atomic positions are those from the X-ray refinement. Note the large errors associated with the oxygen atomic positions

derived from the X-ray data set. Although the precision and accuracy of the structural model found here could certainly be improved for example by increasing the resolution and range of the data, it is clear that Sr_2VO_4 is isostructural with Sr_2CrO_4 , which is a supercell of the K_2SO_4 structure type. Examples of V(IV) in fourfold coordination in oxides are rare, indeed this appears to be the first reported example.

Table III displays bond distances and angles derived from the neutron data refinement. The X-ray results are not included due to the relatively poor precision on the oxygen atomic parameters and to the fact that some of the metal–oxygen distances were found to be unreasonably short, such as Sr2–O6 of 2.10 Å and V2–O4 of 1.38 Å. The V–O distances and angles defining the VO_4 tetrahedra show a large distortion from ideal geometry which may reflect an expected Jahn–Teller distortion; the electronic ground state would be $(e)^1(t_2)^0$ for tetrahedral V(IV). Comparison with the CrO_4 geometry in Sr_2CrO_4 shows a rather similar distortion, and, of course, chromium(IV) is not expected to be Jahn–Teller active with ground state $(e)^2(t_2)^0$. It is also important to note that tetrahedral vanadium(IV) is the one-electron analog of octahedral Cu^{2+} , $(t_2)^6(e)^3$. This will become important in the discussion of magnetic behavior in a later section.

Annealing Experiments

As mentioned orthorhombic Sr_2VO_4 can be prepared by both low and high temperature routes. When this material, first wrapped in platinum foil, is annealed in an evacuated (about 10^{-5} Torr), sealed quartz tube between 800 and 900°C it transforms to the tetragonal K_2NiF_4 -type structure. Annealing at 600°C or below does not produce a structure transition. As the two structures differ greatly in detail, V is octahedrally coordinated in the K_2NiF_4 -type structure but

TABLE II
CRYSTALLOGRAPHIC PARAMETERS FROM NEUTRON AND X-RAY (IN BRACKETS) POWDER
DIFFRACTION DATA

Space group:	$Pna2_1$ (No. 33)				
Unit cell dimensions:	$a = 14.092(4)$ [14.088(1)] Å				
	$b = 5.806(2)$ [5.809(1)] Å				
	$c = 10.106(3)$ [10.110(1)] Å				
Cell content:	8 Sr_2VO_4				
Atom	Site	x	y	z	
Sr(1)	4a	0.132(2) [0.132(1)]	0.221(3) [0.236(2)]	0.000000 [0.000000]	
Sr(2)	4a	0.207(1) [0.205(1)]	0.204(3) [0.194(2)]	0.643(3) [0.627(2)]	
Sr(3)	4a	0.381(1) [0.376(1)]	0.180(3) [0.178(2)]	0.922(2) [0.921(1)]	
Sr(4)	4a	0.444(1) [0.453(1)]	0.228(3) [0.234(2)]	0.275(3) [0.265(1)]	
V(1)	4a	0.021(1) [0.021(1)]	0.778(3) [0.778(3)]	0.120(3) [0.120(3)]	
V(2)	4a	0.282(2) [0.282(2)]	0.701(3) [0.701(3)]	0.791(2) [0.791(2)]	
O(1)	4a	0.122(2) [0.115(3)]	0.360(4) [0.369(9)]	0.234(4) [0.243(5)]	
O(2)	4a	0.243(1) [0.223(4)]	0.001(4) [0.986(8)]	0.410(3) [0.396(8)]	
O(3)	4a	0.137(2) [0.111(5)]	0.889(4) [0.863(9)]	0.190(4) [0.229(6)]	
O(4)	4a	0.302(2) [0.227(3)]	0.142(3) [0.168(9)]	0.137(3) [0.185(7)]	
O(5)	4a	0.453(2) [0.452(5)]	0.767(3) [0.754(9)]	0.262(3) [0.302(6)]	
O(6)	4a	0.289(2) [0.291(5)]	0.459(4) [0.502(9)]	0.367(2) [0.303(6)]	
O(7)	4a	0.975(1) [0.956(5)]	0.034(3) [0.018(9)]	0.054(3) [0.047(7)]	
O(8)	4a	0.011(1) [0.004(4)]	0.574(3) [0.614(9)]	0.010(3) [0.984(7)]	
Overall temperature factor:			0.29(9) [0.96(6)] Å ²		
Nuclear R_N			4.2 [4.6] %		
Weighted profile R_w			5.3 [7.4] %		
Profile R_P			3.8 [5.7] %		
Expected R_E			2.5 [3.4] %		
No. of profile points N :			684		
Independent reflections:			365		
D -spacing range (Å):			1.1–5.7		

Note.

$$\begin{aligned}
 R_N &= \sum |I_{\text{obs}} - I_{\text{cal}}| / \sum I_{\text{obs}}, \\
 R_w &= \{[\sum w(Y_{\text{obs}} - Y_{\text{cal}})^2] / \sum w Y_{\text{obs}}^2\}^{1/2}, \\
 R_P &= \sum |Y_{\text{obs}} - Y_{\text{cal}}| / \sum Y_{\text{obs}}, \\
 R_E &= [(N - P) / \sum w Y_{\text{obs}}^2]^{1/2},
 \end{aligned}$$

where P is the number of parameters.

tetrahedrally coordinated in the Sr_2CrO_4 -type structure, a first-order transition might be expected. The details of this phenomenon are under current investigation.

Magnetic and Electrical Properties

Simple two-probe electrical measurements indicate that at room temperature

Sr_2VO_4 is an insulator, as might be expected given that the VO_4 tetrahedra are isolated in this structure.

The temperature dependence of the magnetic susceptibility is shown in Fig. 1. Note the pronounced relatively broad maximum at about 60°K. This is a clear indication of short range magnetic correlations. Such behavior is quite remarkable again given that

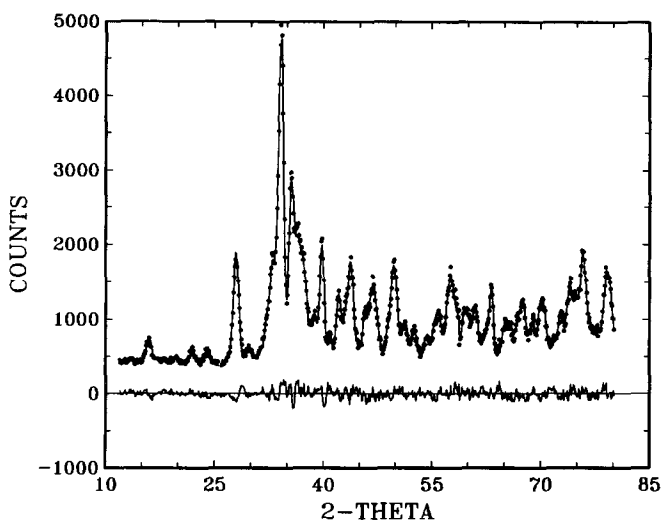


FIG. 1. Powder neutron profile refinement results for orthorhombic Sr_2VO_4 . The solid circles are the profile points, the solid line is the fitted profile, and the lower plot is the difference.

the V(IV) is present as isolated VO_4 tetrahedra. Examination of the crystal structure (Fig. 2) shows no obvious feature such as chains, planes, or clusters of the tetrahedra which would provide a clue to the origin of this unexpected effect. In fact the general shape of the susceptibility curve resembles that of the classic $S = \frac{1}{2}$ dimer model first proposed by Bleaney and Bowers (10).

An attempt was thus made to fit the observed data to the following expression:

$$X_M = C/(T - \theta) + (\bar{g}^2/8T)[1 + (\frac{1}{3})\exp(-2J/kT)]^{-1} + X_{\text{TIP}}$$

The first term is a Curie-Weiss contribution to model the sharp upturn at low temperatures, the second is the Bleaney-Bowers expression per V atom where \bar{g} is the powder-averaged g -factor, and J is the exchange constant. A temperature-independent term, X_{TIP} , is included as has been found for the canonical case of the Cu(II) acetate dimer (11). The results are shown in Fig. 1 and the fit is seen to be excellent. The refined parameters $\bar{g} = 1.88$, $J/k = -52$ K, and $X_{\text{TIP}} = 200 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ are reasonable. The Curie-Weiss constants for the

paramagnetic feature are $C = 0.017 \text{ mol} \cdot \text{K} \cdot \text{cm}^{-3}$ and $\theta = -5.5$ K.

Attempts to fit the data to other short range order models such as the $S = \frac{1}{2}$ Heisenberg linear chain and square planar models

TABLE III

BOND DISTANCES (Å) AND BOND ANGLES (°) IN Sr_2VO_4 DERIVED FROM THE NEUTRON DATA REFINEMENT

V-O distances in VO_4 tetrahedra			
V1-O3 1.88(2)	V2-O1 1.74(2)		
V1-O5 1.75(2)	V2-O2 1.71(3)		
V1-O7 1.76(2)	V2-O4 1.99(3)		
V1-O8 1.65(3)	V2-O6 1.96(2)		
O-V-O bond angle in VO_4 tetrahedra			
O3-V1-O5 103(2)	O1-V2-O2 139(1)		
O3-V1-O7 100(1)	O1-V2-O4 107(2)		
O3-V1-O8 126(1)	O1-V2-O6 97(1)		
O5-V1-O7 104(1)	O2-V2-O4 108(1)		
O5-V1-O8 113(1)	O2-V2-O6 98(1)		
O7-V1-O8 109(2)	O4-V2-O6 97(1)		
Sr-O distances			
Sr1-O1 2.50(3)	Sr2-O2 2.68(3)	Sr3-O1 2.66(4)	Sr4-O1 2.59(3)
Sr1-O2 2.56(3)	Sr2-O3 2.50(3)	Sr3-O2 2.55(3)	Sr4-O4 2.48(3)
Sr1-O3 2.72(3)	Sr2-O4 2.55(2)	Sr3-O3 2.66(3)	Sr4-O5 2.68(3)
Sr1-O4 2.81(3)	Sr2-O5 2.58(3)	Sr3-O4 2.45(4)	Sr4-O6 2.72(3)
Sr1-O5 2.70(3)	Sr2-O6 2.68(3)	Sr3-O5 2.86(3)	Sr4-O7 2.66(3)
Sr1-O6 2.31(3)	Sr2-O7 3.04(2)	Sr3-O6 2.78(3)	Sr4-O8 2.62(3)
Sr1-O7 2.53(3)		Sr3-O7 2.50(3)	
Sr1-O8 2.67(3)		Sr3-O8 2.51(3)	

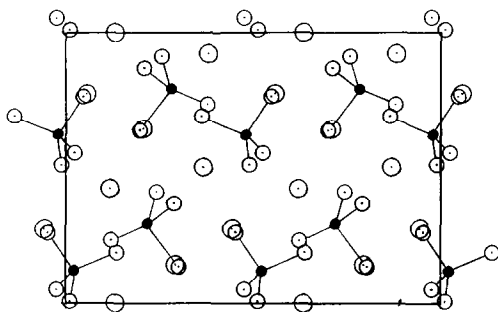


FIG. 2. The crystal structure of the orthorhombic Sr_2VO_4 viewed along the b axis. The small solid circles are V, the small open circles O, and the large open circles Sr.

were much less successful. As mentioned before and as can be seen from Fig. 2, there exists no obvious feature such as pairs of VO_4 tetrahedra coupled directly by V–O–V links in this structure. More tortuous superexchange pathways such as V–O–O–V or V–O–Sr–O–V must be involved. There are a number of such linkages in Sr_2VO_4 ; the one with the shortest O–O distance involves V2–O1–O3–V1. The distances (\AA) are

1.74(2), 2.78(4), and 1.88(2) from left to right with angles V2–O1–O3 of $58(1)^\circ$ and O1–O3–V1 of $109(1)^\circ$.

Magnetic behavior reminiscent of that reported here has been seen before in octahedral Cu(II) salts which are electronically similar to tetrahedral V(IV) as pointed out earlier. For the case of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ both heat capacity and susceptibility data could be fitted with excellent results to the dimer model (12), yet the crystal structure shows no evidence for Cu–Cu pairs; instead, a zig-zig chain arrangement was found (13). In addition to copper nitrate a number of other compounds such as various adducts of Cu(II) propionate also have crystal structures which are polymeric, chain-like, but for which the powder magnetic susceptibility can be modeled very well with the Bleaney–Bowers expression (14).

Finally, the observed J/k value of: -52 K is remarkably high considering the rather convoluted superexchange pathway which must be involved. Recently, a 180° Cu–O–O–Cu pathway in CuSb_2O_6 has been found to give a J/k of very similar magnitude, -43 K (15).

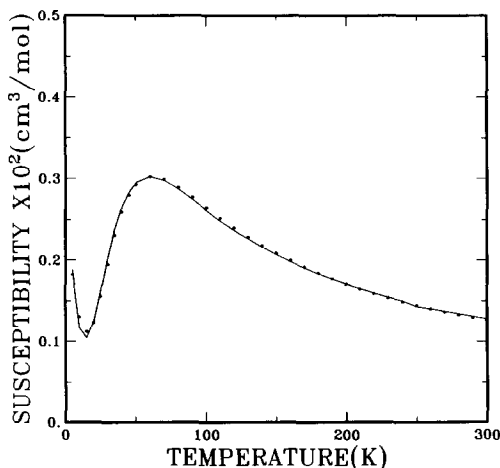


FIG. 3. The magnetic susceptibility of orthorhombic Sr_2VO_4 . The solid line is the fit to the $S = 1/2$ dimer model with Curie–Weiss plus temperature-independent terms. The fitting parameters are given in the text.

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