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Charge order and negative thermal expansion in V$_2$OPO$_4$

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ABSTRACT: The semivalent oxyphosphate V$_2$OPO$_4$ is found to have long range V$^{2+}$/V$^{3+}$ charge ordering up to 605 K where a monoclinic to tetragonal structural transition and a switch from positive to negative thermal expansion are observed. V-V bonding within orbital polymer chains is proposed as the key factor in the novel switch of thermal expansion behavior, as loss of V-V bonding enables transverse oxygen motions to dominate the thermal expansion at high temperatures. Ferrimagnetic order of V$^{2+}$ spin up and V$^{3+}$ spin down states is observed below a magnetic ordering transition at 164 K, and susceptibility measurements evidence local spin pairing correlations to higher temperatures.

INTRODUCTION

Negative thermal expansion (NTE), where the volume of a substance decreases upon heating, is an unusual property that is of fundamental interest and finds application in creating zero expansion materials [1]. There are two basic types of mechanism for NTE. Large-amplitude transverse vibrations or torsions can lead to NTE in insulating framework materials such as Zr(WO$_4$)$_2$ [2,3] or ScF$_3$ [4,5], and changes in band structure associated with electronic or magnetic transitions may result in NTE in metal alloys and ceramics, for example, colossal NTE effects associated with charge ordering in the perovskite BiNiO$_3$ [6]. We report here a novel mechanism where lattice thermal expansion switches from normal, positive behavior (PTE) to NTE driven by the loss of metal-metal bonding associated with charge ordering.

This study is part of an investigation of materials containing orbital molecules, directly bonded clusters of transition metal ions in orbital-ordered solids [7]. Low valent vanadium oxides with short V-V distances are notable for forming large orbital molecules. BaV$_{10}$O$_{15}$ forms triangular V$_3^{2+}$ clusters below a structural and semiconductor-insulator transition at 130 K [8,9,10], and the spinel AlV$_2$O$_4$ is reported to have heptameric V$_7^{3+}$ orbital molecules below the charge order transition at 700 K [11].

We have explored the semivalent oxyphosphate V$_2$OPO$_4$, which was previously reported to have a tetragonal structure at room temperature (Figure 1a) consisting of a stacking along the c axis of non-intersecting chains of face-sharing V$_{2.5}$O$_6$ octahedra, running alternatively parallel to a and b [12]. The intrachain V-V distance of 2.68 Å is very short so direct bonding interactions are expected. A structural transition was reported near 593 K but no details were given. In this paper we report the synthesis, structural and magnetic characterization of V$_2$OPO$_4$ over a wide temperature range, from 4 to 750 K. Separate charge and ferrimagnetic ordering transitions are found, and the former leads to the unusual switch from positive to negative thermal volume expansion that we attribute to the loss of V-V bonding in ‘orbital polymer’ chains.

EXPERIMENTAL SECTION

A polycrystalline sample of V$_2$OPO$_4$ was prepared by high temperature solid state reaction as previously reported by Glaum [6]. The precursor β-VOPO$_4$ was prepared by heating a stoichiometric mixture of NH$_4$VO$_3$ and (NH$_4$)$_2$HPO$_4$ at 600°C in flowing O$_2$ twice for 8 hours [13]. A stoichiometric mixture of β-VOPO$_4$ and V was thoroughly ground, pressed into pellets, and heated in an evacuated sealed silica tube. Good crystallinity and high product purity were obtained after three heating cycles at 1000 °C of ca. 30 hours each, with intermediate regrinding and pelleting.

Phase purity of the product was checked by X-ray powder diffraction (XRD) using a Bruker D2 diffractometer with CuKα radiation and $5°-70°$ 20 range. High resolution synchrotron XRD data has been collected on the I11 diffractometer at the Diamond facility using the wavelength $\lambda = 0.82582Å$ at 270, 180 and 140 K, and from 300 up to 750 K with $\lambda = 0.825775 Å$. For the high temperature experiment, the sample was loaded in a quartz capillary inside a glove bag filled with argon to prevent possible oxidation at high temperature. However, some decomposition or reaction of the product with the quartz was observed at temperatures above 750 K. Time of flight neutron powder diffraction (NPD) data were collected at 298 K and between 10 and 290 K in 20 K steps using a He cryostat on HRPD at the ISIS source. The sample was placed in an aluminum-framed slab can with vanadium windows. All the diffraction data were analyzed using Fullprof software [14].

Magnetic properties were measured in a Quantum Design SQUID magnetometer. Magnetization vs. temperature from 10 to 400 K in a field of 0.1 T, and vs. applied magnetic field from -5 to 5 T at 5, 140 and 160 K, were measured. Resistivity measurements were carried out with the 4 point probe method using a Quantum Design PPMS from 10 to 300 K and in a lab-made apparatus from 300 to 870 K; the sample was placed inside a vacuum furnace and connected to a Keithley 2010 multimeter while the temperature was measured at the sample holder.

Electronic structure calculations were performed using CASTEP (v17.2) [15] using inbuilt on-the-fly pseudopotentials. Plane-wave energy cut-off (700 eV) and k-point density ($5×5×4$ Monkhorst-Pack grid [16]) were both well-converged.
[Partial] density of states ([p]DOS) were produced using OptaDOS (v1.2) with the adaptive peak broadening method [17,18]. Calculations were performed within the appropriate primitive unit cell.

RESULTS AND DISCUSSION

Crystal structure at room temperature. High resolution neutron and synchrotron X-ray diffraction patterns of V$_2$OPO$_4$ at 298 K are not properly indexed with the tetragonal I4$_1$/amd cell as splittings of some peaks are clearly visible as shown in Fig. 1. The peaks can be indexed using a monoclinic C2/c supercell with $a_M = 7.56825$ Å, $b_M = 7.60013(7)$ Å, $c_M = 7.21794(6)$ Å, $\beta_M = 121.2751(5)^\circ$, similar to that of the iron analogue Fe$_2$OPO$_4$ where a partial Fe$^{3+}$/Fe$^{2+}$ charge ordering accompanying the monoclinic distortion below 410 K was reported [19]. Some anisotropic peak broadening was observed and was fitted using Stephens strain model [20], with $S_{200}$ being the dominant parameter.

The relationship between the monoclinic and ideal (high temperature) tetragonal cells of V$_2$OPO$_4$ is shown in Fig. 1a. The transformation from monoclinic to tetragonal including origin shift is shown by matrix (1). For convenience we express the monoclinic cell in a pseudo-tetragonal metric, with 298 K parameters $aT = bT = 5.36282(2)$ Å, $cT = 12.3383(1)$ Å, $\alphaT = 180^\circ - \betaT = 89.7584(5)^\circ$, $\gammaT = 89.7596(7)^\circ$. The proximities of the cell angles to 90° illustrate the small magnitude of the lattice distortion.

$$
\begin{pmatrix}
-0.5 & 0.5 & 1 & 0.5 \\
-0.5 & -0.5 & 0 & 1 \\
0 & 0 & 2 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
$$

The monoclinic distortion maintains uniform distances of 2.68 Å between neighboring V atoms in the chains, so there is no evidence for orbital dimerization as occurs below the Peierls transition in VO$_2$ [21]. Attempts to lower symmetry further generating inequivalent in-chain distances in the refinement did not lead to significant V-displacements or improved fits. The monoclinic distortion creates distinct V1 and V2 sites that alternate along the chains. The average V-O distances in the VO$_6$ octahedra differ significantly as 2.095 and 2.027 Å for V1 and V2. Interpolation of bond valence sums (BVS) [22] give respective values of +2.1 for V1 and +2.7 for V2, showing that V$^{2+}$/V$^{3+}$ charge ordering is present in the monoclinic phase of V$_2$OPO$_4$.

Low temperature magnetic properties. Magnetic susceptibility measurements shown in Figure 2a reveal a magnetic ordering transition at $T_C = 164$ K to a ferro- or ferrimagnetic state, with a divergence between the zero field and field cooled data. Above the transition the inverse susceptibility is not linear and so does not follow standard Curie-Weiss behavior. However, the addition of a constant according to $\chi = C/(T-\theta) + \chi_0$ gives a very good fit to data at 170 - 400 K with fitting parameters $\theta = 165.6$ K, $\chi_0 = 0.00136$ emu.mol$^{-1}$ and $\chi = 0.322$ emu.K.mol$^{-1}$. The latter value gives a paramagnetic moment of $\mu_{eff} = 1.61$ $\mu_B$ per V$_2$OPO$_4$ unit, which is greatly reduced below the ideal value of 3.39 $\mu_B$ for uncoupled V$^{2+}$ and V$^{3+}$ spins. This and the large value of the constant term $\chi_0$ show that strong short-range antiferromagnetic coupling of spins persists in the paramagnetic regime immediately above $T_C$.

![Figure 1. (a) Crystal structure of V$_2$OPO$_4$ showing axes and unit cells for the monoclinic C2/c (in black) and the tetragonal I4$_1$/amd (grey) symmetries. (b) Fit of the monoclinic structure to 298 K synchrotron XRD data. Inset shows the monoclinic splitting of the intense peaks near 14.5° with indexed simulations for I4$_1$/amd and C2/c cells.

Isothermal magnetization vs. magnetic field exhibit a hysteresis loop below $T_C$ (Figure 2b). At 5 K, the saturated magnetization at 5 T is 0.6 $\mu_B$ per formula unit. V$_2$OPO$_4$ has a large coercive field of 0.8 T, characteristic of a moderately hard magnetic material with strong spin anisotropy.

The magnetic structure of V$_2$OPO$_4$ has been solved using the NPD patterns collected at 10 K on HRPD. Magnetic intensities appearing below $T_C$ are superimposed on nuclear peaks and are indexed by the propagation vector (0 0 0). Representation analysis was performed using the Basireps program from the Fullprof suite. Only one of the two possible magnetic representations (Table S3) gives a good fit to the prominent magnetic peak at d $\approx$ 3.8 Å (Figure 3a). This corresponds to a ferromagnetic arrangement of spins within each sublattice, with V1 and V2 spins coupled antiparallel to each other so the overall magnetic order is ferrimagnetic. Temperature variations of the refined moments are shown in Figure 3b. The weak intensities of the magnetic peaks did not enable the spin directions within the monoclinic ac-plane to be determined uniquely from the magnetic fits, and they were constrained to lie parallel to the pseudo-tetragonal c$_T$ axis where they are...
perpendicular to the directions of all spin chains, as shown in Figure 3c.

Figure 2. (a) Magnetic susceptibility of V$_2$OPO$_4$ as a function of temperature measured in a field of 1000 Oe (closed and open symbols for ZFC and FC respectively) and inverse ZFC magnetic susceptibility (right axis, blue symbols) with the fit (orange line) described in the text. (b) Magnetization-field loops at several temperatures.

The ferrimagnetic order of V$^{2+}$ (3d$^1$) spin up and V$^{3+}$ (3d$^2$) spin down states gives a predicted magnetization of 1 $\mu_B$ per formula unit, in fair agreement with the 0.6 $\mu_B$ experimental value at 5 K (Figure 2b). However, the saturated V$^{2+}$ and V$^{3+}$ sublattice moments are reduced from ideal values of 3 and 2 $\mu_B$ to 1.8(6) and 1.5(6) $\mu_B$. Although the antiferromagnetic coupling between neighboring cations within the chains is consistent with predicted superexchange rule [23], the reduction of ordered moments below $T_C$ and the paramagnetic effective moment above $T_C$ also evidences some direct V-V bonding interactions.

**Variable temperature structural studies.** Structure refinements against NPD data showed that the monoclinic charge ordered structure persists down to 10 K. The monoclinic lattice parameters (Table S1) do not evidence any structural transition at $T_C$ = 164 K but a small anomaly in the $\beta$ angle may evidence a slight magnetostriction.

Synchrotron powder X-ray diffraction data collected from 300 up to 750 K show a change in peak splittings and intensities at 605 K (Figures 4 and S2), in agreement with the phase transition around 593 K reported previously [12]. Structure refinements revealed that the structure changes from monoclinic C2/c to tetragonal I4$_1$/amd at 605 K. Temperature variations of the refined lattice parameters are shown in Figure 5 using the pseudo-tetragonal setting of the monoclinic cell (monoclinic parameters are in Figure S1).

The high temperature tetragonal I4$_1$/amd structure has only one unique V site with an average V$^{2.5+}$ oxidation state. Hence the monoclinic to tetragonal structural transition corresponds to the long range charge ordering transition at $T_C$ = 605 K. This is confirmed by the thermal variations of interpolated BVS in Figure 6 where a critical variation in the difference in charge states is seen from ~500 K up to $T_C$. The monoclinic distortion angles $\alpha_T$ and $\gamma_T$ show a similar variation in Figure 5.

The pseudo-tetragonal cell lengths $\alpha_T$ and $c_T$ show a normal positive thermal expansion (PTE) throughout the monoclinic regime as shown in Figure 5. The transition from monoclinic to tetragonal phases appears to be continuous (or quasi-continuous) as no cell volume anomaly or phase coexistence is observed at $T_{CO}$. However $\alpha_T$ shows a dramatic change of slope to negative thermal expansion (NTE) above $T_{CO}$ and this leads to an overall NTE of the lattice volume. Thermal expansion coefficients defined as $\alpha_p = \Delta p/(\rho A T)$ for lattice parameters $p$ are plotted in the lower panel of Figure 5. $\alpha_T$ reaches $-13.3 \times 10^{-6}$ K$^{-1}$ at 750 K and has an average value of $-5.8 \times 10^{-6}$ K$^{-1}$ in the 620-750 K range, comparable to values in other NTE materials [3,24]. Additional datasets collected while cooling from 750 K confirm the reversibility of the structural transition and the PTE to NTE changeover (Figure S3).
switch from PTE to NTE at the 605 K charge ordering transition is driven by a switch in the thermal expansion behavior of the $a_T = b_T$ cell parameters, which correspond to the directions of face-sharing chains of VO$_6$ octahedra. Charge ordering is not in itself expected to drive such a change, but may do so if it also leads to changes in V-V bonding in the chains.

$\text{V}_3\text{OPO}_4$ is an insulating framework material so the NTE above $T_{CO}$ is likely to result from large-amplitude transverse vibrations or torsions, as found in many other framework materials [1]. An increase in amplitude of transverse vibrations of the face-bridging oxygens with temperature would decrease the V-O-V angle and shorten the V-V distance along the chain (shown schematically in the Abstract figure). Accurate oxygen temperature factors are not available from our present synchrotron X-ray refinements, and further neutron scattering experiments will be needed to evidence the expected changes in vibrational motion around the transition.

The change to PTE behavior of the $a_T$ parameter and hence lattice volume below $T_{CO}$ implies a change in bonding. Given the short metal-metal distances, this is most likely an onset of V-V bonding in the chains associated with the charge order. The observed ferrimagnetic order below $T_C = 164$ K is consistent with such bonding through pairing of opposing spin $t_{2g}$ electrons on neighboring V$^{3+}$ and V$^{5+}$ cations. Local ferrimagnetic correlations above $T_C$ are evidenced by the large constant contribution $\chi_0$ to the magnetic susceptibility, and these may be associated with V-V bonding that persists up to $T_{CO}$ and is gradually lost on heating through the critical region above $T_{CO}$ as local charge ordering correlations diminish. V-V distances within the chains remain uniform below $T_{CO}$ so the V atoms form an orbital polymer chain rather than discrete orbital molecules such as the dimers observed in VO$_3$ [21]. Hence the switch from PTE to NTE on warming through the 605 K charge ordering transition is likely due to loss of V-V bonding that enable transverse oxygen motions to dominate the thermal expansion.

Resistivity measurements. The high temperature resistivity (Figure 7) displays a change of slope near 600 K, coinciding with the structural transition at $T_{CO}$. $\text{V}_3\text{OPO}_4$ is semiconducting below and above the transition, and Arhenius fits in the 350-450 K and 620-870 K regions give activation energies of 300 and 400 meV respectively. This demonstrates that loss of long charge ordering does not lead to metallization, but instead $T_{CO}$ marks an order to disorder transition of localized V$^{3+}$ and V$^{5+}$ states.

Figure 4. Temperature evolution of a section of the synchrotron X-ray diffraction intensities showing the monoclinic to tetragonal transition at 605 K.

Figure 5. Pseudo-tetragonal unit cell parameters through the C2/c to I4$_1$/amd transition at 605 K from NPD (circle symbols) and XRD (diamond symbols) and thermal expansion coefficients calculated for the pseudo-tetragonal cell.

Figure 6. Interpolated Bond Valence Sums for the vanadium cations showing the charge ordering transition.
We also attempted to measure the low temperature resistivity of \( \text{V}_2\text{OPO}_4 \) below room temperature, but the sample resistance was too large to be measured accurately below 205 K. The fitted activation energy between 218 and 300 K of 310 meV, is in good agreement with the value obtained in the 350-450 K region of the charge ordered regime.

**Electronic Structure Calculations.** Due to the inherent problems associated with calculating paramagnetic states in strongly-correlated materials using standard DFT methods, magnetically ordered calculations were performed for both the monoclinic and tetragonal models, using the experimental unit cells. An on-site Coulomb repulsion term \( U = 3.5 \text{ eV} \), comparable to values used for \( \text{V}_2\text{O}_3 \) which also contains face-sharing \( \text{VO}_6 \) octahedra [25,26], was used to treat the correlation of V(d) states in calculating the density of states in Figure 8. The experimentally observed monoclinic magnetic model is found to be lowest in energy. The calculated thermal band gap energy of 420 meV is comparable to the above experimental values of 300-310 meV. Projected magnetic moments (from Mulliken analysis [27,28,29]) are 3.04 \( \mu_B \) and -2.07 \( \mu_B \) for \( \text{V}_1 \) (\( \text{V}^{2+} \)) and \( \text{V}_2 \) (\( \text{V}^{3+} \)), respectively, and calculated d-orbital populations are 3.48 and 3.19. The large difference between spin and charge suggests some degree of spin polarized charge transfer between \( \text{V}_1 \) and \( \text{V}_2 \) of the majority spin component.

![Image](image_url)

**Figure 7.** High temperature resistivity showing a change of slope at \( T_{CO} = 605 \text{ K} \).

For the tetragonal model, calculations were less stable, and different magnetic states had more similar energies. The observed (low temperature) magnetic structure gives a semivalent ground state with a small density of states at the fermi level (Figures 8 and S4). Hence, the calculations predict the lowest energy ground states to be the observed charge-ordered model in the monoclinic structure with ferrimagnetic spin order, but a semivalent metallic state is favored for the tetragonal case (Table S2). This does not agree with the observation of a semiconductivity above \( T_{CO} \), but the discrepancy is understandable as the DFT calculation does not allow for the possibility of a localized but disordered \( \text{V}^{2+}/\text{V}^{3+} \) charge state, or for paramagnetism as noted before.

![Image](image_url)

**Figure 8.** Partial density of states for vanadium d and oxygen p states near Fermi level (\( E_F \)) for the charge-order monoclinic and the semi-valent tetragonal phases.

The valence band of the monoclinic phase is dominated by almost dispersionless vanadium d-states (Figure S5). Figure 9a shows a cut through the real-space electron density of the highest occupied band (HOMO), as a weighted sum across reciprocal space. Ideally this corresponds to the majority spin \( t_{2g} \) states of the \( \text{V}_1 \) (\( \text{V}^{2+} \)) sites, but some valence electron transfer to the \( \text{V}_2 \) site is evident. In contrast, the equivalent band representation for the tetragonal semivalent ground state (Figure 9b) shows no electron transfer between V-sites. This supports the above proposal that weak V-V bonding results from the charge ordering in the monoclinic phase, and drives the change from NTE to PTE behavior on cooling below \( T_{CO} \).

![Image](image_url)

**Figure 9.** Electron density sections through the highest occupied (HOMO) bands shown on a linear density scale in the 0 - 0.08 electrons.Å\(^3\) range. The slice is taken through the (20T) plane of the primitive cell (equivalent to monoclinic (22T) and tetragonal (200) planes) and contains a V chain and the interchain bridging oxygen O2. (a) Monoclinic charge-ordered structure showing transfer of charge density from \( \text{V}_1 \) (\( \text{V}^{2+} \)) to \( \text{V}_2 \) (\( \text{V}^{3+} \)) sites. (b) Tetragonal semivalent band structure showing no V-V charge transfer. \( \text{V}_1 \) and \( \text{V}_2 \) labels are for comparison purposes, and correspond to crystallographically identical sites in the tetragonal phase.

**CONCLUSION**

This study has characterized changes of electronic, magnetic, and lattice properties of \( \text{V}_2\text{OPO}_4 \) at two transitions. Long range \( \text{V}^{2+}/\text{V}^{3+} \) charge ordering is observed up to \( T_{CO} = 605 \text{ K} \).
where a monoclinic to tetragonal structural transition and a switch from positive to negative thermal expansion are observed. V-V bonding within orbital polymer chains is proposed as the key factor in the novel switch of thermal expansion behavior, and is consistent with band structure calculations. Ferrimagnetic order of V$^{3+}$ spin up and V$^{4+}$ (3d$^3$) spin down states is observed below $T_c = 164$ K, and magnetic susceptibility measurements evidence local spin pairing correlations to higher temperatures. Hence, the combination of active charge, orbital and spin degrees of freedom in V$_2$OPO$_4$ is shown to give rise to low temperature ferrimagnetism and a new mechanism for switching between positive and negative volume expansion.

ASSOCIATED CONTENT

Supporting Information. Further structural results, electronic structure calculation results, and irreducible representations for V spins in the magnetically ordered structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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