V 3d charge and orbital states in V$_2$OPO$_4$ probed by x-ray absorption spectroscopy

Kota Murota,$^1$ Elise Pachoud,$^2$ J. Paul Attfield,$^2$ Robert Glaum,$^3$
Ronny Sutarto,$^4$ Kou Takubo,$^5$ Daniel I. Khomskii,$^6$ and Takashi Mizokawa$^1$

$^1$Department of Applied Physics, Waseda University, Shinjuku, Tokyo 169-8555, Japan

$^2$Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Edinburgh EH9 3FD, United Kingdom

$^3$Institut für Anorganische Chemie, Universität Bonn, D-53012 Bonn, Germany

$^4$Canadian Light Source, Saskatoon, Saskatchewan S7N 0X4, Canada

$^5$Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan

$^6$II Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany

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Abstract

V 3d charge and orbital states in V$_2$OPO$_4$ have been investigated by means of x-ray absorption spectroscopy (XAS). The electronic structure of V$_2$OPO$_4$ is very unique in that the charge transfer between V$^{2+}$ and V$^{3+}$ in face sharing VO$_6$ chains provides negative thermal expansion as reported by Pachoud et al. [J. Am. Chem. Soc. 140, 636 (2018).] The near edge region of O 1s XAS exhibits the three features which can be assigned to transitions to O 2p mixed into the unoccupied V 3d $t_{2g}$ and $e_g$ orbitals of V$^{2+}$ and V$^{3+}$. The V 2p XAS line shape can be reproduced by multiplet calculations for a mixed valence state with V$^{2+}$ and V$^{3+}$. The polarization dependence of the O 1s and V 2p XAS spectra indicates V 3d orbital order in which $xy$ and $zx$ (or $yz$) orbitals are occupied at the V$^{3+}$ site in the face sharing chains. The occupied $xy$ orbital is essential for the antiferromagnetic coupling between the V$^{2+}$ and V$^{3+}$ sites along the chains while the occupied $zx$ (or $yz$) orbital provides the antiferromagnetic coupling between the V$^{2+}$ and V$^{3+}$ sites between the chains.
I. INTRODUCTION

Transition-metal compounds have been attracting great interest due to their rich lattice and electronic properties which are derived from the transition-metal $d$ and ligand $p$ orbitals [1, 2]. The interplay between the lattice and electronic properties provides an exotic phenomenon known as negative thermal expansion (NTE) through rigid bond formation, magnetoelastic effect, and charge transfer effect [3–6]. The charge transfer mechanism for NTE is characterized by a dramatic valence change of transition metals. For example, BiNiO$_3$ exhibits a valence transition from insulating Bi$^{3+}$Bi$_{0.5}$Ni$_{0.5}$O$_3$ to metallic Bi$^{3+}$Ni$^{3+}$O$_3$ under high pressure [7–9]. La substitution for Bi suppresses the insulating state, and the moderate NTE is realized at ambient pressure in Bi$_{1-x}$La$_x$NiO$_3$ [10–12].

Very recently, Pachoud et al. have reported NTE in V$_2$OPO$_4$ which is driven by charge transfer between V$^{2+}$ and V$^{3+}$ sites [13]. V$_2$OPO$_4$ consists of face and corner sharing VO$_6$ octahedra as shown in Fig. 1. Below 605 K, the V$^{2+}$/V$^{3+}$ charge ordering is accompanied by monoclinic lattice distortion [13]. The face sharing V$^{2+}$ and V$^{3+}$ sites form chains along the [110] or [110] direction of the monoclinic lattice as indicated by the dashed lines in Fig. 1. The corner sharing V$^{3+}$ sites are connected approximately along the [001] direction. The VO$_6$ octahedra in the [110] chains are tilted relative to those in the [110] chains. In Fig. 1, the $x$, $y$, and $z$ axes are along the V-O bonds of the V$^{3+}$ site in the [110] chain while the $x'$, $y'$, and $z'$ axes are along the V-O bonds of the V$^{3+}$ site in the [110] chain. The V$^{2+}$/V$^{3+}$ spins are ferrimagnetically ordered below 165 K. The V$^{2+}$ and V$^{3+}$ spins are antiferromagnetically coupled along the face sharing bond and the V$^{3+}$ spins are ferromagnetically coupled along the corner sharing bond [13]. Above 165 K, the magnetic susceptibility shows a paramagnetic moment of 1.61 $\mu_B$ per V$_2$OPO$_4$ unit, which is greatly reduced from the ideal value for V$^{2+}$ and V$^{3+}$ spins [13]. Above 605 K, the charge ordering disappears and all the V sites become V$^{2.5+}$ in tetragonal lattice structure. Since tetragonal phase with V$^{2.5+}$ has smaller volume than the monoclinic phase with V$^{2+}$ and V$^{3+}$, NTE is realized around 605 K [13]. The NTE in V$_2$OPO$_4$ is seen at relatively high temperature compared to Bi$_{1-x}$La$_x$NiO$_3$. As for the mechanism of the charge transfer transition, the availability of single crystals enables to study role of V $3d$ orbital ordering. Soft x-ray absorption spectroscopy is a powerful technique to study valence and orbital states of V. In the present work, we study V $3d$ orbital states by means of polarization dependent x-ray absorption measurement and cluster model analysis.
II. METHODS

X-ray absorption spectroscopy (XAS) measurement was performed at the REIXS beamline of the Canadian Light Source [15]. The incident soft x-ray is linearly polarized. XAS spectra were taken in the total electron yield (TEY) mode and total fluorescence yield (TFY) mode. The single crystal was mounted in such a way that polarization vectors of the incident soft x-ray are along the [001] axis for the horizontal polarization and along the [221] axis for the vertical polarization.

The XAS spectra can be analyzed by the VO$_6$ cluster model calculations. In the present analysis, the O 2p to V 3d charge transfer process is neglected since the charge transfer energy is around 5 eV or larger in V$^{2+}$ and V$^{3+}$ oxides. In the present cluster model, the ligand field splitting between e$_g$ and t$_{2g}$ level is fixed to 1.6 eV. The Coulomb interaction between the V 3d electrons are given by the Slater integrals $F^2(3d, 3d)$, and $F^4(3d, 3d)$ which can be translated into Racah parameters $B$ and $C$. In the present analysis, $B$ and $C$ are set to 0.117 eV and 0.438 eV [16, 17]. The Coulomb interaction between the V 2p core hole and the V 3d electron is expressed by the Slater integrals $F^2(2p, 3d)$ and $G^1(2p, 3d)$ which are fixed to 3.51 eV and 2.00 eV, respectively (about 80% of the atomic Hartree-Fock values) [18].

III. RESULTS AND DISCUSSION

Figure 2 shows O 1s XAS spectra taken with polarization vector along [001] direction (dashed curves) and with that along [221] direction (solid curves) at various temperatures well below the structural transition temperature at 605 K. The spectra are normalized with respect to intensities at 529 eV and 558 eV. The near edge region from 530 to 535 eV corresponds to the excitations from O 1s to O 2p mixed into unoccupied V 3d levels. In case of LiVO$_2$ with octahedrally coordinated V$^{3+}$ ($t^2_{2g\uparrow}$), the transition to $t^3_{2g\uparrow}$ and those to $t^2_{2g\uparrow}e_{g\uparrow}$, $t^2_{2g\uparrow}t_{2g\downarrow}$, and $t^2_{2g\uparrow}e_{g\downarrow}$ are located around 530 eV and 532 eV respectively [19]. In the O 1s XAS spectra of V$_2$OPO$_4$, the broad and weak peak at 531 eV corresponds to the transition to $t^3_{2g\uparrow}$ at V$^{3+}$. The peaks at 533 eV and 534 eV can be assigned to the transitions to $t^2_{2g\uparrow}e_{g\uparrow}$, $t^2_{2g\uparrow}t_{2g\downarrow}$, and $t^2_{2g\uparrow}e_{g\downarrow}$ at V$^{3+}$ and the transitions from $t^3_{2g\uparrow}$ to $t^3_{2g\uparrow}e_{g\uparrow}$, $t^3_{2g\uparrow}t_{2g\downarrow}$, and $t^3_{2g\uparrow}e_{g\downarrow}$ at V$^{2+}$.3
The peak at 531 eV is enhanced with the polarization vector along the [001] axis. This polarization dependence of the 531 eV peak is more clearly seen in the bulk sensitive TFY spectra and indicates that the unoccupied $t_{2g}$ orbital at $V^{3+}$ is mainly mixed with O 2p$_z$ orbitals along the [001] axis. Therefore, the unoccupied $t_{2g}$ orbital in the $V^{3+}(t_{2g})$ site has either $yz$ or $zx$ symmetry in which the $z$ axis is slightly tilted from the [001] direction and the $x$ axis is approximately along the [201] direction for the $V^{3+}$ octahedra in the [110] chains as indicated in Fig. 1(a). As for the other half of $V^{3+}$ octahedra in the [110] chains, the $z'$ axis is tilted in the other direction from the [001] direction as shown in Fig. 1(a). Although the polarization dependence of the O 1s XAS spectra should be the average of the two kinds of $V^{3+}$ octahedra, it is still roughly consistent with the unoccupied $yz$ or $zx$ ($y'z'$ or $z'x'$) orbital. Indeed, the VO$_6$ octahedron for the $V^{3+}$ site is compressed along the $z$ or $z'$ direction [13], and therefore, the $xy$ ($x'y'$) orbital is stabilized by the ligand field. (The V-O bond length along the $z(z')$ direction is $\sim 1.98 \text{ Å}$ and those along the $x(x')$ and $y(y')$ directions are $\sim 2.09 \text{ Å}$ and 2.05 Å [13].) In addition to the polarization dependence of the 531 eV peak due to the $t_{2g}$ orbital ordering, the peaks at 533 eV and 534 eV also depend on the polarization probably due to the anisotropic hybridization between V 3d and O 2p orbitals by the distortion of the VO$_6$ octahedra. The temperature dependence of the O 1s spectra is rather small indicating the V 3d electronic state is not affected by the magnetic transition at 165 K.

Figure 3 shows V 2p XAS spectra taken with polarization vector along [001] direction (dashed curves) and with that along [221] direction (solid curves) at various temperatures well below the structural transition temperature of 605 K. The spectra are normalized with respect to intensities at 510 eV and 529 eV. The multiplet structure in the near edge region around 514 eV is derived from the $V^{3+}$ component [18]. The overall multiplet structure is rather similar to that of LiVO$_2$ [19] in the surface sensitive TEY spectra. However, the intensity around 523 eV is enhanced suggesting existence of V$^{2+}$. In order to demonstrate the mixed valence of V$^{2+}$ and V$^{3+}$, calculated V 2p spectra for V$^{2+}$ and V$^{3+}$ are mixed to reproduce the experimental results as shown in Fig. 4. The surface sensitive TEY spectra can be explained with $\sim 30\%$ contribution of V$^{2+}$ relative to V$^{3+}$ suggesting a mixed valence state. However, the amount of V$^{2+}$ is much smaller than that expected from the charge order in the bulk. Most probably, the V$^{3+}$ component is enhanced near the surface compared to the bulk value since the surface was exposed to the air. As for the bulk sensitive TFY
spectra, it is difficult to analyze the line shape quantitatively since it is affected by the self absorption effect and the saturation effect. However, as shown in Fig. 3, the intensities around 516 eV and 523 eV (corresponding to 6 eV and 13 eV in the calculation shown in Fig. 4) are enhanced in the TFY spectra compared to the TEY spectra, indicating that the V^{2+} component increases in the bulk sensitive TFY spectra compared to that in the surface sensitive TEY spectra.

In the near edge regions around 514 eV for 2p_{3/2} and around 521 eV for 2p_{1/2}, the V 2p spectral weight is slightly enhanced with polarization vector along the [221] direction. Since the near edge regions correspond to the transitions from V 2p to unoccupied V 3d t_{2g} at the V^{3+} site, the polarization dependence in the near edge regions includes information on the V 3d orbital order. In V_2O_3, Park et al. revealed that the intensity of the near edge regions is enhanced when the a_{1g} orbital along the c axis is unoccupied and the polarization vector is parallel to the c axis [20]. In case of Ti_2O_3, the intensity of the near edge regions is enhanced if the a_{1g} orbital along the c axis is occupied and the polarization vector is perpendicular to the c axis [21]. Here, the a_{1g} orbital is given by a linear combination of the xy, yz, and zy orbitals as \((xy + yz + zx)/\sqrt{3}\). Since the a_{1g} orbital does not change its sign under the rotation about the principal axis or the (111) axis, the relationship between the polarization and the intensity is rather simple.

In the present case of V_2OPO_4, the intensity of the near edge regions is enhanced when the polarization vector is roughly along the x or y axis. This could indicate that the xy orbital is unoccupied at the V^{3+} site. However, since the xy orbital changes its sign by the 90 degrees rotation about the z axis, the relationship between polarization dependence and orbital occupation is less clear than for the a_{1g} orbital. Figure 5 shows the calculated V 2p XAS spectra for the polarizations along the y and z axes for the unoccupied yz case and the unoccupied xy case. In the unoccupied yz orbital case, the near edge regions at 514 eV and 521 eV are slightly enhanced with the polarization vector along the y axis, which is consistent with the experimental result. As for the unoccupied xy orbital case, the near edge regions are completely suppressed with the polarization vector along the z axis inconsistent with the experimental result. The comparison between the experiment and the calculation supports the orbital order with the yz (or zx) orbital unoccupied. The occupied xy orbitals provide a kind of repulsive interaction to the V^{2+} and V^{3+} pairs which is removed by the charge transfer between them. Therefore, the present orbital ordering is consistent with the
In the V chains running along the [110] or [11̅0] directions, the V\(^{2+}\)O\(_6\) and V\(^{3+}\)O\(_6\) octa-
hedra share their faces. Focusing on the V chains along the [110] directions, the XAS results 
indicate that the V \(3d\ t_{2g}\ xy\) and \(zx\) orbitals are occupied at the V\(^{3+}\) site. Here, the \(x\), \(y\), 
and \(z\) axes are close to the [201], [021], and [001] directions of the monoclinic structure as 
shown in Fig. 1(a). (The \(z\) direction is tilted by about 20 degrees from the [001] direction.) 
Since the superexchange pathways for the \(xy\), \(yz\), and \(zx\) orbitals are all active in the face 
sharing V-O-V bond, the V\(^{3+}\) and V\(^{2+}\) sites should have the antiferromagnetic coupling in 
agreement with the neutron result \(^{13}\). This situation is different from the ferromagnetic 
coupling between the face sharing V\(^{3+}\) and V\(^{2+}\) in BaV\(_{10}\)O\(_{15}\) and related systems where the 
a\(_{1g}\) orbital is unoccupied at the V\(^{3+}\) site \(^{22–24}\).

For face sharing octahedra in the chains, it is often convenient to use a\(_{1g}\) and e\(_g^\pi\) trigonal 
orbitals. Their forms are given by \((xy - e^{2\pi ni/3}zx - e^{-2\pi ni/3}yz)/\sqrt{3}\), with \(n = 0\) for the a\(_{1g}\) 
state and \(n = \pm 1\) for two e\(_{g^\pi}\) orbitals (The a\(_{1g}\) orbital points to the (1,1,-1) direction of the 
VO\(_6\) octahedron for the case shown in Fig. 1) \(^2\). One can show that the electron hopping 
along chains are diagonal for these orbitals \(^{25}\), which immediately gives the dominant 
antiferromagnetic coupling along the chains if the same orbitals are occupied at each site.

However, the use of these orbitals is not convenient to treat interchain exchange. Besides 
that, as mentioned above, in V\(_2\)OPO\(_4\) there exists strong distortion of VO\(_6\) octahedra along the 
local \(z\) (or \(z'\)) directions. Therefore, it is more natural to use the local \(xy\), \(zx\) and \(yz\) 
orbitals that we use in this paper. The \(xy\) and \(zx\) orbitals are given by \((a_{1g} + e_{g^++} + e_{g^-})/\sqrt{3}\) 
and \(-(a_{1g} + e^{-2\pi i/3}e_{g^+} + e^{2\pi i/3}e_{g^-})/\sqrt{3}\). Therefore, in the electronic configuration with \(xy\) 
and \(zx\) occupied, the a\(_{1g}\), e\(_{g^+}\), and e\(_{g^-}\) orbitals are equally occupied. Since the a\(_{1g}\), e\(_{g^+}\), and 
e\(_{g^-}\) electrons at the V\(^{2+}\) site can be transferred to the a\(_{1g}\), e\(_{g^+}\), and e\(_{g^-}\) orbitals at the V\(^{3+}\) 
site, the superexchange interaction is antiferromagnetic.

In case of the V chains along the [1\(\overline{1}\)0] directions, the \(z'\) axis is close to the [001] direction 
and the polarization vector in the experiment. It can be assumed that the V \(3d\ t_{2g}\ x'y'\) 
and \(z'x'\) (or \(y'z'\)) orbitals are occupied at the V\(^{3+}\) site in the [1\(\overline{1}\)0] chains. As for the 
superexchange pathways between the V\(^{2+}\) site in the [110] chain and the V\(^{3+}\) site in the 
[1\(\overline{1}\)0] chain (the V-O-V bond angle is about 124 degrees), all the t\(_{2g}\) electrons of the V\(^{2+}\) 
site can be transferred to the \(x'y'\) and \(z'x'\) (or \(y'z'\)) orbitals at the V\(^{3+}\) site which are 
already occupied by electrons. Therefore, the superexchange interaction is expected to be
antiferromagnetic which is also consistent with the neutron result [13].

The superexchange pathways between the two $V^{3+}$ sites in the [110] and [1¯10] chains are mainly given by those between $yz$ and $y'z'$ orbitals (also $zx$ and $z'x'$ orbitals) since the V-O-V bond angle is about 132 degrees [see Fig. 1(a)]. If the $yz$ orbital is unoccupied in the chains running along [110] and the $z'x'$ orbital is unoccupied in the chains running along [1¯10], the two $V^{3+}$ sites along the (001) direction should be ferromagnetic due to the Kugel-Khomskii mechanism [26]. On the other hand, if the $yz$ orbital is unoccupied in the chains running along [110] and the $y'z'$ orbital is unoccupied in the chains running along [1¯10], the superexchange interaction would be antiferromagnetic. The ferromagnetic $V^{3+}$-$V^{3+}$ coupling is consistent with the neutron result [13]. Since the charge transfer from the $V^{2+}$ site to the $V^{3+}$ site costs smaller energy than the other charge transfer processes, the antiferromagnetic couplings between the $V^{2+}$ and $V^{3+}$ sites (both intrachain and interchain) are essential to determine the spin arrangement.

IV. CONCLUSION

In summary, the polarization dependence in near edge regions of O 1s and V 2p XAS spectra indicate that the $xy$ and $zx$ (or $yz$) orbitals are occupied in the $V^{3+}$ site. The V 3$d$ orbital order is consistent with the antiferromagnetic coupling between the face sharing $V^{2+}$ and $V^{3+}$ sites in the chains and the antiferromagnetic coupling between the corner sharing $V^{2+}$ and $V^{3+}$ sites between the chains. In future, the relationship between the orbital order and the negative thermal expansion should be investigated by theoretical calculations and experiments for higher temperature.

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FIG. 1: (a) Crystal structure of $\text{V}_2\text{OPO}_4$ created by VESTA [14]. The dashed lines indicate the face sharing VO$_6$ chains along [110] or [1¯10] directions. The $x$, $y$, and $z$ axes ($x'$, $y'$, and $z'$ axes) are along the V-O bonds of the V$^{3+}$ site in the [110] chain ([1¯10] chain). (b) Electronic configurations for V$^{2+}$ and V$^{3+}$. (c) Photograph of the V$_2$OPO$_4$ crystal and the directions of polarization vector.
FIG. 2: (a) Temperature and polarization dependence of O 1s XAS with TEY mode. (b) Temperature and polarization dependence of O 1s XAS with TFY mode.
FIG. 3:  (a) Temperature and polarization dependence of V 2p XAS with TEY mode.  (b) Temperature and polarization dependence of V 2p XAS with TFY mode.
FIG. 4: Cluster model calculation of V 2p XAS for a mixed valence state of $V^{2+}: V^{3+} = 3:10$. The calculated spectrum is compared with the experimental result taken at 200 K with TEY mode.
FIG. 5: Polarization dependence of the calculated V 2p XAS spectra for V$^{3+}$ with different orbital orders. For the orbital order with V 3d $yz$ unoccupied, polarization dependence of the $t_{2g\uparrow}$ final state is moderate. On the other hand, the orbital order with V 3d $xy$ unoccupied is expected to have strong polarization dependence.