

## Experimental determination of electron states with orbital degrees of freedom

The orbital degree of freedom plays an important role in strongly correlated materials. Several direct observation methods of electron orbitals have been proposed, but they usually focus on the orbital ordered or stable state, and there are few reports on the observation of the degenerate orbitals. Even first-principles calculations cannot easily determine metastable states at finite temperatures. Therefore, the electron state in degenerate orbitals is only vaguely understood.

Recently, our group has proposed the core differential Fourier synthesis (CDFS) method [1]. It allows the direct observation of the 3D distribution of the valence electron density (VED) by synchrotron X-ray diffraction (XRD). It has been successfully applied to determine the electron density in the orbital ordered state and reported in the Research Frontiers 2020. In the work discussed here [2], we used it to determine the electron state with orbital degrees of freedom through the VED distribution.

We investigated the orbital state of vanadium spinel oxide  $\text{FeV}_2\text{O}_4$ . In this system, despite the lack of charge degrees of freedom due to the Mott insulator, both electronic correlations and geometric frustration are present, resulting in an interplay between the different degrees of freedom, such as spin, orbital, and lattice, which leads to three successive phase transitions with decreasing temperature [3]. Although there has been much discussion on the origin of the phase transition, mainly focusing on the orbital ordered state of V, there are few reports of the definitive determination of the electronic state of the high-symmetry cubic phase.

In  $\text{FeV}_2\text{O}_4$ , because the formal charges of Fe and V are +2 and +3, the electron configurations are  $3d^6$  and  $3d^2$ , respectively. The space group of the cubic phase is  $Fd\bar{3}m$ , and because  $\text{FeO}_4$  is a regular tetrahedron, the electron configuration of  $\text{Fe}^{2+}$  is  $e^3t_2^3$ . Owing to the high-spin configuration, one electron on the  $e$  orbital is responsible for the orbital degree of freedom (Fig. 1(b)). By contrast, the octahedral site of  $\text{VO}_6$  has inversion symmetry, and the  $3d$  orbitals of  $\text{V}^{3+}$  are divided into lower triply degenerate  $t_{2g}$  orbitals and higher doubly degenerate  $e_g$  orbitals. If  $\text{VO}_6$  forms a regular octahedron ( $O_h$ ), then  $3d^2$  electrons occupy  $t_{2g}$  in a high-spin configuration (Fig. 1(b)), and  $\text{V}^{3+}$  has spin and orbital degrees of freedom. Therefore, the  $\text{FeV}_2\text{O}_4$  system in the cubic phase has spin and orbital degrees of freedom at both the  $\text{Fe}^{2+}$  and  $\text{V}^{3+}$  sites. However, the  $3d$  state is complicated because of a slight  $D_{3d}$  distortion in the  $\text{VO}_6$  octahedron.

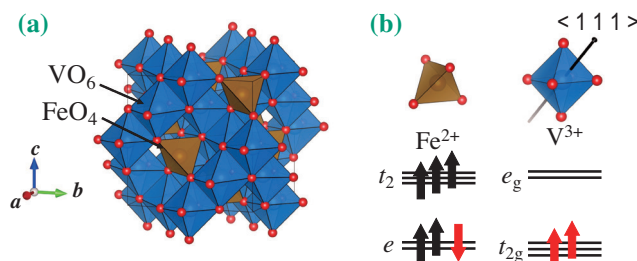


Fig. 1. (a) Crystal structure of  $\text{FeV}_2\text{O}_4$  in the cubic phase. (b) Orbital states of V and Fe in the cubic phase. The black arrow in  $\text{VO}_6$  indicates the  $\langle 111 \rangle$  direction.

The triply degenerate  $t_{2g}$  orbitals are further split into one orbital ( $\varphi_1$ ) and degenerate orbitals ( $\varphi_2$  and  $\varphi_3$ ) by the crystal field formed by the surrounding oxygen. However, it is not clear which energy level is higher,  $\varphi_1$  or degenerate orbitals. It is important to note that the triple degeneracy of the  $t_{2g}$  orbitals is maintained when the effect of the  $D_{3d}$ -type strain is very weak compared with that of the thermal fluctuation. Therefore, we attempted to determine the correct orbital state from the 3D distribution of VED obtained by the CDFS method.

XRD experiments were performed using single crystals at SPing-8 BL02B1. Figure 2(d) shows the observed VED around the V ( $1/2$   $1/2$   $1/2$ ) site at 160 K. The VED around the V site is clearly anisotropic. This VED directly reflects the anisotropy of the  $3d^2$  electrons.

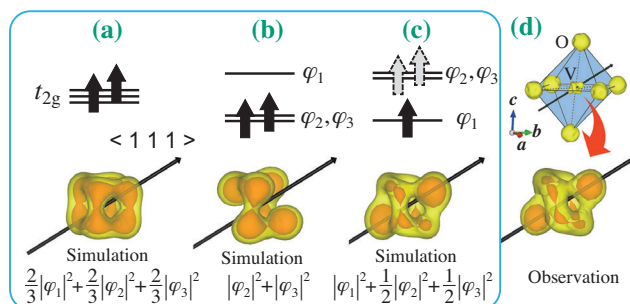


Fig. 2. (a–c) Assumed electron configurations and simulated VEDs of V site. The red part of the VED highlights the characteristic components. The gray dotted arrows in (c) indicate that one electron on double degenerate orbitals occupies both orbitals with equal probability. (d) (upper panel) Observed VED of  $\text{VO}_6$  octahedron with internal coordinates  $(1/2$   $1/2$   $1/2)$  (isosurface level  $4.5e/\text{\AA}^3$ ). The solid line indicates the octahedron and the dotted line indicates the V–O bonds. (lower panel) Observed VED at V site (isosurface level  $4.5e/\text{\AA}^3$  (yellow) and  $5.3e/\text{\AA}^3$  (orange)).

First, we assumed three orbital states as mentioned above, but the VEDs simulated simply from these states did not reproduce the observed one well (Figs. 2(a,b)). However, we found another possible orbital state where  $\varphi_1$  was stabilized. In general, the energy gap of the  $t_{2g}$  orbitals due to the  $D_{3d}$  distortion is small, and Hund's rules are considered. In this case, one electron occupied the lower  $\varphi_1$  and the other one was lifted to the degenerate orbitals. The simulation  $|\varphi_1|^2 + \frac{1}{2}|\varphi_2|^2 + \frac{1}{2}|\varphi_3|^2$  resulted in the VED distribution shown in Fig. 2(c), which perfectly reproduced the experimental result. It is noted that we also succeeded in determining the orbital state at the Fe site. VED analysis by the CDFS method revealed that the degenerate orbitals reflect the anisotropy of their constituent orbitals in the cubic phase.

Here, we reconsider the degenerate orbital. We find that the wavefunctions can also be represented with an arbitrary value of phase  $\theta$  as

$$\begin{cases} \varphi'_2(\mathbf{r}) = \varphi_2(\mathbf{r}) \cos \theta(\mathbf{r}, t) + \varphi_3(\mathbf{r}) \sin \theta(\mathbf{r}, t) \\ \varphi'_3(\mathbf{r}) = -\varphi_2(\mathbf{r}) \sin \theta(\mathbf{r}, t) + \varphi_3(\mathbf{r}) \cos \theta(\mathbf{r}, t) \end{cases}$$

Orbital degrees of freedom mean that  $\theta$  fluctuates in space and time. However, from the diffraction data, it is not clear that  $\theta$  fluctuates in space and time because the VED obtained by XRD measurements is both space- and time-averaged. In fact, assuming

an orbital glass state with  $\theta$  distributed in the whole crystal only spatially, the experimental results can also be reproduced from the  $\theta$  spatial average.

$$\begin{aligned} \frac{1}{2\pi} \int_0^{2\pi} (|\varphi_1|^2 + |\varphi_2 \cos \theta + \varphi_3 \sin \theta|^2) d\theta \\ = |\varphi_1|^2 + \frac{1}{2} |\varphi_2|^2 + \frac{1}{2} |\varphi_3|^2 \end{aligned}$$

Therefore, we investigated the dynamics of  $\text{FeV}_2\text{O}_4$  through phonons to confirm that  $\theta$  fluctuates in space and time. If  $\theta$  fluctuates in time, we expect that electron-phonon coupling will allow the electron orbital fluctuations to affect the phonon behavior. In particular, phonon softening might be observed toward the phase transition where orbital fluctuations are eliminated. Therefore, we performed inelastic X-ray scattering (IXS) at SPing-8 BL43LXU. The softening of the transverse acoustic (TA) mode dispersing along the  $[110]$  and polarized along  $[-110]$  was clearly observed, as shown in Fig. 3. The symmetry of this TA mode is  $E_g$ , which means  $\theta$  fluctuations. Also, as shown in the dispersion diagram of the  $E_g$  TA mode in Fig. 3(c), the softening of the  $E_g$  TA mode was observed up to  $q \sim 0.7$  r.l.u. This softening is different from the usual precursor phenomenon of structural phase transitions but resembles the nematic state of iron-based superconductors, in which orbital degrees of freedom play an important role [4].

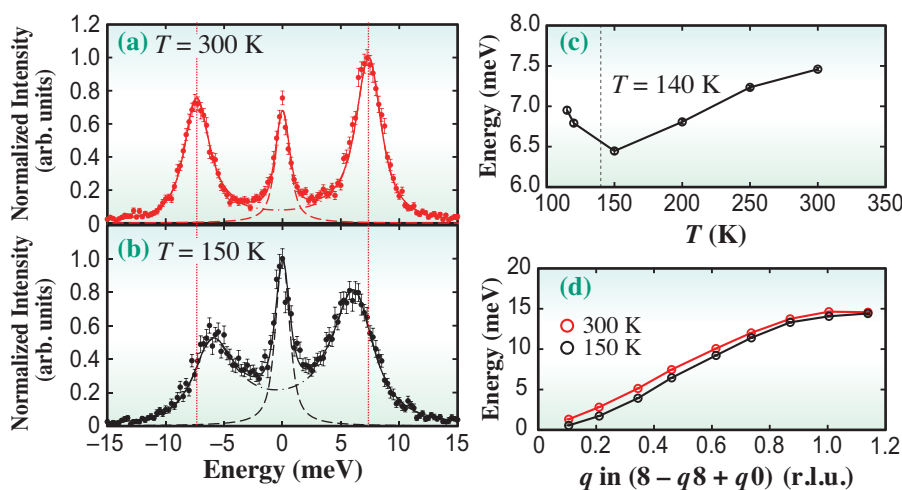


Fig. 3. Energy scan data at  $Q = (7.54 \ 8.45 \ -0.03)$  at (a) 300 K and (b) 150 K. Phonon peaks correspond to the  $E_g$  TA mode. Solid lines indicate the results of fitting using two lines, corresponding to an elastic peak (dashed line) and a pair of phonon peaks (dash-dotted line). The vertical dotted line indicates the phonon energy at 300 K. (c) Temperature dependence of the phonon energy at  $Q = (7.54 \ 8.45 \ -0.03)$ . (d) Phonon dispersions of the  $E_g$  TA mode at 300 K and 150 K.

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