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Do electron distributions with orbital degree of freedom exhibit anisotropy?[†]

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Orbital degrees of freedom appear in partially filled degenerate orbitals and are responsible for a variety of physical properties. Although many methods for directly observing orbital states in ordered states have been proposed, it is difficult to determine degenerate orbital states directly. We found that high-precision diffraction data obtained by synchrotron radiation X-rays can be used to observe only the valence electron density distribution with minimal analytical bias. The results obtained using this method clearly showed the anisotropy of the partially filled degenerate 3d orbital states in spinel vanadium oxide FeV₂O₄. The 3d orbital quantum state was successfully determined from this anisotropy.

Introduction

The interplay of charge, spin, orbital, and lattice degrees of freedom driven by electron correlation is a unifying principle across a wide range of transition metal systems.^{1–5} Such a picture provides a framework for determining whether one-electron physics is inadequate in a particular situation. The orbital degree of freedom in partially filled d-electron orbitals and related aspects such as orbital order, orbital waves, specific magnetic properties, and insulator–metal transitions has aroused considerable interest. Therefore, several methods have been proposed to observe orbital states, such as high harmonics generated from femtosecond laser pulses,⁶ ultraviolet angle-resolved photoelectron spectroscopy,⁷ resonant X-ray scattering,⁸ and non-resonant inelastic synchrotron X-ray

scattering.⁹ Despite the need to observe the orbital degrees of freedom, these experimental methods only allow for determining the orbital ordered or stable state. Even first-principles calculations cannot easily determine metastable states at finite temperatures. Orbital degrees of freedom are realized when degenerate orbitals are partially filled, but since there are few reports of their observation, the electron distribution in degenerate orbitals is only vaguely understood. In the high-temperature region, the anisotropy of degenerate orbitals is expected to be suppressed due to thermal fluctuations caused by the surrounding atoms and crystal field. The anisotropy of two or more degenerate orbitals would still not be uniquely determined, since orbitals with different symmetries are hybridized by quantum mechanical interference. Therefore, it has been widely believed that the degeneracy of localized orbitals blurs anisotropic electronic distributions. However, this physical prediction is yet to be confirmed.

We aimed to observe the valence electron density (VED) distribution to determine the orbital state. Our proposed core differential Fourier synthesis (CDFS) method^{10,11} allows us to directly observe the 3D distribution of the VED by synchrotron X-ray diffraction (XRD). This method calculates the VED; $\rho_v(\mathbf{r})$ in the unit cell by subtracting the structure factor calculated using only the core-shell electrons from the experimental structure factor by the XRD, and then inverse Fourier transforming this difference structure factor as shown in eqn (1). The CDFS is an innovative method that exploits a blind spot in the analysis of diffraction data by minimizing the effect of censoring of the inverse Fourier transform with finite coefficients, which is usually a problem (Fig. S1, ESI[†]). In eqn (1), \mathbf{K} is the scattering vector. $F_{\text{obs}}(|\mathbf{K}|)$ is the absolute value of the experimentally observed crystal structure factor. f_j^{core} is the j th atomic scattering factor with only the core electrons

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contribution. There are several publicly available databases of atomic scattering factors f^{core} for these core-shell electrons. T_j is the j th atomic displacement parameter. P and P^{core} represent the phase factor. P^{core} is with only the core electrons contribution calculated as $P^{\text{core}} = F_{\text{cal}}^{\text{core}}(K)/|F_{\text{cal}}^{\text{core}}(K)|$. n_v is the total number of valence electrons contained in the unit cell. Since $|F(000)|$ is not experimentally observable, we add the n_v/V term to correct the VED distribution data.

$$\rho_v(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}} \left[\left(|F_{\text{obs}}(\mathbf{K})| P - \left| \sum_j f_j^{\text{core}}(\mathbf{K}) T_j e^{-i\mathbf{K}\cdot\mathbf{r}_j} \right| P^{\text{core}} \right) e^{i\mathbf{K}\cdot\mathbf{r}_j} \right] + \frac{n_v}{V} \quad (1)$$

Based on our experience of the endohedral proof of $\text{H}_2@$ ATOCF (open-cage C_{60})¹² and $\text{Li}^+@$ C_{60} ,¹³ the thin VED analysis requires high-brightness synchrotron XRD data. However, the most noteworthy aspect of this method is that the VED analysis can be performed simply by using diffraction data measured with appropriate short-wavelength X-rays, and no assumptions, such as a model of valence electrons, are required.

The configuration of the partially occupied d orbitals leads to peculiar magnetic and electronic transitions, such as the Verwey transition of Fe_3O_4 .¹⁴ In this study, we focus on the orbital state of vanadium spinel oxide FeV_2O_4 , which has an isomorphous structure as magnetite, in the high-temperature phase. 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.^{15–24} FeV_2O_4 has been widely studied from both experimental and theoretical perspectives; however, owing to the intertwining of the multiple degrees of freedom, it is difficult to understand the orbital state completely. AV_2O_4 with other cations at the Fe site has been studied to avoid multiple degrees of freedom. For example, nonmagnetic A-site ($A = \text{Mg}$,²⁵ Zn ,²⁶ Cd ²⁷) and magnetic but orbitally inactive A-site ($A = \text{Mn}$,²⁸ Co ²⁹) have been studied. The role of Fe was also studied in the isomorphous material FeCr_2O_4 .³⁰ By integrating these studies, the crystal structure of FeV_2O_4 is predicted to change from cubic to tetragonal ($a > c$) at 140 K due to Fe orbital ordering, to orthorhombic at 110 K due to Fe-spin-orbital interaction, and to tetragonal ($a < c$) at 65 K due to V orbital ordering. Although there has been considerable discussion on the origin of the phase transition, mainly focusing on the orbital ordered state of V, there are few reports that have definitively determined the electronic state of the high-symmetry cubic phase.

In FeV_2O_4 , because the formal charges of Fe and V are +2 and +3, the electron configurations are $3d^6$ and $3d^2$, respectively. The $S = 2$ spin at the Fe site and the $S = 1$ spin at the V site is determined by the magnetization experiment.¹⁶ The unit cell consists of a 3D structure of 8 FeO_4 tetrahedra and 16 VO_6 octahedra (Fig. 1A). This system has three structural phase transitions with decreasing temperature, but there is only one

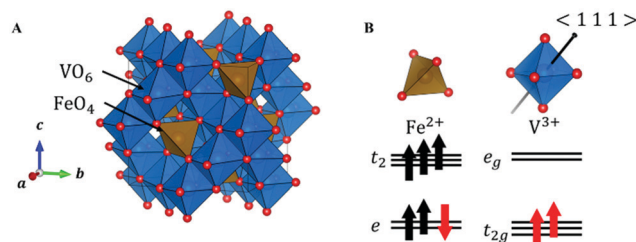


Fig. 1 (A) Crystal structure of FeV_2O_4 in the cubic phase. (B) The orbital states of V and Fe in the cubic phase. The black arrow in VO_6 indicates the $\langle 111 \rangle$ direction.

crystallographically independent site each for Fe, V, and O in all phases. In the cubic phase of the space group $Fd\bar{3}m$, because FeO_4 is a regular tetrahedron, the 3d orbitals of Fe^{2+} split into lower doubly degenerate e orbitals and higher triply degenerate t_2 orbitals. Owing to the high-spin configuration, five electrons with an up-spin form the half-closed shell configuration, and one “down-spin electron” on the e orbital is responsible for the orbital degree of freedom (Fig. 1B). Therefore, Fe^{2+} has both spin and orbital degrees of freedom. In contrast, the octahedral site of VO_6 has inversion symmetry, and the 3d orbitals of V^{3+} are divided into lower triply degenerate t_{2g} orbitals and higher doubly degenerate e_g orbitals. If VO_6 forms a regular octahedron (O_h), then $3d^2$ electrons occupy triple degenerate t_{2g} orbitals in a high-spin configuration (Fig. 1B), and V^{3+} has spin and orbital degrees of freedom. However, the 3d state is complicated because of a slight D_{3d} distortion in the VO_6 octahedron. Therefore, the FeV_2O_4 system has spin and orbital degrees of freedom at both the Fe^{2+} and V^{3+} sites.

The VO_6 octahedron has a D_{3d} -type distortion that satisfies the $\bar{3}m$ site symmetry at the V site. The triply degenerate t_{2g} orbitals are further split into one orbital and two degenerate orbitals by the crystal field formed by the surrounding anions. One orbital wave function is uniquely described by the following formula because the $\langle 111 \rangle$ direction is the quantum axis.

$$\varphi_1(\mathbf{r}) = \frac{1}{\sqrt{3}}(|yz\rangle + |zx\rangle + |xy\rangle) \quad (2)$$

In this formula, x , y , and z are determined to be parallel to lattice vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} , respectively. In contrast, the two wavefunctions of doubly degenerate orbitals of t_{2g} are not uniquely described. When these two orbital wavefunctions are denoted by φ_2 and φ_3 , three wave functions, φ_1 , φ_2 and φ_3 , in t_{2g} have to be orthogonal to each other. Determining the energy level of the post-split orbital is difficult because of the small D_{3d} -type distortion. There are no charge degrees of freedom and the volume of the VO_6 octahedron is conserved. In the case of FeV_2O_4 in the cubic phase, the octahedron of VO_6 extends in the $\langle 111 \rangle$ direction, and the area of the oxygen triangular surface perpendicular to the quantum axis is smaller than that of the regular octahedron. When calculating the V^{3+} - $3d^2$ orbital state using the Q -mode analysis,³¹ the t_{2g} orbitals split into lower doubly degenerate orbitals and higher φ_1 orbital. In contrast, when calculating the V^{3+} - $3d^2$ orbital state using a



point-charge model with the Ewald method³² (for details of the calculation method, see ref. (10)), the t_{2g} orbitals split into the lower φ_1 orbital and higher doubly 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 considerably weaker than 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.

Crystal structure and results of CDFS method

XRD experiments were performed using single crystals on the BL02B1 beamline at the synchrotron facility SPring-8 in Japan [see ESI† Section 1]. Fig. 2D and 4B show the observed VED around the V (1/2 1/2 1/2) and the Fe (1/8, 1/8, 1/8) sites at 160 K. The VED around the V site is more clearly anisotropic than the Fe site. The reason is that only 1/6 of the 3d electrons contribute to the anisotropy in the Fe site, whereas the V site directly reflects the anisotropy of the $3d^2$ electrons. The anisotropy of the VED at the V site was considered as follows:

We defined φ_2 and φ_3 such that the three wavefunctions, including φ_1 , are orthogonal to simulate the 3D VED distribution.

$$\begin{cases} \varphi_2(\mathbf{r}) = \frac{1}{\sqrt{2}}(|yz\rangle - |zx\rangle) \\ \varphi_3(\mathbf{r}) = \frac{1}{\sqrt{6}}(|yz\rangle + |zx\rangle - 2|xy\rangle) \end{cases} \quad (3)$$

When a valence electron occupies the φ_i orbital, $|\varphi_i|^2$ corresponds to VED. Because the CDFS method extracts only the VED, information on the phase of the orbital wave function is not obtained. Here, we expected the effect of the orbital angular momentum l to be negligible and focused mainly on the Jahn–Teller effect.

First, we assume an orbital state where the energy gap of the t_{2g} orbital is smaller than the thermal excitation energy. In this case, the t_{2g} orbital can be regarded as triple degenerate, and φ_1 , φ_2 , and φ_3 orbitals are occupied by the two 3d electrons with equal probability. The VED was simulated as $\frac{2}{3}|\varphi_1|^2 + \frac{2}{3}|\varphi_2|^2 + \frac{2}{3}|\varphi_3|^2$ (Fig. 2A). Next, we assumed the orbital state calculated using Q -mode analysis, in which the degenerate orbitals are stabilized. Because the two 3d electrons occupy the degenerated φ_2 and φ_3 , the VED is described as $|\varphi_2|^2 + |\varphi_3|^2$, as shown in Fig. 2B. The simulated VEDs do not reproduce the observed electron density (Fig. 2D). Next, we focused on the orbital state calculated by the point-charge model. In simple consideration, the two 3d electrons form a spin singlet on stabilized φ_1 , but it does not satisfy $S = 1$ at the V site. 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 occupies the lower φ_1 , and the other one is lifted to the degenerate orbitals and occupies either φ_2 or φ_3 . This electron configuration satisfies $S = 1$. In addition, the simulated VEDs such that the lifted electrons occupy only φ_2 or φ_3 orbital states also did not reproduce the observed VED (Fig. S2) [see ESI† Section 2 for details]. Therefore, we assumed that



Fig. 2 (A–C) Assumed electron configurations and simulated VED of V site. The red part of the VED highlights the characteristic components. The grey dotted arrows in (C) indicate that one electron on double degenerate orbitals occupies both orbitals with equal probability. (D) (Upper panel) Observed VED of 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), $5.3e/\text{\AA}^3$ (red)). (A) Crystal structure of FeV_2O_4 in the cubic phase. (B) The orbital states of V and Fe in the cubic phase. The black arrow in VO_6 indicates the $\langle 111 \rangle$ direction.



the electrons on the double degenerate orbitals occupied both orbitals with equal probability. The simulation as $|\varphi_1|^2 + \frac{1}{2}|\varphi_2|^2 + \frac{1}{2}|\varphi_3|^2$ resulted in the VED distribution shown in Fig. 2C, which perfectly reproduced the experimental result. This result clearly means one electron occupies the lowest φ_1 , and another electron is on the degenerate orbitals composed of φ_2 and φ_3 . VED analysis by the CDFS method found that the degenerate orbitals reflect the anisotropy of their constituent orbitals in the cubic phase.

Here, we reconsider the degenerate orbital. As described above, the double degenerate orbital wavefunctions of t_{2g} are not uniquely described. The wavefunctions can also be represented as follows with an arbitrary phase value θ :

$$\begin{cases} \varphi'_2(\mathbf{r}) = \varphi_2(\mathbf{r}) \cos \theta + \varphi_3(\mathbf{r}) \sin \theta \\ \varphi'_3(\mathbf{r}) = -\varphi_2(\mathbf{r}) \sin \theta + \varphi_3(\mathbf{r}) \cos \theta \end{cases} \quad (4)$$

φ_1 , φ'_2 , and φ'_3 are orthogonal to each other. The orbital degrees of freedom mean that θ fluctuates in time and site j as $\theta_j(t)$. Fig. 3 shows the schematic image of the fluctuating orbital. However, the VED obtained by XRD measurements was space- and time-averaged. The image in which the electron on the degenerate orbital occupies both orbitals with equal probability is a simplified representation. The observed electron density ρ_v with the fluctuated orbital states within the Born–Oppenheimer approximation is

$$\rho_v = \frac{1}{N} \sum_j^{\text{crystal}} \left(|\varphi_{1,j}|^2 + |\varphi_{2,j} \cos \theta_j(t) + \varphi_{3,j} \sin \theta_j(t)|^2 \right) \quad (5)$$

Here, N is the number of V sites in the crystal, j is the label of the V sites in the entire crystal, and t is the time. The linear combination wavefunction of the degenerate orbitals is realized at each V site. However, the simulated VEDs at each V site do not suffice the site symmetry at the V site ($\bar{3}m$) (Fig. S3, ESI[†]). The average of the sum over the entire crystal is observed as the

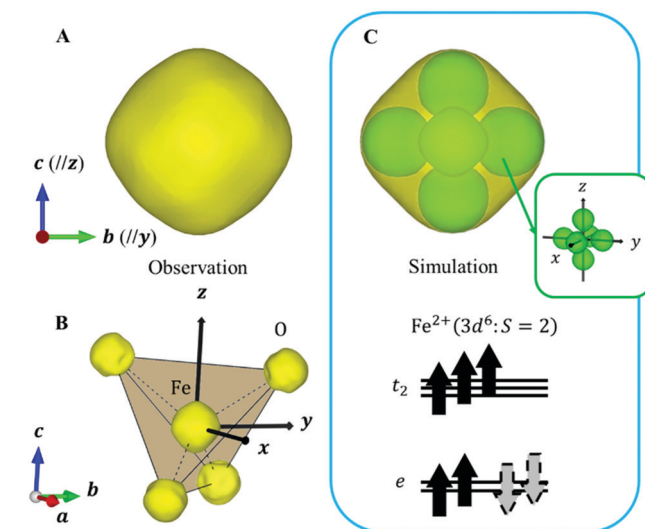


Fig. 4 (A) Observed VED at Fe site (Isosurface level $4.5e/\text{\AA}^3$). (B) Observed VED of FeO_4 tetrahedron with internal coordinates $(1/8\ 1/8\ 1/8)$ (Isosurface level $4.5e/\text{\AA}^3$). The solid line indicates the tetrahedron, and the dotted line indicates the Fe–O bonds. The black arrow indicates the quantum axes. (C) The simulated VED assumes the electron configuration of the bottom figure. The green part of the simulation corresponds to the VED of “down-spin electron” on the degenerated orbitals. The anisotropic shape of the green part is shown in the inset. The grey dotted arrow in the electron configuration indicates that one electron on double degenerate e orbitals occupies both orbitals with equal probability.

electron density. The average is equivalent to:

$$\begin{aligned} \frac{1}{2\pi} \int_0^{2\pi} \left(|\varphi_1|^2 + |\varphi_2 \cos \theta + \varphi_3 \sin \theta|^2 \right) d\theta \\ = |\varphi_1|^2 + \frac{1}{2}|\varphi_2|^2 + \frac{1}{2}|\varphi_3|^2 \end{aligned} \quad (6)$$

Next, we focused on the Fe sites. When the VED of the CDFS analysis is viewed from the \mathbf{a} -axis, the VED has a slight anisotropy extending in the direction of lattice axes \mathbf{a} , \mathbf{b} , and \mathbf{c} at 160 K (Fig. 4A). Applying the same analogy as that applied to the V site, the $\text{Fe}^{2+}\text{-}3d^6$ orbital state should be understood from the VED. The anisotropy of the VED is responsible for

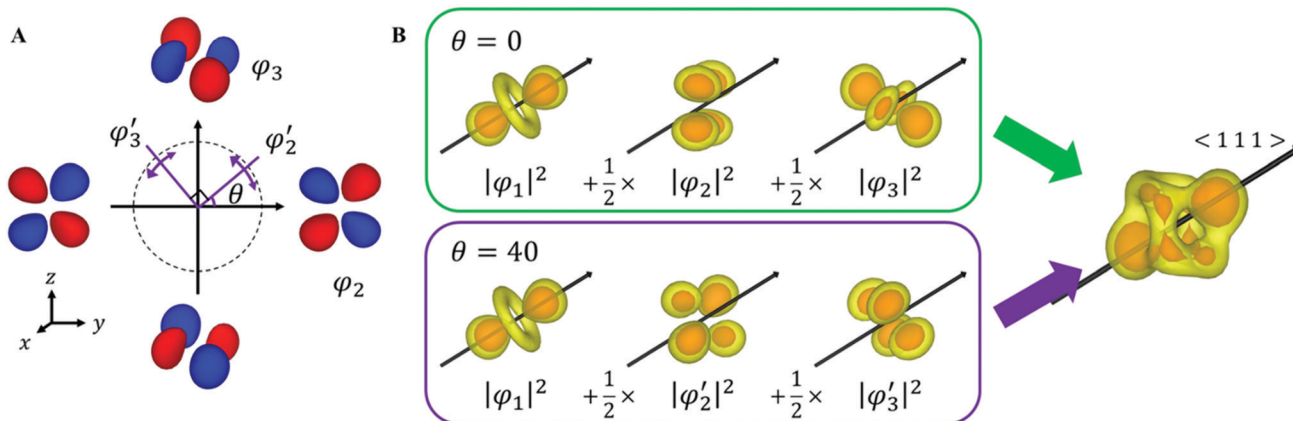


Fig. 3 (A) Schematic of the fluctuating orbital. The red and blue parts indicate the phase of the wavefunction. (B) Simulation with different θ . Simulated VEDs have the same anisotropy even if θ is different.



“down-spin electron” on the e orbitals. In cubic phase, FeO_4 is a regular tetrahedron that satisfies the $\bar{4}3m$ site symmetry at the Fe site, and the e orbitals remain degenerate. The two wave functions of the e orbital of Fe can be expressed as:

$$\begin{cases} \psi_1(\mathbf{r}) = |3z^2 - r^2\rangle. \\ \psi_2(\mathbf{r}) = |x^2 - y^2\rangle. \end{cases} \quad (7)$$

Similar to that for the V site, the wavefunction of “down-spin electron” can also be described as follows using an arbitrary phase value θ' .

$$\psi'(\mathbf{r}) = \psi_1(\mathbf{r}) \cos \theta' + \psi_2(\mathbf{r}) \sin \theta' \quad (8)$$

Because this electron exists on degenerate e orbitals, the averaged orbital state, which is $\frac{1}{2}|\psi_1|^2 + \frac{1}{2}|\psi_2|^2$, is realized (Fig. 4C). Although the anisotropy of the VED around Fe is smaller than that around V, the electron configuration of $\text{Fe}^{2+}3d^6$ is well reproduced in real space.

Since cubic-tetragonal structural transition in FeV_2O_4 occurs at 140 K, it is obvious that the electron orbitals have temporal fluctuations in cubic phase. Depending on the orbital fluctuations, a lattice fluctuation occurs due to the electron–lattice interaction. This phase transition is predicted to be mainly due to Fe orbital order.¹⁸ To confirm the orbital states below the phase transition temperature, direct observation is necessary. In the high-temperature tetragonal phase, a precise structural

analysis of single crystals was performed, paying attention to the domain formation and site symmetry reduction [see ESI† Section 3]. The structural analysis at 120 K shows that the VO_6 octahedron and FeO_4 tetrahedron are slightly deformed, particularly FeO_4 is compressed along the c -axis. This means a “down-spin electron” of Fe occupies the ψ_1 orbital due to Fe orbital order. In fact, when VED was extracted by using CDFS method, the anisotropy of $\text{Fe}^{2+}3d^6$ including ψ_1 orbital asymmetry was observed (Fig. S4, ESI†), but the anisotropy of the V-site orbital was maintained (Fig. S5, ESI†). When the orbital degeneracy of Fe is resolved, the symmetry of FeO_4 is lowered due to JT strain, but it is interesting to see how the phonons behave when the orbital degrees of freedom at the V site is preserved.

Analysis result of inelastic X-ray scattering (IXS)

The distortion in the form of compression/elongation of the FeO_4 tetrahedron coupled with the wave function in eqn (7) corresponds to the E -symmetry. The 8 FeO_4 tetrahedra existing in the unit cell can be divided into two types based on the reversed quantization axis (Fig. S6, ESI†). When these two types of FeO_4 are distorted in the in-phase, this phonon mode is called the E_g mode, and when they are in the anti-phase, this phonon mode is called the E_u mode. The IXS experiments were

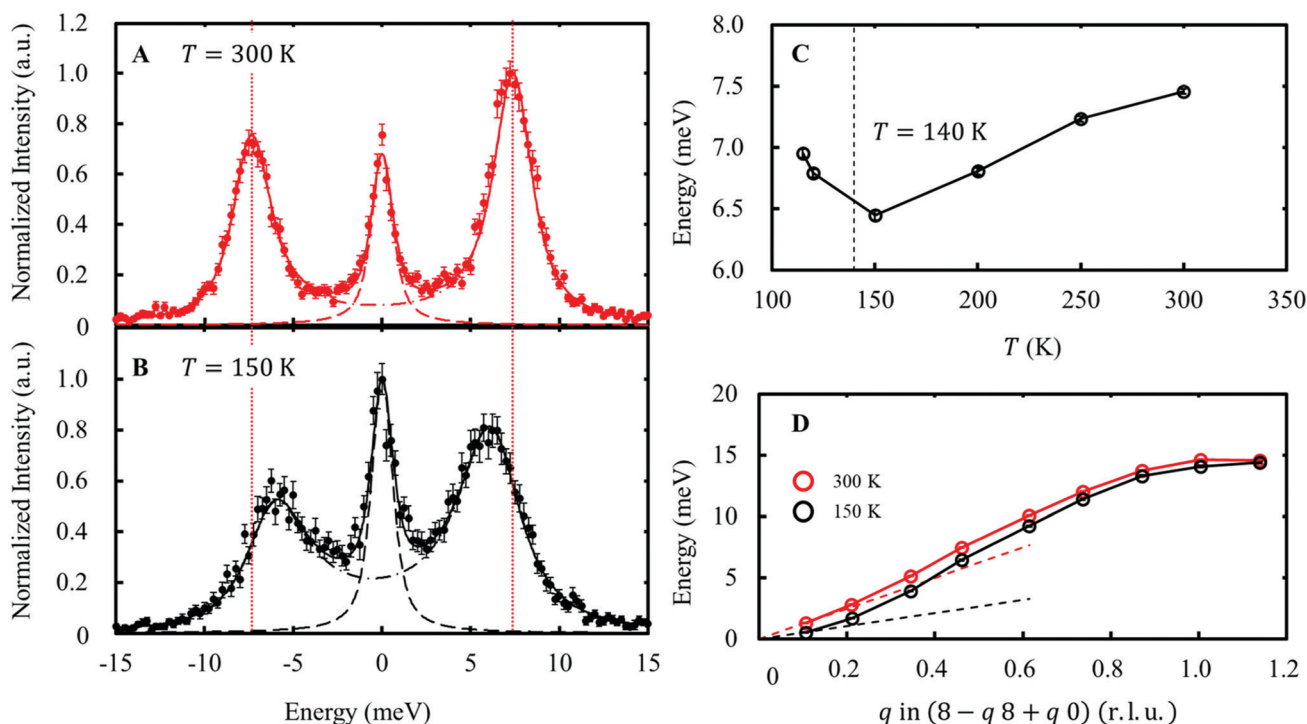


Fig. 5 Energy scan data at $Q = (7.54 \ 8.45 \ -0.03)$ at 300 K (A) and 150 K (B). The phonon peaks correspond to the E_g TA mode. The solid lines indicate fitting results using two lines, corresponding to an elastic peak (dashed line) and a pair of phonon peaks (dash-dotted line). The vertical dotted line indicates the phonon energy at 300 K. (C) The 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. The dashed lines indicate the linear dispersions expected from the elastic stiffness constants at each temperature [see ESI† Section 2.3].



- 13 S. Aoyagi, E. Nishibori, H. Sawa, K. Sugimoto, M. Tanaka, Y. Miyata, R. Kitaura, H. Shinohara, H. Okada, T. Sakai, Y. Ono, K. Kawachi, S. Yokoo, S. Ono, K. Omote, Y. Kasama, S. Ishikawa, T. Komuro and H. Tobita, layered ionic crystal of polar $\text{Li}@C_{60}$ superatoms, *Nat. Chem.*, 2010, **2**, 678.
- 14 E. J. W. Verwey, Electronic Conduction of Magnetite (Fe_3O_4) and its Transition Point at Low Temperature, *Nature*, 1939, **144**, 327–328.
- 15 S. H. Lee, H. Takagi, D. Louca, M. Matsuda, S. Ji, H. Ueda, Y. Ueda, T. Katsufuji, J. H. Chung, S. Park, S. W. Cheong and C. Broholm, Frustrated Magnetism and Cooperative Phase Transition in Spinels, *J. Phys. Soc. Jpn.*, 2010, **79**, 011004.
- 16 T. Katsufuji, T. Suzuki, H. Takei, M. Shingu, K. Kato, K. Osaka, M. Tanaka, H. Sagayama and T. Arima, Structural and Magnetic Properties of Spinel FeV_2O_4 with Two Ions Having Orbital Degrees of Freedom, *J. Phys. Soc. Jpn.*, 2008, **77**, 053708.
- 17 G. J. MacDougall, V. O. Garlea, A. A. Aczel, H. D. Zhou and E. Nagler, Magnetic order and ice rules in the multiferroic spinel FeV_2O_4 , *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **86**, 060414(R).
- 18 Y. Nii, H. Sagayama, A. Aoyagi, R. Sakai, S. Maki, E. Nishibori, H. Sawa, K. Sugimoto, H. Ohsumi and M. Takata, Orbital structures in spinel vanadates AV_2O_4 ($A = \text{Fe}, \text{Mn}$), *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **86**, 125142.
- 19 A. Kismarhardja, J. S. Brooks, H. D. Zhou, E. S. Choi, K. Matsubayashi and Y. Uwatoko, Dielectric properties of single crystal spinels in the series FeV_2O_4 , MnV_2O_4 , and CoV_2O_4 in high magnetic fields, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2013, **87**, 054432.
- 20 S. Nakamura and A. Fuwa, Distinct Evidence of Orbital Order in Spinel Oxide FeV_2O_4 by ^{57}Fe Mössbauer Spectroscopy, *J. Phys. Soc. Jpn.*, 2016, **85**, 014702.
- 21 B. R. Myoung, S. J. Kim, J. T. Lim, T. Kouh and C. S. Kim, Microscopic evidence of magnetic and structure phase transition in multiferroic spinel FeV_2O_4 , *AIP Adv.*, 2017, **7**, 055828.
- 22 Q. Zhang, M. Ramazanoglu, S. Chi, Y. Liu, T. A. Lograsso and D. Vaknin, Magnetic excitations and anomalous spin-wave broadening in multiferroic FeV_2O_4 , *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, **89**, 224416.
- 23 K. Matsuura, H. Sagayama, Y. Nii, N. D. Khanh, N. Abe and T. Arima, X-ray magnetic circular dichroism of an orbital ordered state in the spinel-type vanadium oxide AV_2O_4 ($A = \text{Mn}, \text{Fe}$), *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2015, **92**, 035133.
- 24 D. Dey, T. Maitra and A. Taraphder, Orbital ordering in $\text{Fe}_{1-x}\text{Mn}_x\text{V}_2\text{O}_4$: A first-principles study, *Phys. Rev. B*, 2016, **93**, 195133.
- 25 H. Mamiya, M. Onoda, T. Furubayashi, J. Tang and I. Nakatani, Structural and magnetic studies on vanadium spinel MgV_2O_4 , *J. Appl. Phys.*, 1997, **81**, 5289–5291.
- 26 Y. Ueda, N. Fujiwara and H. Yasuoka, Magnetic and Structural Transitions in $(\text{Li}_x\text{Zn}_{1-x})\text{V}_2\text{O}_4$ with the Spinel Structure, *J. Phys. Soc. Jpn.*, 1997, **66**, 778–783.
- 27 M. Onoda and J. Hasegawa, A distortion of pseudotetramers coupled with the Jahn–Teller effect in the geometrically frustrated spinel system CdV_2O_4 , *J. Phys.: Condens. Matter*, 2003, **15**, L95–L102.
- 28 R. Plumier and M. Sougi, Observation of a first order transition in the ferrimagnetic spinel MnV_2O_4 , *Solid State Commun.*, 1987, **64**, 53–55.
- 29 A. Kismarhardja, J. S. Brooks, A. Kiswandhi, K. Matsubayashi, R. Yamanaka, Y. Uwatoko, J. Whalen, T. Siegrist and H. D. Zhou, $\text{Co}[\text{V}_2]\text{O}_4$: A Spinel Approaching the Itinerant Electron Limit, *Phys. Rev. Lett.*, 2011, **106**, 056602.
- 30 S. Ohtani, Y. Watanabe, M. Saito, N. Abe, K. Taniguchi, H. Sagayama, T. Arima, M. Watanabe and Y. Noda, Orbital dilution effect in ferrimagnetic $\text{Fe}_{1-x}\text{Mn}_x\text{Cr}_2\text{O}_4$: competition between anharmonic lattice potential and spin–orbit coupling, *J. Phys.: Condens. Matter*, 2010, **22**, 176003.
- 31 K. Siratori and K. Kohn, Ground State of a $d\epsilon$ Electron in an Elastic Octahedron of Ligands, *J. Phys. Soc. Jpn.*, 2010, **79**, 114720.
- 32 P. P. Ewald, Die Berechnung optischer und elektrostatischer Gitterpotentiale, *Ann. Phys.*, 1921, **369**, 253–287.
- 33 A. M. Merritt, F. Weber and J. P. Castellán, Th. Wolf, D. Ishikawa, A. H. Said, A. Alatas, R. M. Fernandes, A. R. R. Baron, D. Reznik, Nematic Correlation Length in Iron-Based Superconductors Probed by Inelastic X-Ray Scattering, *Phys. Rev. Lett.*, 2020, **124**, 157001.

