

Orbital-resolved spin-exchange interactions and spin-phonon coupling in CrVO₄

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This report investigates the role of orbital degrees of freedom in CrVO₄, focusing on orbital-driven spin-exchange interactions and spin-phonon coupling through both experiments and first-principles calculations. Combining synchrotron radiation x-ray powder diffraction, Raman spectroscopy, and x-ray absorption fine structure measurements, a significant correlation between magnetic transition and structural modification was identified, revealing spin-lattice coupling at the transition (T_N). This coupling is linked to conventional magnetoelastic interactions, even active above T_N , supported by both experimental and theoretical findings. The calculations revealed crystal field splitting and orbital nondegeneracy resulting from charge transfer in the $3d^3$ system of CrVO₄ due to octahedral symmetry breaking. The study discusses the detailed mechanism of orbital-resolved spin-exchange interactions, leading to one-dimensional A-type antiferromagnetic ordering. Notably, no significant orbital-selective spin-phonon coupling was observed at approximately 200 K ($4T_N$) in CrVO₄, in contrast to earlier studies [A. P. Roy *et al.*, *Phys. Rev. Lett.* **132**, 026701 (2024)]. These findings advance the understanding of the fundamental physics in CrVO₄ and significantly contribute to the field of spin-orbital-lattice physics in transition metal oxides.

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I. INTRODUCTION

Orbital degrees of freedom are a key focus in the study of strongly correlated electron systems due to their unique quantum dynamics and strong entanglement with other degrees of freedom, including spin, charge, and lattice [1–3]. The interactions among these degrees of freedom have attracted significant interest, leading to a deeper understanding of various physical phenomena and potential applications in metals, insulators, and systems undergoing metal-insulator transitions [4–6]. These systems can exhibit diverse ordering types, such as magnetic (spin), charge, and orbital ordering, as well as the cooperative Jahn-Teller (JT) effect driven by lattice distortion [1,7–10]. Recent research has highlighted the importance of multi-orbital systems with strong

spin-orbit coupling (SOC), which is a critical interaction in condensed matter physics [11–14]. SOC plays a significant role in the behavior of topological insulators [15], superconductors [16], Dirac and Weyl semimetals [17,18], and multiferroics [19]. The balance between SOC and other interactions, such as on-site Coulomb repulsion, leads to complex behaviors and exotic states, particularly in transition metal compounds with partially filled d orbitals [20,21]. In cases of small SOC, conventional spin-orbital ordered states can emerge, resulting in notable effects like the JT distortion and strong coupling between orbital and spin degrees of freedom, as described by the Goodenough-Kanamori-Anderson (GKA) rules [10,22]. The incorporation of orbital degrees of freedom and their coupling with spin, particularly through localized spin-orbital models, i.e., Kugel-Khomskii (KK)-type superexchange interactions [2,23], has been shown to influence various phenomena, including enhanced magnetoelectric and spin-phonon coupling in materials like CaBa(Co, Fe)₄O₇ [24] and photoinduced high-temperature magnetism in YTiO₃ [25]. The KK-type superexchange Hamiltonian exhibits hidden symmetries that indicate it does not allow for long-range spin order in a three-dimensional cubic lattice at nonzero temperature, particularly in the absence of spin-orbit interactions [26].

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Orthorhombic CrVO_4 [$Cmcm$ ($D^{17}2h$) ($Z = 4$)] features infinite chains of edge-sharing CrO_6 octahedra connected to corner-sharing VO_4 tetrahedra [27,28]. It exhibits an A-type antiferromagnetic transition at approximately 50 K (T_N), having ferromagnetically ordered sheets that stack antiferromagnetically, and a broad maximum of around 70 K, indicating low-dimensional short-range magnetic ordering [29,30]. This behavior is attributed to the crystal structure, where the edge-sharing CrO_6 chains are aligned parallel to the c axis. The magnetic exchange interactions among Cr^{3+} cations are characterized by short-range antiferromagnetic coupling via superexchange paths ($\text{Cr}-\text{O}-\text{Cr}$) within the chains (intrachain interaction). In contrast, the interchain magnetic exchange interaction is ferromagnetic (FM), following super-superexchange paths ($\text{Cr}-\text{O}\cdots\text{O}-\text{Cr}$) [31–33]. CrVO_4 as a $3d^3$ system with Cr^{3+} ions exhibits a nondegenerate t_{2g}^3 ($S = 3/2$) state under weak SOC, resulting in a quenched orbital moment and negligible SOC energy gain [2,10,34]. The crystal field can lift the orbital degeneracy, influenced by strong Coulomb correlations and hybridization with cations, further enhanced by the JT effect. Additionally, superexchange interactions of the KK type can lead to orbital and magnetic orderings, with the crystal field playing a secondary role in stabilizing these orders [23,35–37]. In general, KK-type interactions typically emerge in orbitally degenerate Mott insulators through second-order superexchange processes. These interactions are especially prominent in perovskite systems such as KCuF_3 , LaVO_3 , and LaMnO_3 , as well as in newer classes of low-dimensional magnetic materials like honeycomb lattices and van der Waals compounds [2,35,38–43]. In these systems, virtual electron hopping between transition metal ions leads to entangled spin-orbital dynamics. However, CrVO_4 does not fall into this category and it lacks the orbital degeneracy and crystal structure motifs that underpin conventional KK-type mechanisms.

A recent study on orthorhombic CrVO_4 has suggested the significant influence of KK-type interactions on its electronic and phononic properties [44]. These findings have suggested that interactions in this system could lead to substantial modifications in electronic states and phonon characteristics at temperatures up to four times the Néel temperature, identifying a strong orbital-selective spin-phonon coupling at 200 K, without any noticeable discontinuity at T_N , indicating a complex interplay of interactions. These findings are both unexpected and notably rare for orthorhombic A-type antiferromagnetic (AFM) materials, which typically exhibit anomalies in phonon frequencies (ω) near T_N , primarily due to strong magnetoelastic coupling. Such anomalies can persist up to approximately $2T_N$, driven by short-range spin correlations even in the paramagnetic regime [45–47].

This discrepancy with prior report [44] motivates a deeper exploration of orbital-driven spin-exchange interactions and spin-phonon coupling in CrVO_4 that we carried out here carefully combining experimental complementary probes and first-principles calculations. The significant spin-lattice coupling in this compound across T_N has been consistently identified through low-temperature synchrotron radiation x-ray diffraction (SR-XRD), Raman spectroscopy, and x-ray absorption fine structure (XAFS) spectroscopy. No significant

structural modifications were observed around 200 K ($4T_N$), which contrasts with the reported presence of unusually strong orbital-selective spin-phonon coupling and KK-type interactions in CrVO_4 . These findings enhance the understanding of the fundamental physics of CrVO_4 and may inform the development of materials with tailored electronic and magnetic properties governed by spin-lattice interactions.

II. MATERIALS AND METHODS

A. Experimental details

Polycrystalline CrVO_4 compound was synthesized by the standard solid-state reaction method. The temperature-dependent SR-XRD of CrVO_4 was performed by using a 12.52-keV ($\lambda = 0.990084 \text{ \AA}$) synchrotron x-ray source, recorded in the temperature range 10–300 K using an image plate (Mar 345) area detector at angle dispersive x-ray diffraction beamline (BL-12), Indus-2, RRCAT, Indore, India. The experimental data were analyzed by the Rietveld refinement method using FULLPROF software and crystal structures at different temperatures were analyzed using VESTA software. Temperature-dependent Raman and XAFS spectroscopy data were used to extract information about the local atomic structure behavior as a function of temperature across the magnetic transitions. The Raman spectra were measured in the 5–300 K range using a liquid He-based flow-type cryostat and a He-Ne laser ($\lambda = 632.8 \text{ nm}$) as the excitation source (laser power $\leq 3 \text{ mW}$ and spot size = $2 \mu\text{m}$) coupled with a Jobin Yvon Horibra LABRAM spectrometer.

The x-ray absorption spectroscopy (XAS) experiments were carried out at the P65 beamline of the PETRA-III synchrotron radiation storage ring DESY (Hamburg, Germany). The XAS measurements were conducted in transmission geometry using the quick-XAS monochromator mode, with roughly 0.5 eV energy resolution. Given the proximity of the vanadium K-edge (5465 eV for metallic V) and chromium K-edge (5989 eV for metallic Cr), both edges were measured within a single scan to optimize the beamtime. We measured 15 temperature points heating the sample across the T_N temperature in the 5–100 K range, ensuring thermal stabilization at each set point before data acquisition. At each temperature, three scans were collected, verified for energy calibration, and averaged. Standard data reduction procedures were applied to the raw V and Cr K-edge XAS spectra, including pre-edge background subtraction, normalization of the edge jump, and extraction of the extended x-ray absorption fine structure (EXAFS) signal $\chi(k)$ [48]. Quantitative structural analysis was performed by fitting the k^2 -weighted experimental spectra $k^2\chi(k)$ to theoretical curves calculated as the sum of partial contributions from various atomic coordination shells (scattering paths) surrounding the absorbing atom (V or Cr). Partial contributions to the theoretical EXAFS signal were calculated using the standard EXAFS model curve with Gaussian disorder approximation [49]. The amplitude and phase functions were calculated using FEFF8 program [50] from atomic clusters obtained by SR-XRD data refinement. The statistically relevant contributions were selected through a trial-and-error procedure, the refinement was optimized refining the lowest-temperature spectra, and the same procedure was applied to

the whole dataset following a well-ascribed procedure [51]. To reduce the number of free parameters and the correlation effects in the data fitting, the same edge energy shift (ΔE_o) and many-body loss S_o^2 parameters were applied to all the spectra as a function of temperature, and the signal multiplicities were fixed to the crystallographic values. This procedure avoids the known correlations between energy scale and interatomic distances, and coordination numbers and disorder factors, allowing high sensitivity to even weak changes of structural parameters as a function of temperature, namely, interatomic distances R and mean square relative displacement σ^2 .

B. Computational details

First-principles calculations were performed within the framework of density functional theory (DFT) and the projected augmented wave (PAW) method as implemented in the Vienna *ab initio* Simulation Package (VASP) [52–54]. The spin-polarized calculations were performed with collinear A-type AFM ordering [29]. A plane-wave energy cut-off of 700 eV was used based on convergence to achieve high accuracy in our calculations. A Γ -centered Monkhorst-Pack grid of $7 \times 7 \times 6$ has been used for Brillouin-zone (BZ) integration within the convergence criterion of 1 meV per formula unit of 12-atom primitive cell [55]. To describe the exchange-correlation energy, we have used the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof description for solids (PBEsol) [56]. The GGA+ U approximation was applied in all calculations to localize the 3d electrons of Cr and correct for the oversimplification of electron correlation within the GGA scheme using an on-site Hubbard interaction U of 4.2 eV, following the method of Dudarev *et al.* [57]. The calculated band gap with this Hubbard U agrees well with the one estimated from optical measurements, and it is consistent with the values employed in other Cr-based compounds [58–61]. The phonon dispersion was calculated with the density-functional-perturbation theory (DFPT) approach within harmonic approximation as implemented in Phonopy [62]. The phonon calculations were performed with a $2 \times 2 \times 2$ supercell of a primitive cell containing 144 atoms. To compute the magnetic exchange, a tight-binding model was constructed based on maximally localized Wannier functions (MLWFs) as implemented in the WANNIER90 program package [63]. The MLWF was constructed by 3d orbitals of Cr and V and 2p orbitals of O. The magnetic exchange was estimated using Green's function approach as implemented in TB2J [64]. Magnon dispersion was calculated using a linear spin wave theory approach by means of the SPINW code [65] using derived exchange coupling (see the Supplemental Material [66] for more details).

We have also employed multireference CASSCF/RASSI-SO/SINGLE-ANISO calculations using the MOLCAS8.2 program package to compute the 3d orbital splitting of Cr [67]. The calculations were performed on a model system with three Cr and six V atoms (see Fig. S1 in the Supplemental Material [66]) to mimic the surroundings of Cr. We have employed the diamagnetic substitution method in our calculation where all the Cr atoms except the one under investigation were replaced by diamagnetic Ga^{3+} . The basis set for our calculations was taken from ANO-RCC library of MOLCAS8.2

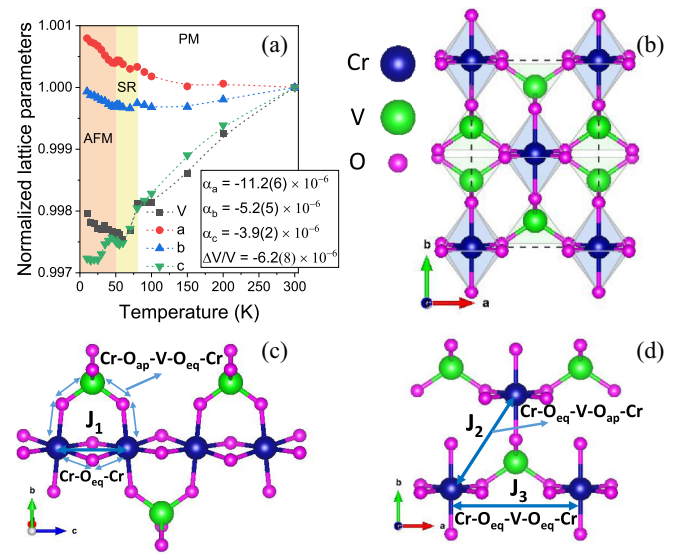


FIG. 1. (a) The variation of normalized lattice parameters and unit cell volume with temperature obtained from Rietveld refinement of the temperature-dependent XRD patterns of CrVO_4 (symbols are the experimental data points, while dashed lines are guided to the eyes only and error bars from Rietveld refinement are smaller than marker sizes). The inset box illustrates the values of the linear thermal expansion coefficients and the corresponding relative volume changes up to 60 K. The observed negative values clearly indicate the presence of negative thermal expansion behavior. (b) The polyhedral form of the orthorhombic (SG: $Cmcm$) crystal structure along c axis drawn in VESTA software using refinement cif file of CrVO_4 at 10 K, and (c), (d) different superexchange interactions pathways for J_1 , J_2 , and J_3 between NN and NNN magnetic Cr^{3+} atoms. Colored regions highlight the transition temperatures in panel (a).

[68,69]. We have used VTZP basis set for Cr and VDZP basis set for Ga, V, and O in our calculations. The scalar relativistic effect was considered using the Douglas-Kroll-Hess (DKH) Hamiltonian [70]. The disk space of our calculations has been reduced by the Cholesky decomposition technique. The CASSCF calculations were performed with three electrons in five 3d orbitals [CAS(3,5)] of Cr in the active space. Within this active space, we have computed energies of 10 quartets and 40 doublets. All these spin-free states have been mixed by RASSI-SO [71] to compute the energies of spin-orbit states. Finally, the orbital splitting of Cr has been deduced with the SINGLE-ANISO module of MOLCAS8.2.

III. DATA ANALYSIS AND RESULTS

A. Spin-lattice coupling

We quantitatively analyzed the temperature-dependent SR-XRD data from CrVO_4 sample (Fig. S3 in the Supplemental Material [66]) using the Rietveld refinement method to identify signatures of spin-lattice coupling. The Rietveld refinement also confirms the CrVO_4 phase purity. Figure 1(a) presents the evolution of lattice parameters and unit cell volume as a function of temperature across T_N . The a and b axes exhibit a smooth and slight compression with increasing temperature, more pronounced along the a axis. The largest anomalies are found along the c axis, which shows a distinct

steplike behavior upon crossing T_N , and on the cell volume, presenting evident negative thermal expansion till about 80 K. We have determined the linear thermal expansion coefficients (α_a , α_b , and α_c in K^{-1}) along the principal crystallographic axes, together with the relative volume change ($\frac{\Delta V}{V}$) over the temperature range up to 60 K for a and b axes and the volume V and the range of 40–60 K for c axis, as presented in the inset box of Fig. 1(a). These results enable a detailed characterization of the anisotropic lattice response at low temperatures. These structural changes are the hallmark of spin-lattice coupling and persist above T_N extending up to approximately 80–100 K. Figure 1(b) shows the crystal structure of CrVO_4 along the c axis and Figs. 1(c) and 1(d) illustrate the various exchange interaction paths observed in CrVO_4 .

Notably, the crystallographic distances within the polyhedral units (Cr/V–O) remain relatively stable across T_N , in contrast to the more pronounced changes observed in the crystallographic distances between transition metal atoms (Cr–Cr and Cr–V) and in the crystallographic bond angles involving metal-ligand connections (Cr–O–Cr and Cr–O–V) [see Figs. S4(a)–S4(c) of the Supplemental Material [66]]. This indicates that the structural changes crossing the transition temperature are not primarily due to distortions of individual polyhedra, but rather due to significant tilting and/or rotation of the CrO_6 and VO_4 polyhedra within the unit cell. Such reorientations contribute to a more pronounced structural distortion along the c axis, as opposed to localized deformations confined within each polyhedron. The Cr atoms of the edge-sharing CrO_6 octahedra are aligned along the c axis; therefore, the relative elongation of the Cr–Cr distance is equal to the relative elongation of the c axis (see Fig. S5 of the Supplemental Material [66]). These findings are further supported by principal component analysis (PCA) and XAS results for CrVO_4 , which offer deeper insight into the temperature-dependent microstructural evolution, confirming the stability of the Cr/V–O bond lengths, against a weak effect in the next-neighbor coordination shells mainly involving Cr–Cr distances along the c axis. These structural distortions represent the microscopic counterpart of evolving spin-lattice interactions. This interplay is further evidenced by the temperature-dependent shifts in both the magnetic exchange strength and the magnon excitation energies, as elaborated later in this work. Moreover, this spin-lattice interaction is also reflected in the temperature-dependent SR-XRD patterns of CrVO_4 (raw data, Fig. S6 of the Supplemental Material [66]), especially at higher 2θ angles, where the emergence and merging of specific reflections near the transition temperature (T_N) provide further evidence of structural modifications (see shaded areas in Figs. S6(b) and S6(c) of the Supplemental Material [66]).

The normalized spectra at the V and Cr K-edges are shown in Fig. 2, in the near-edge (XANES) and EXAFS regions. At first glance, the spectra appear identical with no visible temperature-dependent effects. The pre-edge features of $3d$ metals are known to be especially sensitive to the local coordination geometry around the absorber [72]. In fact, they originate from transitions to empty d states, which are dipole-forbidden, but the hybridization of d levels with oxy-

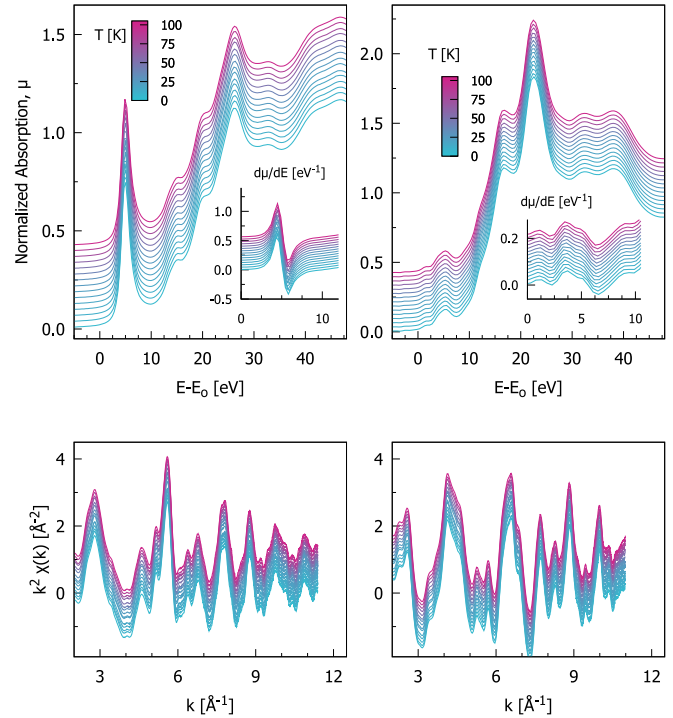


FIG. 2. The V (left panels) and Cr (right panels) K-edge XAFS data as a function of temperature in the XANES (top panels) and k^2 -weighted EXAFS (bottom panels) regions, vertically shifted for the sake of comparison. The inset in the top panels reports the derivative of the absorption signals in the pre-edge region. In the XANES panels, the energy scale is calculated considering the origin at the K-edge of the V and Cr metals. The very equal features in the XANES and EXAFS regions are evident at the V and Cr K-edges.

gen p states may favor dipole-allowed transitions enhancing the pre-edge features, as evident in the vanadium XANES spectra (Fig. 2) in which the tetrahedral symmetry (T_d) allows the pd hybridization. In the case of octahedral symmetry (O_h), this hybridization is absent, which results in the weak pre-edge features observed in the chromium XANES spectra. The weak pre-edge features observed at Cr K-edge suggest undistorted CrO_6 octahedra. Noticeably, modifications of the local coordination symmetry modify the pd hybridization, reflecting in large changes of the pre-edge features that became sensitive fingerprints of tiny changes of local coordination geometry [72]. The data in Fig. 2 demonstrate very unchanged pre-edge features, as evident also looking at the pre-edge derivatives in the insets of Fig. 2, suggesting no changes of CrO_6 and VO_4 polyhedra geometry across the magnetic transition temperature.

To highlight the most subtle changes in the XAFS spectra, we first used the PCA, which has demonstrated special sensitivity to very tiny spectral changes [51] and helps in individuating relationships between variables driving further data analysis procedures. Figure S7 of the Supplemental Material [66] reports the PCA loading as a function of temperature for the Cr and V XAFS spectra. Looking at the Cr K-edge [Fig. S7(a) of the Supplemental Material [66]], the first (PC1) and second (PC2) principal component loadings reveal a spe-

TABLE I. The average local atomic structure around vanadium and chromium was determined by the EXAFS data analysis. The interatomic distances (R_{EXAFS}) and mean square relative displacements (σ_o^2) averaged over the temperature range (5–100 K) are shown, and in parentheses is the standard deviation on the last digit of the parameter distribution. The interatomic distances obtained from the low-temperature SR-XRD Rietveld refinement ($R_{\text{SR-XRD}}$) are reported for the sake of comparison.

K edge	Shell	N	$R_{\text{SR-XRD}}$ (Å)	R_{EXAFS} (Å)	σ_o^2 ($\times 10^3$ Å ²)
V	V–O ₁	2	1.6420	1.6343(7)	5.80(10)
	V–O ₂	2	1.7847	1.7602(5)	
	V–Cr	6	3.3614	3.3560(4)	4.43(6)
	V–V ₁	2	3.8070	3.7531(9)	4.86(31)
	V–V ₂	4	4.4708	4.4775(9)	3.61(19)
	Cr–O	6	2.0000	1.9449(3)	4.71(2)
Cr	Cr–Cr	2	2.9963	2.9701(22)	2.80(6)
	Cr–V	6	3.3614	3.3396(3)	5.03(8)

cific evolution of the spectra across the transition temperature and the cluster analysis (K -means) clearly distinguishes the two regions below and above T_N . On the contrary, the PCA analysis of the vanadium XAFS spectra shows no trend as a function of temperature (Fig. S7b of the Supplemental Material [66]). This finding points out a dominant relationship between the Cr local structure and the magnetic transition around 50 K, while the local order around V does not change appreciably.

The quantitative analysis of the EXAFS spectra allows deeper insight into the structural modifications occurring tuning the temperature across the transition temperature T_N . The V K-edge spectra were fitted using five coordination shells, namely two oxygen neighbor shells V–O_{1,2} at 1.634 Å (two neighbors) and 1.760 Å (two neighbors), respectively, a V–Cr shell (six neighbors) at 3.356 Å, and two V–V_{1,2} shells at 3.753 Å (two neighbors) and 4.478 Å (four neighbors). The same disorder factor σ^2 was used for V–O_{1,2} shells. The Cr K-edge data were fitted using only three main contributions: an oxygen neighbor shell Cr–O at 1.944 Å (six neighbors), a Cr–Cr shell (two neighbors) at 2.970 Å, and one Cr–V shell at 3.339 Å (six neighbors). The average interatomic distances found by EXAFS analysis are in good agreement with the lattice distances refined from low-temperature SR-XRD (Table I). The interatomic distances and σ^2 parameters as a function of temperature are reported in Fig. 3. The neighbor shell distances around V are unchanged as a function of temperature, the semidispersion in the whole temperature range being less than 10^{-3} Å for the first three shells. No specific trend is found related to the magnetic transition, except for σ^2 of the V–V₁ and V–V₂, where the increase could simply be due to increased thermal disorder. The local structure that does not change must be linked to the lack of effects in multivariate analyses of vanadium XAFS data. Around Cr, the Cr–O and Cr–V shells are very unchanged across the whole temperature range, but the Cr–Cr distances, corresponding to the distance of Cr sites along the c axis [Fig. 1(c)], evidently increase above T_N . This effect must be related to the differences individuated by PCA and cluster analysis and to the peculiar trend of the c axis resulting from XRD analysis. Therefore,

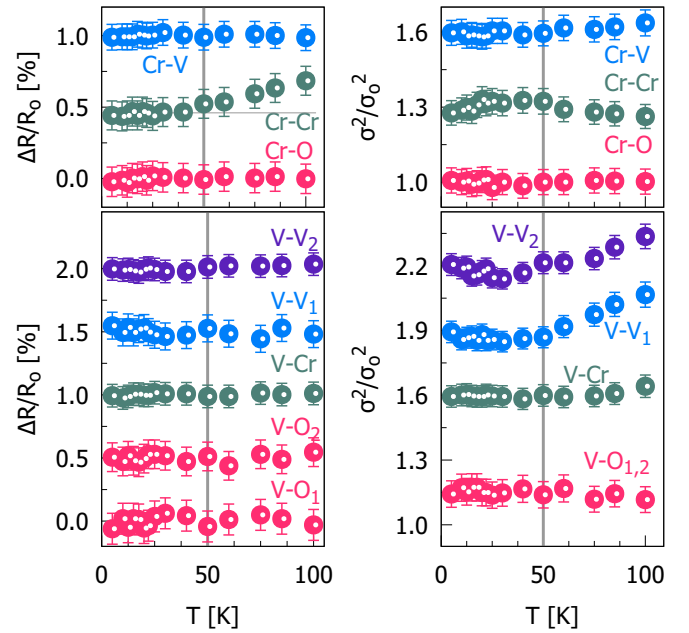


FIG. 3. Structural parameters from the refinement of the Cr (top panels) and V (bottom panels) EXAFS spectra. The left panels show the relative changes of interatomic distances $\Delta R = R(T) - R_o$, with respect to their temperature-averaged values R_o . The right panels report the ratios between temperature-dependent mean square relative displacement $\sigma^2(T)$ and their temperature-averaged values σ_o^2 . The data of the different shells are vertically shifted for clarity. The vertical gray lines indicate the magnetic transition temperature T_N and the horizontal gray line (top left panel) highlights the raising of Cr–Cr shell distance above T_N .

our XRD and XAS findings coherently provide insights into the microstructural effects related to the evolution of the spin-lattice coupling in CrVO₄, highlighting the stability of bond lengths within the polyhedral structure and the potential role of lattice distortions due to mainly magnetoelastic coupling in the system rather than strong spin-orbital-driven lattice coupling.

B. First-principles calculations

Multireference CASSCF/RASSI-SO/SINGLE-ANISO calculations reveal that the typical crystal field splitting of the d orbitals of Cr³⁺ into t_{2g} and e_g subsets in the CrO₆ octahedral environment occurs due to octahedral crystal field, even in the presence of the highly positive V⁵⁺ (d^0) in the VO₄ tetrahedra. The orbital degeneracy is further lifted by structural distortion from the ideal octahedral symmetry. The barycenters of the t_{2g} and e_g levels are found to be separated by 1.59 eV, a typical value for a transition metal system (Fig. S8 of the Supplemental Material [66]). The calculated band structure of CrVO₄ shows a direct band gap of 2.45 eV, which aligns well with the experimentally measured value of 2.62 eV [Fig. S9(a) of the Supplemental Material [66]]. The first-principles calculations also reveal that the valence band maximum is dominated by 3d orbitals of Cr and 2p orbitals of oxygen, while the conduction band minimum is mainly dominated by 3d orbitals of V and Cr

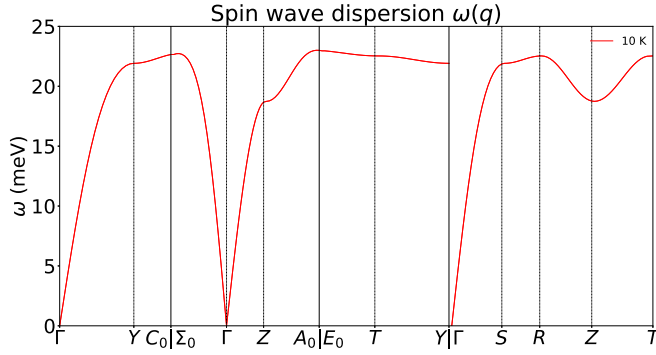


FIG. 4. Magnon dispersion of CrVO_4 at $T = 10$ K. The red line contains two quasidegenerate modes, one for each magnetic atom. Four Brillouin-zone regions are represented, separated by solid black lines.

[Fig. S9(b) of the Supplemental Material [66]]. However, a non-negligible population of e_g orbitals below the Fermi level is observed from the computed PDOS due to the symmetry breaking from ideal octahedra and ligand to metal charge transfer [Fig. S9(c) of the Supplemental Material [66]]. This implies that the exchange interactions in CrVO_4 can occur through both t_{2g} and e_g orbitals. In CrVO_4 , the magnetic structure can indeed be modeled by considering a nearest-neighbor (NN) intrachain exchange interaction J_1 and two next-nearest-neighbor (NNN) interchain exchange interactions J_2 and J_3 [Figs. 1(c) and 1(d) and Fig. S10 of the Supplemental Material [66]]. To elucidate the orbital contribution to the magnetic exchange pathways, first we employed a tight-binding Hamiltonian derived from MLWFs [63]. It offers the calculations of magnetic exchange using Green's function approach as implemented in TB2J [64]. This method uses local spin rotation as a perturbation, which circumvents the limitations of energy mapping analysis, where obtaining convergence for some metastable configurations is challenging. The estimated exchange couplings at 10 K agree well [$J_1 = -2.87$ meV, $J_2 = 0.32$ meV, and $J_3 = -0.56$ meV, $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$, where the positive sign corresponds to the FM and the negative sign corresponds to the AFM interaction; see Table SI of the Supplemental Material [66]] with the theoretical calculation reported for CrVO_4 [44]. Additionally, we computed the magnon spectra using linear spin wave theory, considering both nearest-neighbor and next-nearest-neighbor interactions derived from DFT. Our calculations reveal two quasidegenerate magnetic quasiparticle modes, consistent with the A-type AFM ordering of Cr atoms along the c axis (Fig. 4). Figure S11 of the Supplemental Material [66] shows the magnon frequency at the Z point of the Brillouin zone ($q = [001]$) and exchange interactions (J_1 and J_2) as a function of temperature, indicating typical damping with increasing temperature but displaying an anomalous behavior near the Néel temperature (T_N), where the frequency increases. Beyond 60 K, spin waves are progressively damped with increasing temperature (see Supplemental Material [66]). These results are consistent with our previous observations of lattice distortion across T_N obtained by combining XRD and XAS analyses.

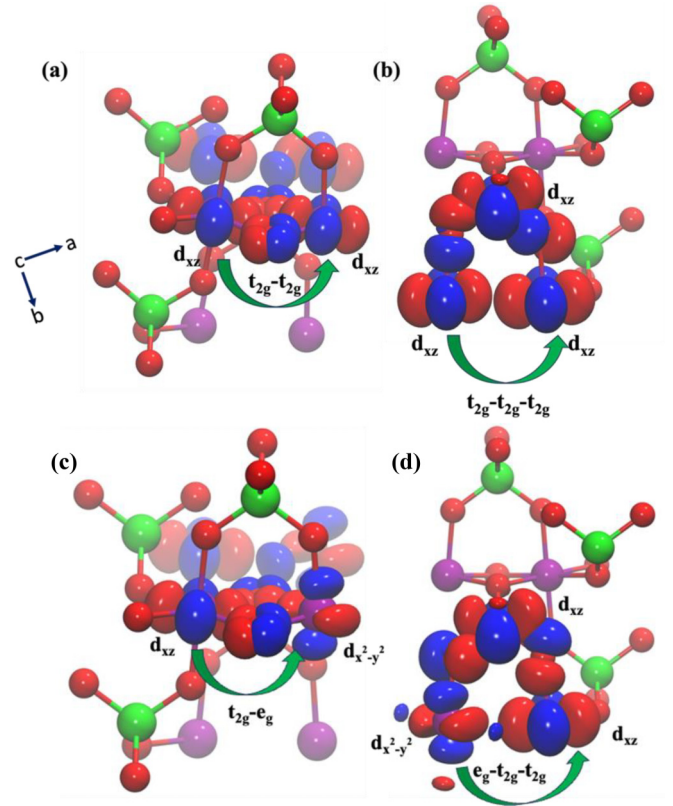


FIG. 5. The calculated maximally localized Wannier functions illustrate the dominant atomic orbitals involved in the antiferromagnetic interaction for (a) the short pathway of the J_1 magnetic exchange and (b) the long pathway of the J_1 magnetic exchange and the dominant atomic orbitals involved in the ferromagnetic interaction for (c) the short pathway of the J_1 magnetic exchange and (d) the long pathway of the J_1 magnetic exchange.

A. J_1 Spin exchanges

The intrachain magnetic exchange J_1 occurs through two dominant superexchange pathways: (1) $\text{Cr}-\text{O}_{\text{eq}}-\text{Cr}$ in the a - c plane and (2) $\text{Cr}-\text{O}_{\text{ap}}-\text{V}^{5+}-\text{O}_{\text{ap}}-\text{Cr}$ confined in the b - c plane, where eq and ap describe the equatorial and apical oxygen atoms, respectively. The orbital-resolved magnetic exchange reveals that J_1 originates from two competitive pathways, $t_{2g}-t_{2g}$ and $t_{2g}-e_g$, where the former contributes to the antiferromagnetic coupling and the latter contributes to the ferromagnetic coupling (see Table SII of the Supplemental Material [66]). The $t_{2g}-t_{2g}$ interactions occur between the d_{xz} orbitals of the two Cr atoms [Figs. 5(a) and 5(b)]. On the other hand, the $t_{2g}-e_g$ interaction occurs between the d_{xz} and $d_{x^2-y^2}$ orbitals of two Cr atoms [Figs. 5(c) and 5(d)]. This brings up the question of why the J_1 exchange remains antiferromagnetic, even though the $\text{Cr}-\text{O}_{\text{eq}}-\text{Cr}$ bond angle is nearly 90° . According to the GKA rule, the interactions should be ferromagnetic as the $\text{Cr}-\text{O}_{\text{eq}}-\text{Cr}$ angle is close to 90° [73,74], because orbitals are arranged in such a way that the p -orbital tails of one $\text{Cr}-\text{O}_{\text{eq}}$ unit are nearly orthogonal to the other $\text{O}_{\text{eq}}-\text{Cr}$ unit [Figs. 6(a)–6(c)] such that the symmetric (ψ_+) and antisymmetric (ψ_-) combination of them remains nearly degenerate ($\Delta e = E(\psi_+) - E(\psi_-)$, see Ref. [59]). Therefore, the AFM contribution to the magnetic exchange should be

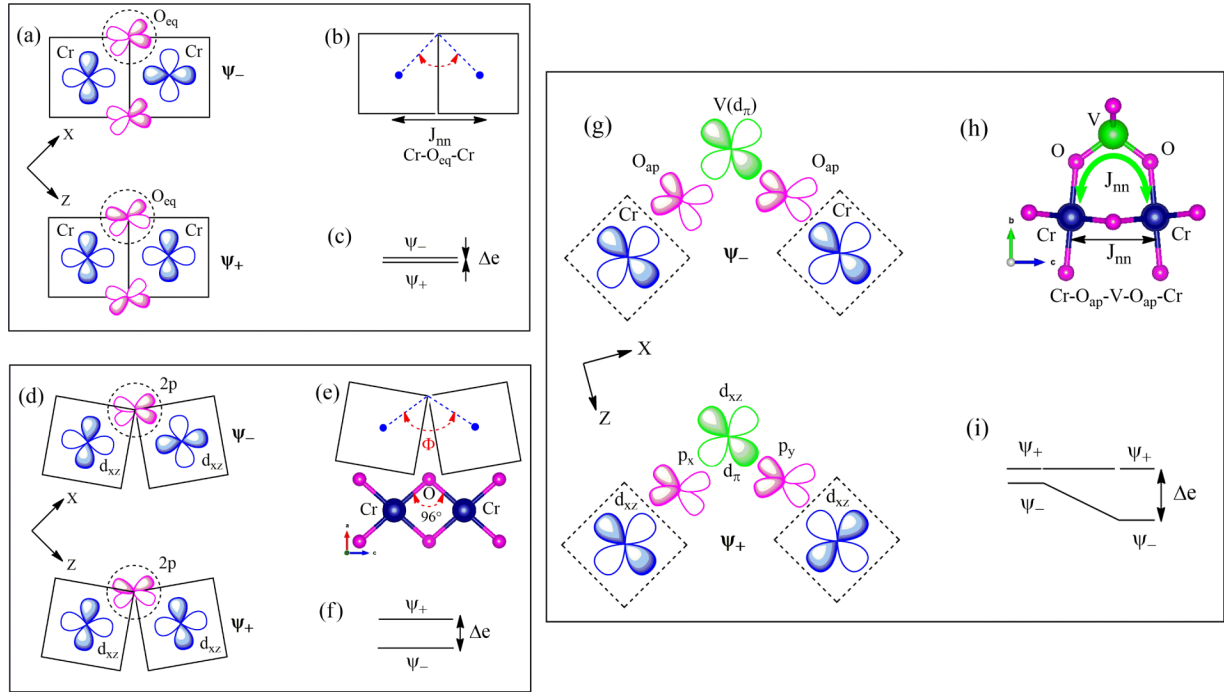


FIG. 6. (a)–(c) A Cr–O–Cr spin-exchange interaction with $\angle M-L-M$ angle $\phi = 90^\circ$ occurring in a Cr_2O_6 dimer. The symmetric (ψ_+) and antisymmetric (ψ_-) combinations of the two magnetic orbitals shown in panel (a), a Cr_2O_6 dimer, made by two edge-sharing coplanar CrO_4 square planes, shown in panel (b), and the energy split Δe between the two (ψ_+ and ψ_-) in panel (c). (d)–(f) A Cr–O–Cr spin-exchange interaction (J_1) with $\angle M-L-M$ angle $\phi > 90^\circ$ (here, $\phi = 96^\circ$). The in-phase and out-of-phase combinations of the two magnetic orbitals in panel (d), the energy split Δe between the two in panel (f), and two noncoplanar CrO_4 square planes as in panel (e). (g)–(i) The exchange interaction (J_1) between the two magnetic orbitals in the $\text{Cr-O}\cdots\text{V}^{5+}\cdots\text{O-Cr}$ spin exchange found in CrVO_4 when the $L\cdots L$ contact is bridged by a d^0 metal cation V. (g) The symmetric and antisymmetric combinations (ψ_+ and ψ_- , respectively) of the two magnetic orbitals; (i) the energy split Δe between ψ_+ and ψ_- is large when the bonding interaction O $2p$ tails of the ψ_- state with the $d\pi$ orbital of V. The detailed expressions have been presented in the text.

nearly zero where the AFM contribution is proportional to Δe . In CrVO_4 , the $\angle M-L-M$ angle deviates from 90° (approximately 96°), causing the p -orbital tails at the bridging ligands L to lose their orthogonality, resulting in a nonzero overlap integral. This leads to energy differences between the ψ_+ and ψ_- combinations of the orbitals, resulting in $\Delta e > 0$ and a nonzero contribution to J_{AFM} [Figs. 6(d)–6(f)]. The involvement of the ligand $2s$ orbital in developing AFM ordering in CrVO_4 is often overlooked for simplicity. This interaction also has an antisymmetric effect on ψ_+ , which shifts the energy of ψ_+ ($E(\psi_+)$) to higher values [Fig. 6(f)] [75]. Furthermore, the violation of GKA rule can be ascribed to the long $\text{Cr-O}_{\text{ap}}-\text{V}^{5+}-\text{O}_{\text{ap}}-\text{Cr}$ exchange pathway. The presence of bridging d^0 metal cation (V^{5+}) brings ψ_- lowers in energy through favorable overlap via p_x orbital of Cr-O_{ap} , d_{xz} orbital of V, and p_y orbital of another $\text{O}_{\text{ap}}-\text{Cr}$ [Figs. 6(g)–6(i)] while ψ_+ is unchanged. Thus, the energy separation between ψ_+ and ψ_- increases, which leads to a strong AFM exchange [59,76]. This is also in agreement with the literature study where Bansal and co-workers proposed that the transfer of an electron from p_x orbital of Cr-O_{ap} with the p_y orbital of $\text{O}_{\text{ap}}-\text{Cr}$ via bridging V leads to the AFM exchange [44]. The interaction through the V bridge might also arise from the strong covalent interaction between the O $2p$ and V $4s$ orbitals, which can be characterized by sp^3 hybridization, as demonstrated by NMR studies of ^{51}V in

CrVO_4 [32]. Similarly, ^{51}V NMR studies of the quasi-one-dimensional compound $\text{BaCu}_2\text{V}_2\text{O}_8$ have shown nonzero spin densities at the vanadium sites, indicating the involvement of VO_4 tetrahedra in both intrachain and interchain exchange interactions [77].

B. J_2 and J_3 spin exchanges

In the interchain spin exchange, two types of super-superexchange paths are identified: $\text{Cr-O}_{\text{eq}}-\text{V}^{5+}-\text{O}_{\text{ap}}-\text{Cr}$ (J_2) and $\text{Cr-O}_{\text{eq}}-\text{V}^{5+}-\text{O}_{\text{eq}}-\text{Cr}$ (J_3). In the J_2 super-superexchange path, the $\text{O}\cdots\text{O}$ contact involves different types of oxygen atoms, with one O_{eq} atom situated in the equatorial plane and another O_{ap} atom oriented along an axially elongated direction, nearly perpendicular to the equatorial plane. This configuration results in complex and relatively rare orbital-resolved exchange interactions, which are not extensively documented in the existing literature. The orbital-resolved magnetic exchange reveals that J_2 is dominated by $t_{2g}-t_{2g}-t_{2g}$ interactions where d_{yz} orbital of one Cr interacts with the d_{yz} orbital of another Cr via d_{yz} orbital of bridging V (Table SIII and Fig. S12(a) of the Supplemental Material [66]). In the $\text{Cr-O}_{\text{eq}}-\text{V}^{5+}-\text{O}_{\text{ap}}-\text{Cr}$ path, the arrangement of the two magnetic orbitals leads to nearly orthogonal p -orbital tails, resulting in a negligible total overlap integral with the $3d\pi$ of V [see Fig. S12(a) of the Supplemental Material [66]]. This results in

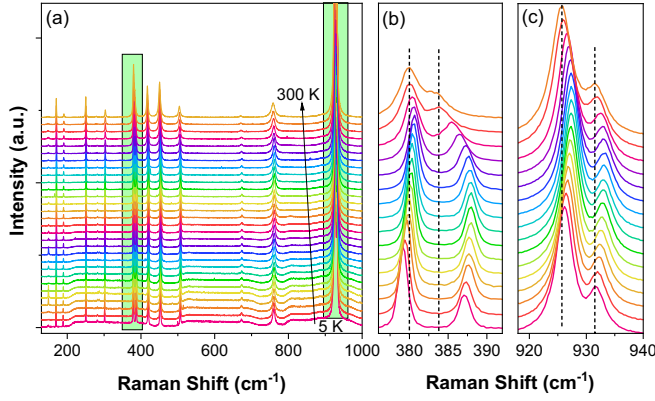


FIG. 7. (a) Temperature-dependent Raman spectra of CrVO_4 at the temperature range 5–300 K. (b), (c) Enlarged view of the regions highlighted in green in panel (a) showing the variation of peak positions as a function of temperature, indicating the signature of spin-phonon coupling.

a relatively small Δe , indicating a diminished contribution to the J_{AFM} . However, the J_{FM} interaction does not vanish, as the electron density overlap from the p-orbital tails of differently oriented oxygen atoms remains nonzero, owing to the $\text{O} \cdots \text{O}$ contact being close to the van der Waals distance [78].

In the interchain spin-exchange path J_3 , two parallel CrO_4 equatorial planes are corner shared with VO_4 tetrahedra, where the O $2p$ orbital tails of the two magnetic orbitals are well separated by the $\text{O} \cdots \text{O}$ contacts. The orbital-resolved magnetic exchange reveals that J_3 is mediated by the interaction between d_{yz} orbital of one Cr with the d_{xy} orbital of another Cr via the d_{yz} orbital of bridging V (Table SIV and Fig. S12(b) of the Supplemental Material [66]). Here, O $2p$ tails of the magnetic orbitals strongly interact with the bridging V through favorable overlap, thereby lowering the energy level of ψ_- , while ψ_+ remains unaffected by the V $3d\pi$ orbital. This interaction increases the energy split Δe between ψ_+ and ψ_- in the $\text{Cr}-\text{O}_{\text{eq}}-\text{V}^{5+}-\text{O}_{\text{eq}}-\text{Cr}$ exchange paths, consequently resulting in weak antiferromagnetic J_3 . However, the magnetic properties of CrVO_4 are predominantly influenced by the one-dimensional character of the CrO_2 ribbon chain via the J_1 exchange path, with J_2 also contributing favorably to this one-dimensional AFM chainlike behavior as observed in LiCuVO_4 [79,80].

C. Spin-phonon coupling

We have utilized temperature-dependent Raman spectroscopic data to gain a better understanding of how the local atomic structure behaves as temperature changes during a magnetic transition. Raman spectroscopy, specifically, is a technique that allows us to examine the strength of atomic interactions by studying directly the vibrations of molecules at the atomic level. By doing so, one can observe how the evolution of magnetic order is connected to alterations in the dynamics of the atomic lattice, providing valuable insights into the relationship between atomic structure and magnetic behavior with temperature. Figure 7 presents the temperature-dependent (5–300 K) Raman spectra of CrVO_4 . The data clearly indicate that the overall Raman spectral signature remains consistent across T_N , confirming the absence of any

structural phase transition and impurity phase, which aligns with the XRD measurements. The temperature-dependent Raman spectra were analyzed using a Lorentzian fitting to extract quantitative details regarding the changes observed across the transition. In general, the temperature-dependent frequency change in the phonon mode can be written as [47,81,82]

$$\Delta\omega(T) = \Delta\omega_{\text{qh}}(T) + \Delta\omega_{\text{anh}}(T) + \Delta\omega_{(\text{e-ph})}(T) + \Delta\omega_{(\text{s-ph})}(T), \quad (1)$$

where $\Delta\omega_{\text{qh}}(T)$ represents the quasi-harmonic contribution arising solely from the thermal expansion of the lattice. The change in frequency owing to intrinsic anharmonicity is given by $\Delta\omega_{\text{anh}}(T)$. $\Delta\omega_{(\text{e-ph})}(T)$ and $\Delta\omega_{(\text{s-ph})}(T)$ are the electron-phonon and spin-phonon coupling terms, respectively. The term $\Delta\omega_{\text{qh}}(T)$ is neglected here and $\Delta\omega_{(\text{e-ph})}(T)$ is absent in CrVO_4 due to the insulating nature. Therefore, the change in frequency of the phonon modes with temperature can be explained as

$$\Delta\omega(T) = \Delta\omega_{\text{anh}}(T) + \Delta\omega_{(\text{s-ph})}(T). \quad (2)$$

The behavior of anharmonic phonons with temperature, resulting from phonon-phonon interactions, offers valuable insights into the underlying physics. Consequently, the Raman shift ($\Delta\omega$) and linewidth (Γ) of selected modes as a function of temperature were fitted using an anharmonic model. The temperature dependence of the phonon frequency due to cubic anharmonicity (three-phonon process) is given by [83]

$$\Delta\omega_{\text{anh}}(T) = \omega_0 + C \left[1 + \frac{2}{e^x - 1} \right]. \quad (3)$$

Similarly, the temperature dependence of phonon linewidth due to quartic anharmonicity (four-phonon process) can be written as [83]

$$\Delta\Gamma_{\text{anh}}(T) = C \left[1 + \frac{2}{e^x - 1} \right] + D \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right], \quad (4)$$

where $x = \frac{\hbar\omega_0}{(2k_B T)}$, $y = \frac{\hbar\omega_0}{(3k_B T)}$, ω_0 is the Raman frequency at absolute zero, and C and D are cubic and quartic anharmonic coefficients for frequency (ω) and linewidth (Γ), respectively. The analysis revealed that the Raman shifts ($\Delta\omega$) of the studied modes deviate significantly from the expected anharmonic behavior when the temperature drops below approximately 80 K (T_{SR}), particularly concerning the magnetic short-range transition. However, two Raman modes associated with a combination of bending modes involving both Cr and V, along with distorted polyhedra, and bending modes with rigid polyhedra (at 190 and 302 cm^{-1}), exhibit anomalous phonon softening from the room temperature compared to the anharmonic behavior of other modes, as shown in Figs. 8(a) and 8(b). This peculiar behavior of these modes might be associated with strong intrinsic anharmonic phonon-phonon interactions in the CrVO_4 lattice along with spin-phonon coupling and merits further investigation [82,84]. Unlike other phonon modes, the cubic-anharmonic model could not explain the behavior of these modes since their frequency decreases upon cooling in the entire temperature range. For all other

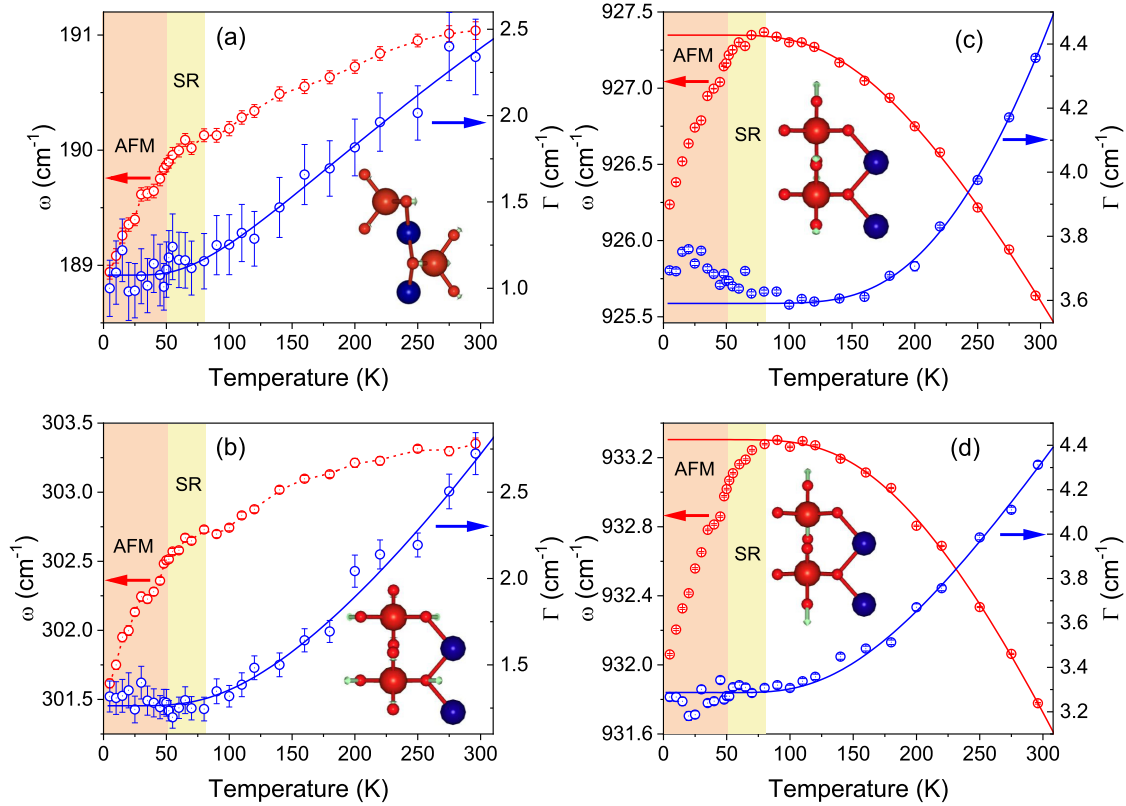


FIG. 8. The temperature dependence of Raman shifts (ω , cm^{-1}) (red) and linewidth (Γ , cm^{-1}) (blue) of selected modes corresponding to (a) A_g (190 cm^{-1}), (b) A_g (303 cm^{-1}), (c) A_g (926 cm^{-1}), and (d) B_{3g} (932 cm^{-1}). Error bars denote one standard deviation obtained from fitting. The symbols are the experimental data points, and the solid red lines in panels (c) and (d) and blue lines in panels (a)–(d) are the anharmonic models that fit ω and Γ , respectively, as described in the text. Transition temperatures are highlighted by colored regions.

modes, no discontinuity in $\Delta\omega$ and Γ was observed at 200 K, while we noted significant anomalous changes at T_N ($\simeq 50 \text{ K}$) in $\Delta\omega$ [Figs. 8(c) and 8(d), and Figs. S13 and S14 of the Supplemental Material [66]], suggesting spin-phonon coupling at the transition. To investigate the spin-phonon coupling further, we have calculated Raman frequencies from the first-principles phonon calculations. The calculations reveal that the structures are dynamically stable with temperature, as there are no negative frequencies (see phonon dispersion and projected density of states in Fig. S15 of the Supplemental Material [66]). According to group theory, CrVO_4 will have 15 Raman-active modes at Γ point ($5A_g$, $4B_{1g}$, $2B_{2g}$, and $4B_{3g}$). The temperature dependence of the frequency of the calculated Raman modes agrees well with the experimental results (see Figs. S13 and S14, and Table SV of the Supplemental Material [66]).

To further analyze the temperature-induced shifts in eigenfrequencies, we calculated the differences between the measured frequencies ($\Delta\omega_{\text{exp}}(T)$) and the predicted anharmonic behavior ($\Delta\omega_{\text{anh}}(T)$) (represented by solid red lines in Fig. 8 and Figs. S13 and S14 of the Supplemental Material [66]). These differences for selected modes are illustrated in Fig. S16 of the Supplemental Material [66]. Notably, a significant influence of spin-phonon coupling on the eigenfrequencies is observable below 80 K, driven by strong FM spin fluctuations in the interchain exchange interactions within the a - b plane, resulting in short-ranged spin-spin correlations

(generally observed in A-type AFM materials). Pronounced short-range spin fluctuations in CrVO_4 have already been revealed through magnetic susceptibility (see Fig. S17 of the Supplemental Material [66]) and NMR measurements reported in prior studies [30,32]. The results can be compared with theoretical models, where the frequency shift is expressed in terms of spin-spin correlation function $\langle S_i \cdot S_j \rangle$ between the nearest neighbors on two opposite sublattices as [45,84–87]

$$\Delta\omega_{\text{s-ph}}(T) = \frac{2}{\omega\mu} \frac{\partial^2 J}{\partial u^2} \langle S_i \cdot S_j \rangle = \lambda_{\text{sph}} S^2 \Phi(T). \quad (5)$$

In this equation, $\langle S_i \cdot S_j \rangle$ is spin-spin correlation factor (indicates the statistical average of adjacent spins), $\lambda_{\text{sph}} (= \frac{2}{\omega\mu} \frac{\partial^2 J}{\partial u^2})$ is the spin-phonon coupling coefficient, S^2 is the average of adjacent spins (here, $S^2 = \frac{9}{4}$, for $\text{Cr}^{3+} 3d^3$), and $\Phi(T) = [1 - (\frac{T}{T_{\text{SR}}})^\gamma]^\gamma$ is the normalized order parameter that is directly proportional to the average magnetization $M(T)$, where T_{SR} is short-range magnetic ordering temperature and γ is critical exponent. The calculated spin-phonon coupling coefficients (λ_{sph}) are provided in Table II. The phonon scattering can be attributed to the presence of weak spin-phonon (lattice) coupling, which becomes active even above the T_N temperature (50 K) due to the emergence of short-range magnetic ordering ($\approx 80 \text{ K}$)-induced lattice strains in the system. This finding is consistent with NMR studies of CrVO_4 , which

TABLE II. The fitting parameters of the anharmonic model fit to ω and Γ and the spin-phonon coupling coefficients (λ_{sph}) of the various Raman modes derived phenomenologically.

Assigned modes	ω (cm ⁻¹) (300 K)	ω_0 (cm ⁻¹)	C (ω)(cm ⁻¹)	C (Γ)(cm ⁻¹)	D (Γ)(cm ⁻¹)	λ_{sph} (cm ⁻¹) (Expt.)
T(B _{1g})	170	178.96 (4.35)	-8.18 (4.36)	0.94 (0.03)	-0.06 (0.03)	0.74 (0.09)
T(A _g)	191			1.13 (0.02)	-0.05 (0.02)	
R(B _{1g})	250	254.69 (0.65)	-2.98 (0.65)	0.88 (0.07)	0.08 (0.07)	0.51 (0.06)
ν_2 (A _g)	303			1.11 (0.12)	0.15 (0.13)	
R(B _{1g})	380	384.56 (1.37)	-3.89 (1.39)	0.92 (0.15)	0.36 (0.15)	0.65 (0.04)
ν_4 (B _{3g})	383	395.89 (0.44)	-7.96 (0.45)	-0.36 (0.75)	1.84 (0.76)	0.67 (0.26)
ν_2 (A _g)	417	423.13 (0.19)	-2.77 (0.20)	1.45 (0.07)	0.13 (0.08)	0.76 (0.26)
ν_4 (B _{2g})	450	459.40 (0.32)	-5.46 (0.33)	1.77 (0.05)	0.18 (0.06)	0.70 (0.05)
ν_4 (B _{3g})	504	512.19 (0.37)	-4.50 (0.39)	2.41 (0.05)	-0.01 (0.05)	0.89 (0.41)
ν_3 (B _{1g})	670	681.14 (1.86)	-7.34 (1.89)	3.35 (6.22)	1.14 (6.27)	0.61 (0.26)
ν_3 (A _g)	759	776.03 (1.67)	-14.25 (1.69)	6.88 (0.58)	0.37 (0.60)	0.69 (0.04)
ν_1 (A _g)	926	932.64 (0.35)	-5.29 (0.36)	-4.98 (1.56)	8.57 (1.56)	0.57 (0.03)
ν_3 (B _{3g})	931	940.68 (0.86)	-7.37 (0.37)	3.42 (0.19)	-0.13 (0.19)	0.67 (0.03)

reported the onset of short-range spin fluctuations at 77 K [32]. The renormalization of phonon frequencies above T_N can be explained by in-plane ferromagnetic correlations $\langle S_i \cdot S_j \rangle$, which exist even in the paramagnetic phase. Similar behavior has been observed in other A-type AFM materials, as well as in other types of manganese and vanadate materials [45]. The absence of anomalies in ω and Γ at 200 K, within the limits of instrument resolution, indicates that no significant interactions between phonons and other degrees of freedom occur below this temperature. However, the anomaly in ω and Γ at T_N can be attributed to the onset of long-range AFM ordering. This is associated with the two-ion contribution to magnetoelastic coupling through the (super)exchange interactions [45,46,88] and/or phonon scattering resulting from short-range spin fluctuations that induce lattice strains above T_N [89,90].

IV. DISCUSSION

The study of CrVO₄ using advanced computational and experimental methods reveals significant insights into its electronic structure, magnetic behavior, and spin-phonon interactions. CrVO₄ exhibits crystal field splitting of Cr³⁺ in the CrO₆ octahedral environment, despite the presence of V⁵⁺ in VO₄ tetrahedra, which was not considered in prior study [44], resulting in a splitting between t_{2g} and e_g orbitals with a splitting energy of 1.59 eV. The material exhibits valence and conduction bands primarily composed of Cr and V 3d states, with notable O 2p hybridization. Therefore, the result shows a non-negligible population of e_g orbitals due to symmetry breaking of the regular octahedral, suggesting that exchange interactions occur through both orbitals t_{2g} and e_g . The magnetic structure is governed by both intrachain (J_1) and interchain (J_2, J_3) exchange interactions. J_1 , primarily mediated by Cr–O–Cr and Cr–O–V–O–Cr pathways, remains AFM despite a Cr–O_{eq}–Cr bond angle suggesting FM coupling, due to symmetry and orbital overlap. The V⁵⁺ bridge in J_1 enhances AFM exchange through favorable orbital interactions. J_2 and J_3 involve more complex interactions through oxygen bridges, with J_2 dominated by t_{2g} – t_{2g} – t_{2g} interactions and J_3 by d_{yz} – d_{xy} interactions. J_1 is the primary contributor

to AFM behavior, driven by the one-dimensional CrO₂ chain along the c axis.

XANES and EXAFS analyses reveal that the valence states of vanadium (V⁵⁺) and chromium (Cr³⁺) remain stable across the magnetic transition and hence the Cr/V–O_n coordinations. However, notable structural changes occur in the local environment around Cr when the temperature rises above T_N . Specifically, there is an increase in the Cr–Cr interatomic distances associated with edge-sharing CrO₆ octahedra, accompanied by a decrease in the Cr–Cr mean square relative displacement σ^2 . This combination indicates a significant microstructural reconfiguration, which likely plays a critical role in modulating the superexchange interactions (J_1) within the system. Furthermore, these observations also suggest a conventional magnetoelastic response of the material rather than strong spin-orbital-lattice entanglement.

The SR-XRD analysis corroborates these findings, showing significant changes of lattice constant mainly along the c axis (and consequently in the volume) crossing T_N , while smoother effects are shown along the a and b axes. Raman spectroscopy reveals that the magnetic transitions do not correspond to structural phase transitions, but phonon modes show deviations in anharmonic behavior near T_N . This suggests that spin-phonon coupling influences the system, particularly above T_N , where short-range magnetic ordering begins. Softening of bending phonon modes involving Cr and V occurs with decreasing temperature in the whole temperature range, distinct from other phonon modes, which show anomalies near T_N . Phonon modes associated with this coupling soften as temperature decreases, contributing to the long-range AFM ordering and magnetoelastic coupling observed in the system. The magnetic and structural properties of CrVO₄ are intricately linked to spin-lattice interactions, polyhedral tilting, and spin-phonon coupling, which all play significant roles in its magnetic transition behavior. However, in our study, no anomalous change in the phonon frequencies (ω) or linewidths (Γ) of all the modes was observed at 200 K, suggesting that no significant spin-phonon coupling occurs below this temperature, within the resolution limits of our instruments.

This contrasts with the recent findings of Roy *et al.* [44], which reported orbital-driven spin-phonon coupling at 200 K (about $4T_N$) for CrVO_4 suggesting a significant influence of KK-type interactions on its electronic and phononic characteristics at temperatures up to four times the Néel temperature ($T_N = 50$ K), without any noticeable discontinuity at T_N . However, these rare and unexpected findings contrast with typical orthorhombic A-type AFM materials [45–47], which usually show phonon frequency (ω) anomalies near T_N from strong magnetoelastic coupling, often persisting above T_N due to short-range spin correlations, according to our findings. A careful examination of the Raman data reported by Roy *et al.* near T_N reveals deviations from expected anharmonic phonon behavior, suggestive of underlying spin-phonon interactions. However, this region receives limited attention in their analysis, possibly due to challenges in data quality near T_N . By focusing primarily on the higher-temperature regime (~ 200 K), their study may underrepresent potential spin-related contributions to phonon anomalies at T_N . Consequently, the observed phonon renormalization effects are attributed mainly to interactions with other degrees of freedom manifesting below 200 K, potentially overlooking a key signature of spin-lattice coupling commonly observed in correlated systems. In addition, the interpretation by Roy *et al.* assumes that the VO_4 tetrahedra in CrVO_4 suppress the conventional octahedral crystal field splitting of Cr^{3+} ions, leading to partial occupancy of both the t_{2g} and e_g orbitals. This assumption appears questionable, as it overlooks the actual crystal field environment and lacks the key microscopic mechanisms of orbital-resolved spin-exchange interactions. Therefore, our results suggest that the presence of strong orbital-selective spin-phonon coupling driven by KK-type interactions in CrVO_4 is questionable, indicating that the earlier observations may have been influenced by Cr_2O_3 impurity phase. However, in a recent study, this type of phonon behavior with temperature has been observed in the Cr_2O_3 system [91] as observed by Roy *et al.* [44] in CrVO_4 .

V. CONCLUSIONS

This study highlights the key role of orbital degrees of freedom in CrVO_4 , particularly in orbital-driven spin-exchange interactions and spin-phonon coupling at T_N . Both experimental data and first-principles calculations show spin-lattice coupling near the transition temperature (T_N), driven by magnetoelastic interactions. XAS confirms that V and Cr valence states and local coordination remain stable, while polyhedral tilting around Cr plays a critical role in magnetic transitions by affecting superexchange interactions (J_1). The magnetic results reveal a one-dimensional A-type antiferromagnetic ordering at 50 K, influenced by orbital-resolved spin-exchange interactions. Phonon softening near T_N con-

tributes to long-range AFM ordering and magnetoelastic coupling and spin-phonon coupling above T_N , driven by short-range spin fluctuations. The lack of anomalies in ω and Γ of any of the modes at $4T_N$ within instrument resolution excludes the existence of any strong orbital-selective spin-phonon coupling in CrVO_4 . These findings not only enhance our understanding of the electronic and physical properties of CrVO_4 but also offer a significant contribution to the broader field of spin-orbital-lattice physics in transition metal oxides.

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DATA AVAILABILITY

The data supporting this study's findings are available within the article.

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