

Magnetic structure and interactions in the quasi-one-dimensional antiferromagnet CaV_2O_4

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CaV_2O_4 is a spin-1 antiferromagnet, where the magnetic vanadium ions have an orbital degree of freedom and are arranged on quasi-one-dimensional zigzag chains. The first- and second-neighbor vanadium separations are approximately equal suggesting frustrated antiferromagnetic exchange interactions. High-temperature susceptibility and single-crystal neutron-diffraction measurements are used to deduce the dominant exchange paths and orbital configurations. The results suggest that at high temperatures CaV_2O_4 behaves as a Haldane chain, but at low temperatures, it is a spin-1 ladder. These two magnetic structures are explained by different orbital configurations and show how orbital ordering can drive a system from one exotic spin Hamiltonian to another.

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The magnetism of low-dimensional and frustrated systems is a current research topic. Often, such phenomena arise from the crystal structure, e.g., well-separated chains or planes of magnetic ions can lead to low-dimensional magnetism while triangular structures combined with antiferromagnetic interactions give rise to frustration (e.g., Ref. 1). More recently the role of orbitals on exchange paths has been investigated and materials where direct exchange is the dominant magnetic interaction are particularly sensitive to orbital occupation and overlap. In some cases the structure gives rise to orbital configurations and exchange interactions that could not be deduced from a simple inspection of magnetic ion separations. Recent studies of vanadium spinels suggest that geometrically frustrated systems with an orbital degree of freedom can relax frustration via orbital ordering which gives rise to preferred exchange pathways.²⁻⁶ In some cases there is a lowering of the dimensionality of the magnetism with dominant antiferromagnetic interactions coupling the magnetic moments into spin-1 chains (Haldane chains)^{2,3} or into pairs (dimers).⁶ Here we investigate CaV_2O_4 where the vanadium ions interact predominantly via direct exchange and are arranged on zigzag chains. The intrachain V-V distances are approximately equal, suggesting competing first- and second-neighbor antiferromagnetic exchange interactions. However, we find that the magnetism is more complex than this simple picture suggests and is strongly influenced by the orbital ordering of the vanadium ions.

Unlike many similar AV_2O_4 systems that are spinels, CaV_2O_4 crystallizes in the CaFe_2O_4 -type structure with orthorhombic space group $Pn\bar{m}$ at room temperature. The magnetic V^{3+} ions possess spin $S=1$ due to two unpaired electrons in the $3d$ shell and are arranged in two inequivalent (although similar) zigzag chains of slightly distorted edge-sharing VO_6 octahedra running along the crystallographic c direction (see Fig. 1).

The octahedral environment partially removes the degeneracy of the $3d$ orbitals and both electrons occupy the lower-

lying t_{2g} levels. The combination of edge-sharing octahedra which allows the overlap of t_{2g} orbitals and V-V distances of $\approx 3 \text{ \AA}$ favors direct exchange interactions.⁷ Such interactions are antiferromagnetic and highly sensitive to both orbital occupation and vanadium separation.^{7,8} Superexchange via oxygen can also contribute to the coupling; however, the V-O-V intrachain bond angles range from 92.5° to 99.3° , implying that these interactions are weak. The structure suggests chains consisting of two competing antiferromagnetic interactions, J_{zz}^n along the zigzags and J_{leg}^n along the legs where the superscript n takes the values 1 or 2 for the two inequivalent chains. The V-V distances along the zigzags and legs are the same for the two chains with $d_{zz}^1 = d_{zz}^2 = 3.08 \text{ \AA}$ and $d_{\text{leg}}^1 = d_{\text{leg}}^2 = 3.01 \text{ \AA}$, and the exchange constants should also be similar $J_{zz}^1 \approx J_{zz}^2$ and $J_{\text{leg}}^1 \approx J_{\text{leg}}^2$. The interchain coupling is weak and frustrated and occurs via superexchange interactions with V-O-V angles ranging from 122.0° to 131.2° . This material is therefore potentially a quasi-one-

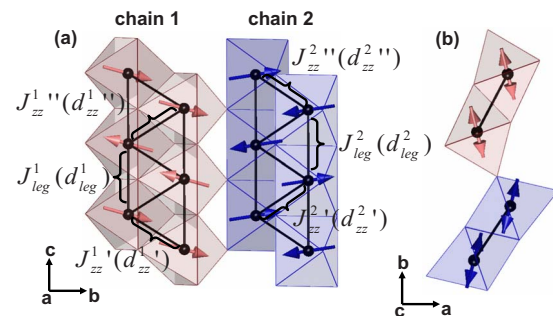


FIG. 1. (Color online) The double chain structure of CaV_2O_4 projected onto the (a) b - c and (b) a - b planes. The two inequivalent VO_6 octahedra are highlighted in pink (chain 1) and blue (chain 2). Arrows indicate the direction of the ordered moments and the intrachain exchange constants for the monoclinic phase are labeled. In the orthorhombic phase $J_{zz}^1 = J_{zz}^2 = J_{zz}^n$, $J_{\text{leg}}^1 \approx J_{\text{leg}}^2$ and $J_{\text{leg}}^1 \approx J_{\text{leg}}^2$.

dimensional (1D) spin-1 antiferromagnet with frustrated first (J_{zz}) and second (J_{leg}) neighbor interactions.

CaV_2O_4 undergoes a structural phase transition at $T_s \approx 141$ K to a monoclinic phase with space group $P2_1/n(P2_1/n11)$ resulting in $\alpha = 90.767(1)^\circ$ and a small change in lattice parameters.⁹ Below T_s , the zigzag distances become inequivalent ($d_{zz}' \neq d_{zz}''$), which lifts the degeneracy of the interactions along the zigzags so that at low temperatures, $J_{zz}' \neq J_{zz}''$ (see Fig. 1). However, a single distance d_{leg}'' and interaction (J_{leg}'') remain along the legs. The monoclinic distortion changes the V-V and V-O distances in slightly different ways for the two chains; therefore the set of interactions characterizing each chain are probably similar but not identical (see Ref. 9 and supplementary information¹⁰).

Below $T_N \approx 51$ – 78 K, CaV_2O_4 develops long-range antiferromagnetic order with a magnetic propagation vector $\mathbf{k} = (0, \frac{1}{2}, \frac{1}{2})$.^{11–15} Experimental investigations of powder and single-crystal samples using various techniques found that the ordered spin moment had a strongly reduced value of $1.0\mu_B \leq \mu \leq 1.59\mu_B$ (compared to $2\mu_B$ available for $S=1$) and that the average spin direction is along the b axis.^{11–15} The reduced ordered moment as well as a broad maximum in the dc susceptibility at $T \approx 250$ – 300 K (Refs. 13, 14, and 16) indicate low-dimensional and/or frustrated behavior. Neutron powder-diffraction experiments find a collinear spin structure at low temperatures.^{11,12} In contrast, nuclear magnetic resonance (NMR) measurements indicate that the structure consists of two collinear substructures that are canted with respect to each other.¹⁴

Herein we discuss the first single-crystal neutron diffraction and high-temperature dc susceptibility measurements on CaV_2O_4 using the samples described in Ref. 13. Remarkably the susceptibility indicates that the material behaves as a $S=1$ Heisenberg chain above T_s instead of a zigzag chain with $J_{leg} \approx J_{zz}$ as anticipated from the crystal structure. Neutron diffraction is used to determine the magnetic structure at 6 K and reveals that below T_s , the exchange interactions are those of a $S=1$ ladder. These results can be explained by two different orbital configurations at high and low temperatures and imply that orbital ordering drives the system between the two spin Hamiltonians.

The static magnetic susceptibility of CaV_2O_4 was measured over a temperature range $3 \leq T \leq 1000$ K using a vibrating sample magnetometer (Quantum Design) at the Laboratory for Magnetic Measurements, HZB. Data were collected on samples of volume ≈ 6 mm³ with a magnetic field of 1 T applied along the crystallographic axes. The background corrected susceptibility is shown in Fig. 2. The low-temperature data are in agreement with previous measurements.^{13,14} The high-temperature data ($700 \leq T \leq 950$ K) were fitted to the Curie-Weiss law giving a g factor of 1.958(4) and a paramagnetic Curie temperature of $\Theta = -418(5)$ K. This yields an effective moment of $\mu_{exp} = 2.77(18)\mu_B$, as commonly found in V^{3+} materials. In addition the sum of the magnetic exchange couplings in the orthorhombic phase, $J_{zz} + J_{leg} = -(3/2)k_B\Theta[S(S+1)]^{-1} = 27.0(4)$ meV, was obtained assuming identical chains.

To extract further information about the high-temperature exchange interactions in CaV_2O_4 , exact diagonalization cal-

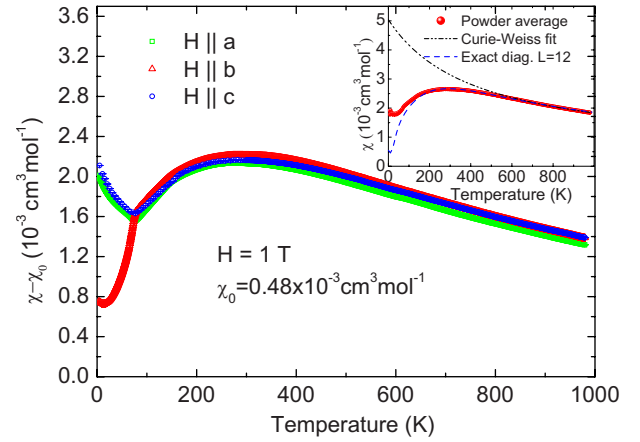


FIG. 2. (Color online) Single-crystal dc magnetic susceptibility of CaV_2O_4 for all three crystallographic directions. The inset shows the powder averaged data fitted to Curie-Weiss and exact diagonalization models.

culations for a spin-1 chain (up to 12 spins) with nearest-neighbor (J_{zz}) and next-nearest-neighbor (J_{leg}) interactions were performed.¹⁷ This model was fitted to the data in the orthorhombic phase ($200 \leq T \leq 950$ K) and the best agreement was found for $J_{zz} = 19.85(1)$ meV and $J_{leg} = 0.75(4)$ meV (inset of Fig. 2), while a second solution was found for $J_{zz} = 3.02(1)$ meV and $J_{leg} = 18.60(8)$ meV. These results show that one of the exchange interactions is much stronger than the other, rather than both being approximately equal and frustrated as expected from the crystal structure. The two solutions are in fact magnetically equivalent since either J_{zz} is dominant (single spin-1 chain) or J_{leg} is dominant (two spin-1 chains).

Single-crystal neutron-diffraction experiments were performed to obtain the low-temperature magnetic structure of CaV_2O_4 using the instruments SXD at the ISIS facility, Rutherford Appleton Laboratory, and E4 and E5 at the BER II reactor, HZB, Germany. Only the E5 measurements are reported here. E5 is a four-circle single-crystal diffractometer with a two-dimensional position-sensitive ³He detector. A pyrolytic graphite monochromator selected an incident wavelength of $\lambda = 2.36$ Å and the cylindrical sample ($d = 4$ mm, $h = 6$ mm) was cooled by a closed-cycle refrigerator. Data were collected above the structural and magnetic phase transitions at 160 K and in the antiferromagnetically ordered phase at 6 K.

The orthorhombic-monoclinic structural transition gives rise to two twin domains occupying equal volume fractions. This is observed as split contributions at the nominal Bragg positions of the orthorhombic cell with $l \neq 0$. Figure 3 shows the magnetic Bragg intensity at 6 K for $(0, \frac{1}{2}, \frac{1}{2})$ (orthorhombic notation). The two peaks could be indexed in the monoclinic setting as $(0, \frac{1}{2}, \frac{1}{2})$ from twin 1 and $(0, \frac{1}{2}, \frac{1}{2})$ from twin 2, and the large difference in their intensities is due to the difference in their magnetic structure factors. It is important for the magnetic refinement to accurately determine the intensity of the twin peaks separately; however, since the monoclinic splitting is relatively small, most of the twin pairs partially overlap, making it impossible to use conven-

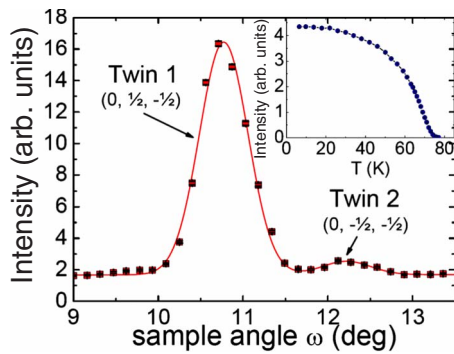


FIG. 3. (Color online) Magnetic intensity as a function of sample angle ω at the orthorhombic $(0, \frac{1}{2}, \frac{1}{2})$ position for $T=6$ K. The temperature dependence of the integrated magnetic Bragg intensity of twin 1 $(0, \frac{1}{2}, \frac{1}{2})$ is shown in the inset.

tional integration routines. Therefore manual fitting and correction was done, and by applying the twin law $(h, k, l)_{\text{Twin1}} \sim (h, -k, l)_{\text{Twin2}}$, it was possible to identify the peaks and create a separate intensity list for each. In addition, a list containing the summed intensities of both twins was created for the peaks which could not be separated. Note that due to the resolution function of neutron powder diffractometers, the splitting cannot be observed in the powder measurements,^{11,12} thus the twinned peaks are summed resulting in a significant loss of information.

The magnetic structure refinement was carried out with these three lists simultaneously using the program FULLPROF.¹⁸ As a starting point we used the two collinear solutions proposed from the previous neutron powder-diffraction work which were compatible with symmetry analysis.^{11,12} They provide good fits to our single-crystal data with magnetic residual factors of $R_F=0.13$ and 0.15 , respectively. A close inspection, however, reveals that they systematically fail to assign a nonzero intensity to the small contributions such as the $(0, \frac{1}{2}, \frac{1}{2})_{\text{Twin2}}$ peak (Fig. 3). We therefore considered canted versions of these models and found much better agreement. The best solution has a magnetic residual factor of $R_F=0.048$ and is illustrated in Fig. 1.

The spins are found to be collinear within each zigzag chain with antiparallel alignment along the legs and alternating antiparallel-parallel alignment along the zigzags. The two inequivalent chains are canted with respect to each other by equal and opposite amounts from the b axis. The total canting angle between the chains is $37(2)^\circ$ with projections in the a - b and b - c planes of $29(1)^\circ$ and $24(2)^\circ$, respectively. The refined magnetic moment sizes per V atom are strongly reduced from the expected value $\langle \mu \rangle = gS\mu_B \approx 2\mu_B$, with $0.97(1)\mu_B$ and $1.01(1)\mu_B$ for the two chains, respectively, consistent with the value of $1.06(6)\mu_B$ obtained from the powder diffraction.^{11,12} NMR measurements revealed the existence of two antiferromagnetic substructures, canted about the b axis¹⁴ by a total canting angle of $19(1)^\circ$ and the ordered spin moment was found to lie in the range 1.02 – $1.59\mu_B$. Unlike single-crystal neutron diffraction, however, NMR is unable to determine which spins form the two substructures or the relative ordering within them. Here we show that each substructure is a zigzag chain.

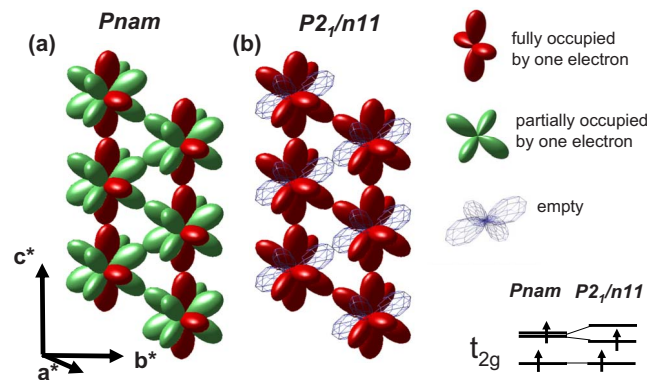


FIG. 4. (Color online) The orientation and occupancy of the vanadium t_{2g} orbitals for an example chain in the (a) high-temperature ($Pnam$) phase and (b) low-temperature ($P2_1/n11$) phase. (Lower right) t_{2g} energy-level diagram for both phases.

To gain further insight into the magnetism of CaV_2O_4 we examine the orbital occupation and direct exchange mechanism more deeply. The three t_{2g} orbitals have lobes pointing along the three intrachain directions d_{leg}^n , $d_{\text{zz}}^{n'}$, and $d_{\text{zz}}^{n''}$, respectively, which correspond to the three exchange paths J_{leg}^n , $J_{\text{zz}}^{n'}$, and $J_{\text{zz}}^{n''}$. As there are only two electrons in the $3d$ shell, it is important to know which orbitals are occupied since only filled orbitals give rise to strong antiferromagnetic exchange interactions. The degeneracy of the t_{2g} orbitals can be lifted by distortions in the VO_6 octahedra and an examination of the V-O distances can be used to deduce the orbital energy-level diagram. In CaV_2O_4 those structural distortions are less pronounced than for classical Jahn-Teller systems with e_g orbital order [e.g., LaMnO_3 (Ref. 19)]. However, magnetism and orbital physics in t_{2g} systems are very sensitive to structural changes and even small distortions can have a dramatic impact on the physics.^{20,21}

In the high-temperature orthorhombic phase of CaV_2O_4 the octahedra are compressed and the d_{leg}^n orbital (with lobes along d_{leg}^n) is shifted to lower energy while the higher-energy $d_{\text{zz}}^{n'}$ and $d_{\text{zz}}^{n''}$ orbitals are degenerate and symmetrically equivalent.¹⁰ The d_{leg}^n orbital is therefore occupied by one of the two electrons leading to a strong antiferromagnetic leg interaction J_{leg}^n , while the remaining electron will partially occupy the two degenerate d_{zz}^n orbitals so that the zigzag interactions are identical ($J_{\text{zz}}^{n'}=J_{\text{zz}}^{n''}$) and significantly weaker than J_{leg}^n .²² The predicted high-temperature orbital states are illustrated in Fig. 4(a). Our susceptibility analysis reveals that one of the intrachain exchanges is much stronger than the other although it is unable to distinguish which; this orbital arrangement combined with the slightly shorter $d_{\text{leg}}^n=3.01$ Å compared to $d_{\text{zz}}^n=3.08$ Å suggests that the dominant interaction is J_{leg}^n .

The orthorhombic-to-monoclinic transition at $T_s=141$ K gives rise to two inequivalent zigzag distances ($d_{\text{zz}}^{n'}$ and $d_{\text{zz}}^{n''}$) and exchange interactions ($J_{\text{zz}}^{n'}$ and $J_{\text{zz}}^{n''}$). In addition it further distorts the octahedra and completely lifts the orbital degeneracy. We therefore expect two of the three orbitals to be completely occupied, giving rise to two strong antiferromagnetic exchange interactions, while the remaining orbital is

unfilled resulting in no interaction. The issue is then to identify the unfilled orbital. In theory it should be possible to estimate the orbital energy-level diagram by inspecting the octahedral environment as for the orthorhombic phase; however, this is difficult because the V-O distances are all unequal and the V ions are somewhat off center.^{9,10} Instead we turn to the magnetic structure to provide the answer. Figure 1 shows that the magnetic moments coupled by J_{leg}^n and $J_{\text{zz}}^{n'}$ have an antiparallel alignment while the moments coupled by $J_{\text{zz}}^{n''}$ are parallel. This observation suggests that the leg exchange interaction (J_{leg}^n) and one of the zigzag interactions ($J_{\text{zz}}^{n'}$) are strongly antiferromagnetic while the second zigzag interaction ($J_{\text{zz}}^{n''}$) is weak. This in turn implies that the d_{leg}^n and $d_{\text{zz}}^{n'}$ orbitals are occupied, while the $d_{\text{zz}}^{n''}$ orbital is unoccupied as illustrated in Fig. 4(b). Such an arrangement where every second interaction along the zigzags is strong, combined with a strong leg exchange, is a spin-1 ladder.^{23–25}

To summarize, our investigation reveals the role played by orbital ordering in driving the spin-1 quasi-1D antiferromagnet CaV_2O_4 from one exotic spin Hamiltonian to another. High-temperature dc susceptibility combined with an inspection of the VO_6 octahedra reveal that in the orthorhombic phase, there is partial orbital degeneracy and a single exchange interaction (J_{leg}) dominates. The system can therefore be viewed as a 1D, spin-1, Heisenberg antiferromagnet or Haldane chain. The orbital degeneracy is lifted in the monoclinic phase, long-range antiferromagnetic order de-

velops, and single-crystal neutron diffraction reveals a canted magnetic structure. The structure implies that the low-temperature orbital configuration gives rise to different exchange interactions and results in an antiferromagnetic spin-1 ladder. Two other realizations of this system^{23,26} are organic, unlike CaV_2O_4 . Theory suggests that the spin-1 ladder has gapped excitations where the gap is considerably smaller than the Haldane gap ($\Delta_{\text{Haldane}}=0.41J_{\text{leg}}$), e.g., for rung couplings in the range expected for CaV_2O_4 of $0.2J_{\text{leg}} \leq J'_{\text{zz}} \leq 1.0J_{\text{leg}}$, the gap is $0.16J_{\text{leg}} \geq \Delta_{\text{ladder}(S=1)} \geq 0.08J_{\text{leg}}$.²⁴ Assuming that the low-temperature value of J_{leg} is similar to the high-temperature values obtained from susceptibility ($18 \leq J_{\text{leg}} \leq 27$ meV)—an assumption that is valid since the d_{leg}^n orbital is occupied by one electron in both structural phases—the expected gap size should lie in the range $1.5 \leq \Delta_{\text{ladder}(S=1)} \leq 4.4$ meV. This small gap value explains why CaV_2O_4 is able to order below $T_N=71$ K in the presence of weak interladder coupling. Further work is in progress including band-structure calculations to explore the low-temperature orbital splitting and inelastic neutron scattering to measure the magnetic excitation spectrum.

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