I. INTRODUCTION

Low-dimensional frustrated spin systems have rich phase diagrams arising from a complex interplay of thermal and quantum fluctuations and competing magnetic interactions at low temperatures. While spin $S = 1/2$ antiferromagnetic (AF) chains\(^1\) and odd-leg ladders\(^2,3\) have gapless magnetic excitations, $S = 1$ chains and $S = 1/2$ even-leg ladders with nearest-neighbor (NN, $J_1$) interactions exhibit a finite energy gap between the ground state and the lowest excited magnetic states. However, numerical calculations have shown that the influence of frustrating next-nearest-neighbor (NNN, $J_2$) interactions play a significant role and depending on the $J_2/J_1$ ratio, can lead to incommensurate helical spin structures which may be gapped or gapless.\(^4,5,6,7,8\) Such a system is described by the XXX Hamiltonian:\(^4\)

$$\mathcal{H} = \sum_{\rho=1}^{2} J_{\rho} \sum_{l} (S_{l}^{z} S_{l+\rho}^{z} + S_{l}^{y} S_{l+\rho}^{y} + \lambda S_{l}^{z} S_{l+\rho}^{z}),$$

(1)

where $S_{l}$ is the spin operator at the $l$th site, $J_{\rho}$ is the AF interaction between the NN ($\rho = 1$) and NNN ($\rho = 2$) spin pairs, and $\lambda$ is the exchange anisotropy. For $j \equiv J_2/J_1 > 1/4$, the classical AF chain exhibits incommensurate helical long-range ordering described by the wave vector $q = \arccos[-1/(4j)]$ and a finite vector chirality $\vec{\kappa} = S_{l} \times S_{l+1}$ which describes the sense of rotation (left or right handed) of the spins along the helix. In the large-$j$, small-$\lambda$ limit of the $S = 1$ chain, one finds a corresponding phase where spin correlations decay, as required for a one-dimensional system, although only algebraically, but chirality is still long-range ordered. This phase is called the chiral gapless phase and is seen to exist for all spin quantum numbers $S$.\(^6,7\) For smaller $j$, a chiral gapped phase is observed in the $S = 1$ chain\(^8\) with chiral long-range order and exponentially decaying spin correlations.

The above chiral phases are ground state phases of a spin system. In a related prediction, Villain suggested three decades ago that a long-range ordered vector chiral phase can exist above the Néel temperature $T_N$ of a quasi-one-dimensional spin chain system showing helical magnetic ordering below $T_N$.\(^9\) This chiral phase would have a transition temperature $T_0 > T_N$ that could be detected using heat capacity measurements.\(^2\)

The compound CaV$_2$O$_4$, containing crystallographic $V^{4+}$ spin $S = 1$ zigzag chains, has been suggested as a model experimental system to study the above chiral gapless phase.\(^10,11\) CaV$_2$O$_4$ crystallizes in the CaFe$_2$O$_4$...
structure at room temperature with the orthorhombic space group $Pnam$ and with all the atoms in distinct Wyckoff positions 4(c) $(x, y, 1/4)$ in the unit cell. As shown in Figs. 1 and 2, two zigzag chains of distorted edge- and corner-sharing VO$_6$ octahedra occur within the unit cell and run parallel to the $c$-axis, with the Ca ions situated in tunnels between the chains. Two sets of crystallographically inequivalent V atoms occupy the two zigzag chains, respectively. The VO$_6$ octahedra within a zigzag chain share corners with the octahedra in the adjacent zigzag chain. Within each zigzag chain, in order to be consistent with our theoretical modeling later in Sec. IV of the paper, the nearest neighbors are defined to be those on different legs of the zigzag chain where the NN V-V distance is 3.07 Å. The NNN V-V distance (3.01 Å) is defined to be along a leg of the zigzag chain. The similarity between these two distances in CaV$_2$O$_4$ suggests that $J_1 \approx J_2$, which would result in geometrically frustrated AF interactions in this insulating low-dimensional system.

Previous studies on polycrystalline samples of CaV$_2$O$_4$ have offered contrasting views on the nature of the magnetic ground state. Magnetic neutron diffraction measurements on CaV$_2$O$_4$ (Ref. 13) gave clear evidence for the presence of long-range antiferromagnetic ordering at 4.2 K (the temperature dependence was not studied, and the Néel temperature was not determined). A doubled magnetic unit cell along the $b$ and $c$ directions was found with AF propagation vector $(0 \pm \frac{1}{2} \pm \frac{1}{2})$ and three collinear AF models with the V ordered moments parallel to the $b$-axis were considered. Interestingly, the ordered moment was found to be 1.06(6) $\mu_B$/V atom, where $\mu_B$ is the Bohr magneton. This value is a factor of two smaller than the value $gS\mu_B = 2.0 \mu_B$/V atom expected for a spin $S = 1$ with spectroscopic splitting factor ($g$-factor).

FIG. 1: End-on (top) and inclined (bottom) views along the $c$-axis of the CaV$_2$O$_4$ structure showing the V zigzag chains with the V atoms in distorted edge- and corner-sharing octahedral coordination by oxygen.

FIG. 2: Top panel: the skeletal structure of CaV$_2$O$_4$ showing the zigzag V-V chains. The large spheres represent V atoms, the small dark spheres Ca atoms, and the small light spheres O atoms. Middle and bottom panels: cross-sections of the $b$-$c$ and $a$-$b$ planes, with the V and O atoms labeled as described in Table II. The Ca atoms have been omitted for clarity.
$g = 2$. Magnetic susceptibility measurements$^{10,11}$ showed a broad maximum at $\sim 250$ K, indicating the onset of strong short-range AF ordering in a low-dimensional spin system upon cooling. The data also showed a finite value at the lowest temperatures, indicating that an energy gap for spin excitations did not occur, consistent with the neutron diffraction measurements. However, these magnetic susceptibility data also showed a bifurcation below $\sim 20$ K between low field (100 Oe) zero-field-cooled and field-cooled measurements that was suggestive of a spin-glass-like freezing rather than long-range AF ordering. $^{51}$V nuclear magnetic resonance (NMR) measurements$^{10,11}$ showed a nuclear spin-lattice relaxation rate $1/T_1 \propto T$ at low temperatures from 2 K to 30 K, of unknown origin, but again indicating lack of an energy gap for magnetic excitations. The authors$^{10,11}$ proposed a chiral gapless ordered phase at low temperatures in accordance with theoretical predictions for a $S = 1$ frustrated XY or XXZ chain. The chiral phase implies a helical spin arrangement in contrast to the collinear spin models proposed$^{13}$ in the neutron diffraction study. Furthermore, the observation of a $^{51}$V nuclear resonance at the normal $^{51}$V Larmor frequency$^{10,11}$ at temperatures at and below 4 K is not consistent with the long-range antiferromagnetic ordering found at 4 K from the neutron diffraction measurements$^{10,11}$ since such ordering produces a very large static local magnetic field of order 20 T at the positions of the V nuclei.

In order to resolve the above inconsistencies regarding the magnetic ground state of CaV$_2$O$_4$ and to search for interesting physics in this system associated with possible geometric frustration within the zigzag spin chains, we have for the first time (to our knowledge) grown single crystals of this compound, and report herein crystal structure, static magnetization and magnetic susceptibility $\chi(T)$, ac magnetic susceptibility $\chi_{ac}(T)$, heat capacity $C_p(T)$, and anisotropic linear thermal expansion $\alpha_i(T)$ ($i = x, y, z$) measurements over the temperature $T$ range 1.8 to 350 K on polycrystalline and single crystal samples. Our $\chi(T)$ and $\chi_{ac}(T)$ measurements do not show any signature of a spin-glass transition around 20 K as previously reported$^{10,11}$ We instead observe long-range antiferromagnetic (AF) ordering at sample-dependent Néel temperatures $T_N \approx 51–76$ K.

We have recently reported elsewhere the results of $^{17}$O NMR measurements on a polycrystalline sample of CaV$_2$O$_4$ and find a clear signature of AF ordering at $T_N \approx 78$ K$^{14}$ We find no evidence of a $^{51}$V NMR signal at the normal Larmor frequency at temperatures between 4 K and 300 K, in conflict with the above previous $^{51}$V NMR studies which did find such a resonance$^{10,11}$ In single crystals, at temperatures below 45 K we do find a zero-field $^{51}$V NMR signal where the $^{51}$V nuclei resonate in the static component of the local magnetic field generated by the long-range AF order below $T_N \approx 70$ K$^{14}$ The ordered moment at 4.2 K in the crystals was estimated from the zero-field $^{51}$V NMR measurements to be $1.3(3) \mu_B/(V$ atom), somewhat larger than but still consistent with the value 1.06(6) $\mu_B/(V$ atom) from the above neutron diffraction measurements$^{13}$ An energy gap $\Delta$ for antiferromagnetic spin wave excitations was found with a value $\Delta/k_B = 80(20)$ K in the temperature range 4–45 K, where $k_B$ is Boltzmann’s constant. This energy gap was proposed to arise from single-ion anisotropy associated with the $S = 1 V^{3+}$ ion. A model for the antiferromagnetic structure at 4 K was formulated in which the magnetic structure consists of two substructures, each of which exhibits collinear antiferromagnetic order, but where the easy axes of the two substructures are at an angle of $19(1)^\circ$ with respect to each other. The average easy axis direction is along the $b$-axis, consistent with our magnetic susceptibility measurements to be presented here, and with the easy-axis direction proposed in the earlier neutron diffraction measurements$^{13}$ Our magnetic neutron diffraction studies of the antiferromagnetic structure of CaV$_2$O$_4$ single crystals are qualitatively consistent with the NMR analyses; these results together with high-temperature ($T \leq 1000$ K) magnetic susceptibility measurements and their analysis are presented elsewhere$^{15}$

We also find that CaV$_2$O$_4$ exhibits a weak orthorhombic to monoclinic structural distortion upon cooling below a sample-dependent temperature $T_S = 108–147$ K, discovered from our neutron and x-ray diffraction measurements to be reported in detail elsewhere$^{15}$ In our two annealed single crystals only, anomalies in the heat capacity and thermal expansion are also found at $T_S \approx 200$ K. From high-energy x-ray diffraction measurements reported here, we find that in one of the crystals the anomaly is most likely primarily due to the metal-insulator and structural transitions in V$_2$O$_3$ impurity phase that grows coherently in the crystal when it is annealed. In the other crystal, we still find a small anomaly in the heat capacity at $T_S$ but where the transition in the V$_2$O$_3$ impurity phase is at much lower temperature. Hence we infer that there is an intrinsic transition in our two annealed CaV$_2$O$_4$ crystals at $T_S$ with an unknown origin. We speculate that this transition may be the long-sought chiral ordering transition envisioned by Villain$^9$ that was mentioned above.

From our inelastic neutron scattering results to be published elsewhere$^{16}$ we know that the magnetic character of CaV$_2$O$_4$ is quasi-one-dimensional as might be inferred from the crystal structure. The largest dispersion of the magnetic excitations is along the zigzag chains, which is along the orthorhombic $c$-axis direction, with the dispersion along the two perpendicular directions roughly a factor of four smaller. This indicates that the exchange interactions perpendicular to the zigzag chains are roughly an order of magnitude smaller than within a chain. We therefore analyze the magnetic susceptibility results here in terms of theory for the $S = 1 J_1$-J$_2$ linear Heisenberg chain, where $J_1(J_2)$ is the (next-)nearest-neighbor interaction along the chain. With respect to the interactions, this chain is topologically the same as a zigzag chain where $J_1$ is the nearest-neighbor interaction between
spins in the two different legs of the zigzag chain and $J_2$ is the nearest-neighbor interaction between spins within the same leg. We utilize exact diagonalization to calculate the magnetic susceptibility and magnetic heat capacity for chains containing up to 14 spins $S = 1$, and quantum Monte Carlo simulations of the magnetic susceptibility and heat capacity for chains of 30 and 60 spins. We obtain estimates of $J_1, J_2/J_1$, the temperature-independent orbital susceptibility $\chi_0$, and the zero-temperature spin susceptibilities in $\text{CaV}_2\text{O}_4$ from comparison of the theory with the experimental $\chi(T)$ data near room temperature. Remarkably, we find that one of the two exchange constants is very small compared to the other near room temperature, as opposed to $J_1/J_2 \approx 1$ that is expected from the crystal structure. Thus, with respect to the magnetic interactions, the zigzag crystallographic chain compound acts instead like a linear $S = 1$ Haldane spin chain compound. In Ref. 15, we propose that partial orbital ordering is responsible for this unexpected result, and suggest a particular orbital ordering configuration. In Ref. 15, we also deduce that below $T_\textrm{S} \sim 150$ K, the monoclinic distortion results in a change in the orbital ordering that in turn changes the nature of the spin interactions from those of a Haldane chain to those of a $S = 1$ two-leg spin ladder. Here we also compare the theory for the magnetic heat capacity with the results of our heat capacity experiments. We estimate the coupling $J_\perp$ between these chains that leads to the long-range AF order at $T_N$.

The remainder of this paper is organized as follows. The synthesis and structural studies are presented in Sec. II. The magnetization, magnetic susceptibility, heat capacity and thermal expansion measurements are presented in Sec. III. In Sec. IV we consider the origin of the heat capacity and thermal expansion anomalies at $T_\textrm{S1} \approx 200$ K. We then analyze the $\chi(T)$ data in terms of the predictions of exact diagonalization calculations and quantum Monte Carlo simulations to obtain $J_1, J_2/J_1$ and $\chi_0$. Using the same $J_1$ and $J_2/J_1$ parameters, we compare the predicted behavior of the magnetic heat capacity with the experimentally observed heat capacity data. We also obtain an estimate of the interchain coupling $J_\perp$ giving rise to long-range AF order at $T_N$. A summary of our results is given in Sec. V.

II. SYNTHESIS, SINGLE CRYSTAL GROWTH, AND CRYSTAL STRUCTURE OF $\text{CaV}_2\text{O}_4$

A. Synthesis and Crystal Growth

Polycrystalline $\text{CaV}_2\text{O}_4$ was synthesized via solid state reaction by first mixing $\text{V}_2\text{O}_3$ (99.995%, MV Labs) with $\text{CaCO}_3$ (99.995%, Aithaca Chemicals) or CaO obtained by calcining the CaCO$_3$ at 1100 °C. The chemicals were ground inside a He glove-box, pressed and sintered at 1200 °C for 96 hours in flowing 4.5%H$_2$-He, as well as in sealed quartz tubes when using CaO, with interme-

diate grindings. Phase purity was confirmed by powder x-ray diffraction (XRD) patterns obtained using a Rigaku Geigerflex diffractometer with Cu Ka radiation in the angular range $2\theta = 10$–90° accumulated for 5 s per 0.02° step. Thermogravimetric analysis (TGA) at 800 °C using a Perkin Elmer TGA 7 was used to check the oxygen content by oxidizing the sample to $\text{CaV}_2\text{O}_6$. A typical oxygen content of $\text{CaV}_2\text{O}_6$ was determined, consistent with the initial stoichiometric composition $\text{CaV}_2\text{O}_4$.

$\text{CaV}_2\text{O}_4$ was found to melt congruently in an Ar arc furnace with negligible mass loss by evaporation. Therefore crystal growth was attempted by pulling a crystal from the melt in a triarc furnace (99.995% Ar) using a tungsten seed rod. The triarc furnace was custom made for us by Materials Research Furnaces, Inc. Using 15–20 g premelted buttons of $\text{CaV}_2\text{O}_4$, pulling rates of 0.2–0.5 mm/min were used to grow ingots of about 3–6 mm diameter and 3.0–4.7 cm length. The length of the ingot was limited by contraction of the molten region as power was lowered to control the crystal diameter. Obtaining a single grain was difficult because small fluctuations in the arcs coupled with high mobility of the $\text{CaV}_2\text{O}_4$ melt easily caused nucleation of new grains. Out of multiple growth runs, a reasonably large single grain section could be cut out of one of the ingots. The as-grown ingot from the triarc furnace and a single crystal isolated and aligned from it are shown in Figs. (8a) and (b), respectively. Due to the tendency for multiple nucleations in the triarc furnace, an optical floating zone (OFZ) furnace was subsequently used for crystal growth. Growth rates and Ar atmosphere flow rates were optimized to successfully grow large crystals of 4–5 mm diameter and 4–5 cm length starting from sintered polycrystalline rods with masses of 8–10 g. An as-grown rod from the OFZ furnace is shown in Fig. (8c).

Powder XRD of crushed sections from the triarc grown ingots as well as from the OFZ grown crystals showed single phase $\text{CaV}_2\text{O}_4$. Laue x-ray diffraction patterns of a single-grain section confirmed its single-crystalline character and the crystal was found to grow approximately along its crystallographic c-axis. The crystals were oriented and cut to obtain faces aligned perpendicular to the principal axes. They were measured as grown (only for the triarc grown crystals) as well as after annealing in flowing 5%H$_2$-He gas at 1200 °C for up to 96 hours.

B. Powder and Single Crystal X-ray and Neutron Diffraction Measurements

Rietveld refinements of the powder x-ray diffraction data obtained at room temperature were carried out using the program DBWS9807. The refined powder XRD patterns from a polycrystalline sample and crushed pieces of the triarc and optical floating zone grown crystals are shown in Fig. 4 and the refinement results are presented in Tables II and III. The XRD of the powdered
were measured with a two-dimensional position sensitive detector, 90 mm × 90 mm in area. The sample was mounted in a closed-cycle refrigerator, where the temperature was controlled between 290 K and 6 K. A structural phase transition at temperature \( T_S \) from the high temperature orthorhombic structure to a low temperature monoclinic structure was found. This transition is reflected in Fig.\( \text{E} \) by a sudden change in the (0 3 1) Bragg peak intensity which occurs at a temperature \( T_S \approx 112 \text{ K} \) for the as-grown triarc crystal, and \( \approx 141 \text{ K} \) and \( \approx 147 \text{ K} \) for the annealed triarc and OFZ-grown crystals, respectively. Due to twinning the orthorhombic (0 3 1) reflection splits below the structural phase transition into the (0 3 1) and (0 3 1) monoclinic reflections. The total integrated intensity at this position increases at \( T_S \) because of the increased mosaic which results in a reduction of the extinction effect. The peak in the intensity at 105 K for the as-grown triarc crystal is an experimental artifact due to multiple scattering. The lattice parameters of the low temperature monoclinic phase differ very little from the orthorhombic phase and the monoclinic angle \( \alpha \approx 89.3^\circ \) is close to 90\(^\circ\). This result and the smoothly varying signatures in the thermodynamic properties suggest that the structural transition is of second order and involves a small distortion of the orthorhombic structure. Full details of the neutron and x-ray diffraction structural measurements and results will be presented elsewhere.

A higher temperature anomaly in the temperature dependence of the lattice parameters of a powder sample was observed by x-ray diffraction over a temperature range of 175–200 K. This transition with \( T_{S1} \approx 200 \text{ K} \) was also observed in the magnetic susceptibility, thermal expansion, and heat capacity measurements of two annealed single crystals as described in Sec. III below. In the next section we investigate whether there is a structural aspect to this phase transition.

### C. High Energy X-ray Diffraction Measurements on Annealed \( \text{CaV}_2\text{O}_4 \) Single Crystals

In order to unambiguously determine the crystallographic structure of \( \text{CaV}_2\text{O}_4 \) at various temperatures, to characterize structural phase transitions, and to check the crystal perfection, high-energy x-ray diffraction measurements (\( E = 99.43 \text{ keV} \)) using an area detector were performed on two annealed single crystals at the Advanced Photon Source at Argonne National Laboratory. At this high energy, x-rays probe the bulk of a crystal rather than just the near-surface region and, by rocking the crystal about both the horizontal and vertical axes perpendicular to the incident x-ray beam, an extended range of a chosen reciprocal plane can be recorded. For these measurements, a crystal was mounted on the cold-finger of a closed-cycle refrigerator surrounded by the heat shield and vacuum containment using Kapton windows to avoid extraneous reflections associated with Be or the aluminum housing. Two orientations of the crystal, with either the [001] or [100] direction parallel to the incident beam, were studied allowing the recording of the (hk0) or (0kl) reciprocal planes. For each data set, the horizontal angle, \( \mu \), was scanned over a range of

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**FIG. 3:** Single crystals of \( \text{CaV}_2\text{O}_4 \) grown using (a), (b) a triarc furnace (a numbered division on the scale is 1 mm) and (c) an optical floating zone furnace (compared with a U.S. penny).
TABLE I: Structure parameters at room temperature for CaV$_2$O$_4$ forming in the CaFe$_2$O$_4$ structure, refined from powder XRD data. Space Group: Pnam (#62); Z = 4; Atomic positions: 4(c), (x, y, 1/4); Profile: Pseudo-Voigt. The overall isotropic thermal parameter $B$ is defined within the temperature factor of the intensity as $e^{-2B \sin^2 \theta/\lambda^2}$.

| Sample  | Synthesis                  | $a$ (Å) | $b$ (Å) | $c$ (Å) | $B$ (Å$^2$) | $R_{wp}$ (%) | $R_p$ (%) |
|---------|----------------------------|---------|---------|---------|-------------|-------------|-----------|
| an-2-116 | 1200 °C solid state          | 9.2064(1) | 10.6741(1) | 3.0090(1) | 2.33(4)    | 11.17       | 8.24      |
| an-2-50  | Triarc as grown             | 9.2241(11) | 10.6976(13) | 3.0046(1) | 1.72(5)    | 12.05       | 9.27      |
| an-2-50  | Triarc annealed 1200 °C     | 9.2054(3) | 10.6748(3) | 3.0042(1) | 1.58(5)    | 14.54       | 10.95     |
| an-3-074 | OFZ annealed 1200 °C        | 9.2089(2) | 10.6774(3) | 3.0067(1) | 0.75(5)    | 17.46       | 12.77     |

TABLE II: Atomic positions ($x, y, 1/4$) for CaV$_2$O$_4$ obtained by Rietveld refinement of powder XRD data at room temperature for four samples.

| Sample Number | Synthesis                  | $x, y$ | $x, y$ | $x, y$ | $x, y$ |
|---------------|----------------------------|---------|---------|---------|---------|
| an-2-116      | Solid State (1200 °C)      | 0.7550(3), 0.6545(2) | 0.7562(4), 0.6536(3) | 0.7542(4), 0.6544(3) | 0.7536(4), 0.6550(3) |
| an-2-50-c1    | Triarc (as grown)         | 0.4329(2), 0.6117(1) | 0.4320(3), 0.6120(2) | 0.4336(3), 0.6120(2) | 0.4331(3), 0.6114(2) |
| an-2-50-c1    | Triarc (annealed)$^a$     | 0.2083(6), 0.1615(5) | 0.2128(8), 0.1593(7) | 0.2049(8), 0.1603(8) | 0.2074(9), 0.1635(9) |
| an-3-074      | Triarc (annealed)$^a$     | 0.5190(7), 0.7823(5) | 0.5153(11), 0.7812(7) | 0.5166(0), 0.7806(7) | 0.5169(11), 0.7797(8) |

$^a$Two-phase sample containing $\sim 1\%$ V$_2$O$_3$ as determined from Rietveld refinement.

TABLE III: Bond angles V–O–V and bond lengths V–V for CaV$_2$O$_4$ at room temperature refined from powder XRD data and calculated using Atoms for Windows, version 5.0. The V$_1$–O and V$_2$–O bond lengths varied from 1.92 Å to 2.08 Å. The accuracy of the bond angles calculated is ±0.1 °.

| Sample Number | Synthesis                  | $V_1$–O$_1$–$V_1$ (NN)$^a$ | $V_1$–O$_4$–$V_1$ (NN)$^a$ | $V_1$–V$_1$ (NN)$^a$ | $V_1$–O$_3$–V$_1$ (NNN)$^b$ | $V_2$–O$_2$–V$_2$ (NN)$^a$ | $V_2$–O$_3$–V$_2$ (NN)$^a$ | $V_2$–V$_2$ (NN)$^a$ | $V_2$–O$_3$–V$_2$ (NN)$^b$ | $V_1$–V$_2$ (Å)$^a$ | $V_1$–O$_1$–V$_2$ (Å)$^a$ | $V_1$–V$_2$ (Å)$^b$ | $V_1$–O$_3$–V$_2$ (Å)$^b$ | $V_1$–V$_2$ (Å)$^b$ |
|---------------|----------------------------|--------------------------|--------------------------|------------------------|-----------------------------|--------------------------|--------------------------|------------------------|--------------------------|------------------|---------------------|------------------|----------------------|------------------|
| an-2-116      | Sintered powder (1200 °C)  | 93.9                      | 93.6                      | 3.009                  | 99.3                         | 93.1                      | 96.8                      | 3.009                  | 97.3                      | 3.058             | 121.7               | 3.583            | 131.6               | 3.647            |
| an-2-50-c1    | Triarc (as grown)         | 92.9                      | 93.0                      | 3.005                  | 99.9                         | 93.0                      | 95.6                      | 3.005                  | 98.0                      | 3.058             | 122.9               | 3.588            | 132.2               | 3.652            |
| an-2-50-c1    | Triarc (annealed)$^a$     | 95.0                      | 94.4                      | 3.004                  | 101.8                        | 93.7                      | 97.5                      | 3.004                  | 97.1                      | 3.055             | 121.8               | 3.582            | 132.2               | 3.652            |
| an-3-074      | Optical float zone        | 3.077                      | 3.071                      | 3.004                  | 3.004                        | 3.071                      | 3.075                      | 3.004                  | 3.004                      | 3.055             | 121.0               | 3.589            | 132.2               | 3.643            |

$^a$Interchain angles and distances parallel to $a$-axis

$^b$Interchain angles and distances parallel to $b$-axis
FIG. 4: Rietveld refinement of room temperature powder XRD data of CaV$_2$O$_4$ showing $I_{\text{obs}}$ (+), $I_{\text{calc}}$ (.), difference (–), and peak positions (·) for (a) a polycrystalline sample, (b) an as-grown triarc crystal, (c) an annealed triarc crystal, and (d) an annealed optical floating zone (OFZ) crystal. The annealed single crystal samples contain small XRD peaks from $\sim 1–2$ mol% of V$_2$O$_3$, shown as the lower sets of peak position markers.

FIG. 5: Temperature variation of intensity of the (0 3 1) structural Bragg peak across the orthorhombic to monoclinic structural transition temperature ($T_S$) in single crystal samples of CaV$_2$O$_4$ measured by neutron diffraction. The (0 3 1) peak is present in both the orthorhombic and monoclinic phases.

$\pm 2.4$ deg for each value of the vertical angle, $\eta$, between $\pm 2.4$ deg with a step size of 0.2 deg. The total exposure time for each frame was 338 sec. The x-ray diffraction patterns were recorded with different intensities of the incident beam that were selected by attenuation to increase the dynamic range to a total of $10^7$ counts. A beam size of 0.3 x 0.3 mm$^2$ was chosen to optimize the intensity/resolution condition and to allow probing different sections of the crystal by stepwise translations of the crystal in directions perpendicular to the incident beam.

1. Annealed Triarc-Grown Crystal

Figure 6 shows the (hk0) diffraction plane of the annealed triarc sample an-2-50-c1 at 205 K. The reciprocal space image reveals well-defined diffraction spots that correspond to the “primary” CaV$_2$O$_4$ lattice, as well as spots that can be indexed to an impurity phase inclusion of V$_2$O$_3$ coherently oriented with respect to the CaV$_2$O$_4$. No additional reflections were observed. Indeed, we find two coherent twins of V$_2$O$_3$ related by an inversion across a mirror plane of the CaV$_2$O$_4$ lattice as depicted by the black and white rectangles in the left panel of Fig. 6. By comparing the integrated intensities of reflections from the two phases, we estimate that V$_2$O$_3$ comprises a volume fraction of approximately 1–2 percent of the sample. This is in excellent agreement with the result of the x-ray diffraction analysis of the polycrystalline sample prepared from the same annealed crystal that was described above. The volume fraction of V$_2$O$_3$ varies only slightly in different parts of the crystal probed by scanning the x-ray beam over the crystal. This indicates that the inclusions of V$_2$O$_3$ are approximately equally distributed over the volume of the crystal.

Upon lowering the temperature of the crystal to 165 K, below $T_{S1} \sim 200$ K, we observe changes in the V$_2$O$_3$ structure consistent with the known first-order rhombohedral-to-monoclinic structural transition at 170 K (measured on heating). In particular, the upper left corners of both panels of Fig. 6 show enlarged
views of the region near the (380) reflection from CaV$_2$O$_4$ and the (220) reflection (in hexagonal notation) for the rhombohedral lattice of V$_2$O$_3$. Below $T_{S1}$, the (220) reflection splits into three reflections in the monoclinic phase. The temperature dependence of this transition is displayed in Fig. 7. Here, we note that there is a finite range of coexistence between the rhombohedral and monoclinic phases of V$_2$O$_3$ (see the inset to Fig. 7) and the transition itself has a hysteresis of roughly 5–10 K.

Several points regarding Figs. 6 and 7 are relevant to our interpretation of the specific heat and thermal expansion measurements of the annealed triarc crystal (an-2-50-c1) to be presented below in Figs. 15 and 16 respectively. First, we note that over the temperature range 50–1 to be presented below in Figs. 15 and 16, respectively. The annealed triarc crystal (an-2-50-c1) was reoriented so that the CaV$_2$O$_4$ O$_4$ crystal (an-2-50-c1), oriented with the (hk0) plane coincident with the scattering plane at $T = 205$ K (left panel) and 165 K (right panel). The white circles in the lower center of each pattern depict the excluded areas around the primary x-ray beam direction. Several peaks corresponding to the main phase, CaV$_2$O$_4$, as well as the coherently oriented second phase, V$_2$O$_3$, are labeled by indices (hkl) and (hkl)$^*$, respectively. For V$_2$O$_3$, the hexagonal Miller indices for the rhombohedral lattice are used. The insets of both panels display enlarged regions of the diffraction pattern to highlight the rhombohedral-to-monoclinic transition for V$_2$O$_3$.

For the low-temperature monoclinic phase of CaV$_2$O$_4$ two possible space groups have been considered\textsuperscript{22} The space groups $P\ 2_1/n\ 1\ 1$ and $P\ n\ 1\ 1$ can be separated by testing the occurrence or absence of (0k0) reflections with $k$ odd, respectively. The systematic absence of such reflections was proven by recording (hkl) planes with varying conditions to evaluate the sporadic occurrence of these reflections by Rengers or multiple scattering. The space group $P\ 2_1/n\ 1\ 1$ is confirmed for the low-temperature phase of the studied CaV$_2$O$_4$ crystal. No changes in the diffraction pattern were observed related to the onset of antiferromagnetic order in CaV$_2$O$_4$ below $T_N = 69$ K.

The details of the orthorhombic-to-monoclinic transition at $T_S$ for CaV$_2$O$_4$ are shown in Fig. 8 where we plot the monoclinic distortion angle as a function of temperature. The monoclinic angle was determined from the splitting of the peaks along the b-direction through the position of the (042) reflection. Below $T_S = 138(2)$ K, the monoclinic angle evolves continuously, consistent with a second order transition, and saturates at approximately 89.2 deg at low temperatures.
FIG. 7: Integrated intensity of selected reflections in the high-energy x-ray diffraction pattern related to the rhombohedral (top panel) and monoclinic (bottom panel) phases of $\text{V}_2\text{O}_3$ as a function of temperature for the annealed triarc crystal (an-2-50-c1). The direction of the temperature change is indicated by arrows. The inset displays the pattern observed at 180 K (with increasing temperature) for the (220) reflection from $\text{V}_2\text{O}_3$ in the coexistence temperature range. This region is the same as that displayed in the insets of Fig. 6.

2. Annealed OFZ-Grown Crystal

The annealed optical floating zone crystal (an-3-074 OFZ) shows a diffraction pattern similar to that of the annealed triarc-grown crystal (an-2-50-c1) in measurements of $(hk0)$ planes at room temperature. The observed $\text{V}_2\text{O}_3$ inclusions are again coherently oriented with respect to the Ca$\text{V}_2\text{O}_4$ lattice. The intensities of the diffraction peaks related to $\text{V}_2\text{O}_3$ are similar to those in the annealed triarc crystal (an-2-50-c1) and also vary only slightly upon scanning different spots of the crystal which indicates a homogeneous distribution of the $\text{V}_2\text{O}_3$ inclusions with a similar volume fraction. However, the temperature dependence of the diffraction pattern is different for the two crystals. Measurements taken on cooling show that in the annealed floating-zone crystal (an-3-074 OFZ), the shape and position of the peaks originating from $\text{V}_2\text{O}_3$ are stable from room temperature down to 130 K where the onset of the structural transition occurs. Around 120 K strong changes are observed similar to the observations around 180 K in the annealed triarc crystal (an-2-50-c1). Below 110 K, the transition to the low-temperature monoclinic structure of $\text{V}_2\text{O}_3$ is complete. Therefore, the temperature for the rhombohedral-to-monoclinic transition is reduced by $\sim 60$ K compared to the corresponding temperature in the annealed triarc crystal (an-2-50-c1).
III. MAGNETIZATION, MAGNETIC SUSCEPTIBILITY, HEAT CAPACITY AND THERMAL EXPANSION MEASUREMENTS

In the following, we describe our results of magnetization, magnetic susceptibility, heat capacity, and thermal expansion measurements of both polycrystalline and single crystal samples. These and additional measurements consistently identify temperatures at which the antiferromagnetic transition ($T_N$), the orthorhombic-to-monoclinic structural transition ($T_S$), and the transition temperature at $\sim$ 200 K ($T_{S1}$) occur in these samples. In Table IV, we summarize these transition temperatures for the different samples obtained using the various measurements.

### A. Magnetization and Magnetic Susceptibility Measurements

The static magnetic susceptibility versus temperature $\chi(T) \equiv M(T)/H$ of a polycrystalline sample as well as of the oriented crystals was measured using a Quantum Design MPMS SQUID magnetometer in a 1 T field from 1.8 K to 350 K, where $M$ is the magnetization of the sample and $H$ is the magnitude of the applied magnetic field. In addition, low field (100 Oe) zero-field-cooled and field-cooled ($zfc$, $fc$) measurements of $M(T)$ at fixed $H$ were carried out from 1.8 K to 100 K. A Quantum Design MPMS ac SQUID magnetometer was used to measure the ac susceptibility $\chi_{ac}(T)$ of the annealed triarc grown crystal from 5 to 100 K in an ac field $H_{ac} = 1$ Oe and frequency 10 Hz. The powder was contained in polycarbonate capsules mounted in clear plastic straws. Each crystal was glued to a small piece of clear plastic transparency sheet with GE 7031 varnish or Duco cement, which was then aligned inside the plastic straws with the $a$, $b$ or $c$ axis direction parallel to the external magnetic field. $M(H)$ isotherms were measured in fields up to $H = 5.5$ T at various temperatures.

The $\chi(T)$ in $H = 1$ T is plotted in Fig. 10 for a CaV$_2$O$_4$ polycrystalline sample and for aligned single crystals grown using a triarc furnace and using an optical floating zone (OFZ) furnace. Each crystal was cooled (zfc, fc) measurements of $\chi$, magnetic susceptibility $\chi$ (peak of $d(\chi T)/dT$), heat capacity $C_p$ (peak of $\Delta C_p$), thermal expansion $\alpha$ (peak of $\alpha(T)$), except for $T_S$ where the onset of $\alpha$ slope change is used], powder synchrotron x-ray diffraction (XRD), single crystal neutron diffraction (ND), and single crystal high-energy x-ray diffraction (HEXRD) measurements for polycrystalline (powder) and single crystal CaV$_2$O$_4$ samples. The single crystals were grown using either a triarc furnace or an optical floating zone (OFZ) furnace.

| Sample     | Synthesis   | Method   | $T_N$ (K) | $T_S$ (K) | $T_{S1}$ (K) |
|------------|-------------|----------|-----------|-----------|--------------|
| an-2-116   | powder      | XRD      | 76        | 147       |              |
|            | 1200 °C     |          | 75        | 144       |              |
|            |             | XRD      |           | 150       | 200          |
| an-2-50    | Triarc crystal | $\chi$ | 51        | 108       |              |
|            | as-grown    | $C_p$    | 51        | 108       |              |
|            |              | ND       | 53        | 112       |              |
| an-2-50    | Triarc crystal | $\chi$ | 68        | 133       | 195          |
|            | annealed 1200 °C | $C_p$ | 68        | 133       | 193          |
|            |              | $\alpha$ | 68        | 136       | 198          |
|            |              | ND       | 69        | 141       |              |
|            |              | HEXRD    | 138(2)    | 192(7)$^c$|              |
| an-3-074   | OFZ crystal | $\chi$  | 69        | 136       | 192          |
|            | annealed 1200 °C | $C_p$ | 71        | 132       | 191          |
|            |              | ND       | 69        | 147       |              |

$^a$No clear signature of a transition corresponding to $T_{S1}$ was observed.

$^b$Not measured for this sample.

$^c$The error bar reflects the hysteresis on warming and cooling.
FIG. 10: Magnetic susceptibility $\chi$ versus temperature in a field of 1 T of CaV$_2$O$_4$ (a) polycrystalline sample, (b) as-grown triarc-grown single crystal, (c) annealed triarc-grown single crystal, and (d) annealed OFZ-grown single crystal. The axes ($a$, $b$, or $c$) along which the measurements were carried out are as indicated. The insets show $d(\chi(T))/dT$ versus $T$ to highlight the transition temperatures. The oscillatory behavior of $d(\chi(T))/dT$ at the higher temperatures, most pronounced in the inset in (b), is an artifact generated by the SQUID magnetometer.

FIG. 11: Zero-field-cooled and field-cooled susceptibility of CaV$_2$O$_4$ in a field of 100 Oe measured on (a) polycrystalline powder, (b) unannealed triarc grown single crystal (c) annealed triarc grown single crystal, and (d) annealed OFZ grown single crystal. Part (c) also shows the ac-susceptibility $\chi^\prime_{ac}(T)$ along the easy $b$-axis of the annealed crystal measured in a field $H_{ac} = 1$ Oe at a frequency of 10 Hz. The antiferromagnetic transition temperatures $T_N$ are marked as shown.

small anisotropies which typically showed $\chi_b > \chi_a > \chi_c$. However, occasionally variations of $\pm5\%$ in the absolute value of $\chi_i(T)$ were observed between different runs for the same crystal axis $i$ that we attribute to sample size and positioning effects (radial off-centering) in the second order gradiometer coils of the Quantum Design MPMS SQUID magnetometer.\textsuperscript{26,27}

The ordering temperatures observed are marked by vertical arrows in Fig. 10 and are highlighted in the plots of $d(\chi(T))/dT$ versus $T$ shown in the insets. The various transition temperatures are summarized in Table IV. As is typical for a low-dimensional antiferromagnetic system, the polycrystalline sample shows only a very weak cusp at $T_N = 76$ K due to averaging over the three principal...
axis directions, but it is still well-defined as observed in the $d(\chi(T))/dT$ vs $T$ plot shown in the inset of Fig. 11(a).

In a related study, $^{17}$O NMR measurements on a polycrystalline sample of $^{17}$O-enriched CaV$_2$O$_4$ gave a clear signature of antiferromagnetic ordering at 78 K. In contrast to the polycrystalline sample, the as-grown crystal in Fig. 10(b) shows a clear and distinct antiferromagnetic ordering temperature but with a much lower value $T_N \approx 51$ K. After annealing the crystals, Figs. 10(c) and 10(d) show that $T_N$ increases to $\approx 69$ K, closer to that observed in the polycrystalline sample. However, the powder average of the annealed single crystal susceptibility below $T_N$ does not match the susceptibility of the polycrystalline sample. The reason for this disagreement is unclear at this time. In any case the slow upturn in the susceptibility of the powder sample below 40 K in Fig. 10 is evidently intrinsic, due to the powder average of the anisotropic susceptibilities, and is not due to magnetic impurities.

The zero-field-cooled (zfc) and field-cooled (fc) $\chi(T)$ measured in a field of 100 Oe for polycrystalline and single crystal samples of CaV$_2$O$_4$ are plotted in Figs. 11(a)–(d). Also shown in Fig. 11(c) is the real part of the ac susceptibility $\chi'_ac(T)$ along the easy $b$-axis direction of the annealed triarc crystal measured in an ac field of amplitude 1 Oe at a frequency of 10 Hz. A small irreversibility is observed in Fig. 11 in all samples between the zfc and fc susceptibilities below $\sim 30$ K. However, the $\chi'_ac(T)$ measurement in Fig. 11(c) does not show any peak in that temperature region, ruling out spin glass-like spin freezing which was suggested to occur in powder samples from earlier reports. The slight irreversibility observed may be associated with antiferromagnetic domain wall effects.

In Fig. 12 we show isothermal $M(H)$ measurements up to $H = 5.5$ T at 1.8 K for the polycrystalline sample and for the annealed triarc-grown single crystal. The behavior is representative of all samples measured.

We find that $M$ is proportional to $H$ at fields up to at least $\sim 2$ T, indicating the absence of any significant ferromagnetic impurities and the absence of a ferromagnetic component to the ordered magnetic structure.

### B. Heat Capacity Measurements

The heat capacity $C_p$ versus temperature $T$ of a sintered polycrystalline pellet of CaV$_2$O$_4$ as well as of crystals (as-grown and annealed) was measured using a Quantum Design PPMS system at $T = 1.8$ to 200–300 K in zero applied magnetic field. The $C_p(T)$ was also measured of a polycrystalline sintered pellet of isostructural nonmagnetic CaSc$_2$O$_4$ whose lattice parameters and formula weight are very similar to those of CaV$_2$O$_4$. The CaSc$_2$O$_4$ sample was synthesized from Sc$_2$O$_3$ (99.99%, Alfa) and CaCO$_3$ (99.995%, Aithaca) by reacting a stoichiometric mixture in air at 1000 °C for 24 hr and then at $1200 ^\circ$C for 96 hr with intermediate grindings, and checked for phase purity using powder XRD.

In Fig. 13 we plot the measured $C_p(T)$ of four CaV$_2$O$_4$ samples and of isostructural nonmagnetic CaSc$_2$O$_4$. The difference $\Delta C_p$ versus $T$ for the four CaV$_2$O$_4$ samples is plotted in Fig. 14(a). Here $\Delta C_p$ is the difference between the heat capacity of CaV$_2$O$_4$ and that of CaSc$_2$O$_4$, but where the temperature axis of $C_p$ for CaSc$_2$O$_4$ was multiplied by a scaling factor to take account of the difference in the formula weights of CaV$_2$O$_4$ and CaSc$_2$O$_4$. This factor is given by $[M_M(CaSc_2O_4)/M_M(CaV_2O_4)]^{1/2}=0.9705$ where $M_M$ is the molar mass of the respective compound. If the lattice heat capacity of CaV$_2$O$_4$ and the (renormalized) heat capacity of CaSc$_2$O$_4$ had been the same, the difference $\Delta C_p(T)$ would presumably have been the magnetic heat...
The entropy versus temperature associated with the \( \Delta C_p(T) \) data of each sample in Fig. 14(a) is shown in Fig. 15, obtained by integrating \( \Delta C_p(T) \) over temperature. This figure shows the same data as in Fig. 14(a) except for vertical offsets to separate the data sets. The symbol \( T_N \) labels the long-range antiferromagnetic transition and \( T_S \) labels the high temperature orthorhombic to low temperature monoclinic structural transition. An additional transition at \( T_M \sim 200 \) K is seen in the two annealed single crystals. The small anomaly for the AFZ crystal and for the triarc crystal that rides on top of the broader peak appear to be intrinsic to CaV\(_2\)O\(_4\). The broad peak in the latter crystal appears to be due to coherently grown V\(_2\)O\(_3\) impurity phase that grows during annealing (see text).

The entropy versus temperature associated with the \( \Delta C_p(T) \) data of each sample in Fig. 14(a) is shown in Fig. 15(b), obtained from \( \Delta S(T) = \int_0^T [\Delta C_p(T)/T] dT \). In Fig. 15(b), \( \Delta S \) is normalized by the entropy \( 2R\ln(2S+1) = 2R\ln(3) \) for two moles of fully disordered spins \( S = 1 \), where \( R \) is the molar gas constant. As noted above, at least at low temperatures, we associate \( \Delta S(T) \) with the magnetic entropy of the system. At the antiferromagnetic ordering temperature \( T_N \), the normalized value of \( \Delta S(T_N)/2R\ln(3) \approx 6-8\% \) is very small and is about the same for all samples. This small value indicates that short-range antiferromagnetic ordering is very strong above \( T_N \) and the data in Fig. 15(b) indicate that the maximum spin entropy of the system is not attained even at room temperature. This is qualitatively consistent with our estimate \( J_1 \approx 230 \) K obtained below in Sec. 11 by comparison of our \( \chi(T) \) data with calculations of \( \chi(T) \).

The small observed magnetic entropy at \( T_N \) is consistent with the values of the heat capacity discontinuities \( \Delta C_{AF} \) at \( T_N \) in Fig. 15 as follows. In mean field theory,
for a system containing $N$ spins $S$ the discontinuity in the magnetic heat capacity at the ordering temperature for either ferromagnetic or antiferromagnetic ordering is predicted to be

$$\Delta C_{AF} = \frac{5}{2}N k_B (2S + 1)^2 - 1 \left(\frac{2S + 1)^2}{2S + 1}\right).$$

where $N$ is the number of spins and $k_B$ is Boltzmann’s constant. Using $S = 1$ relevant to $\text{V}^{3+}$ and $N k_B = 2 R$, where $R$ is the molar gas constant, one obtains $\Delta C_{AF} = 4 R = 33.3 \text{ J/mol K}$, where a “mol” refers to a mole of CaV$_2$O$_4$ formula units. From Fig. 15 the experimental $\Delta C_{AF}$ is about 0.5 to 2 J/mol K, which is only 1.5–6% of the mean field value. This small jump in $C_p(T_N)$ is consistent with the above small value of $\Delta(S(T_N))$. When short range magnetic ordering removes most of the magnetic entropy of a system at high temperatures, then thermal effects associated with three-dimensional magnetic ordering of the system at low temperatures will necessarily be much smaller than otherwise expected.

### C. Thermal Expansion Measurements

The thermal expansion of the annealed triarc grown CaV$_2$O$_4$ crystal an-2-50-c1 was measured versus temperature using capacitance dilatometry from 1.8 to 300 K along the three orthorhombic axes $a$, $b$ and $c$. The crystal is the same annealed triarc crystal measured by magnetic susceptibility and heat capacity in Figs. 10 and 11(c) and in Figs. 13–15 respectively. In Fig. 16 the linear coefficients of thermal expansion are plotted versus temperature (left-hand scale), along with the volume thermal expansion coefficient (right-hand scale). At high temperatures $T \sim 300 \text{ K}$ the $\alpha$ values tend to become temperature independent. Below 200 K, the ordering transitions observed above in the magnetic susceptibility and heat capacity are reflected in distinct anomalies in the thermal expansion coefficients at the corresponding temperatures. The ordering temperatures observed are summarized above in Table IV.

### IV. ANALYSIS OF EXPERIMENTAL DATA

#### A. Origin of the Transition at $T_{S1} \sim 200 \text{ K}$ in Annealed CaV$_2$O$_4$ Single Crystals

From Table V above, the relative volume change of the annealed triarc crystal an-2-50-c1 on heating through $T_{S1}$ from the thermal expansion data is $\Delta V/V = -1.4 \times 10^{-4}$. This value is about 1% of the value for pure V$_2$O$_3$ at its transition. The height of the heat capacity anomaly above “background” in Fig. 15 for this crystal is $\approx 2.5 \text{ J/mol K}$, which is about 0.8% of the value at the structural transition for pure V$_2$O$_3$. These estimates are both consistent with our estimates from x-ray diffraction.

### TABLE V: Relative length changes along the orthorhombic $a$-, $b$- and $c$-axis directions and of the volume $V$ that are associated with the three transitions at $T_N \approx 70$ K, $T_S \approx 140$ K, and $T_{S1} \approx 195$ K in annealed triarc CaV$_2$O$_4$ single crystal an-2-50-c1. The temperature $T$ range over which the changes were measured are as indicated.

| $T$ range (K) | $T_N$ | $T_S$ | $T_{S1}$ |
|---------------|-------|-------|----------|
| $\Delta a/a$ ($10^{-5}$) | 1.2 | 4.9 | -7.5 |
| $\Delta b/b$ ($10^{-5}$) | -4.3 | -0.9 | -0.1 |
| $\Delta c/c$ ($10^{-5}$) | 1.1 | 19.6 | -6.3 |
| $\Delta V/V$ ($10^{-5}$) | -2.0 | 23.6 | -13.9 |
data in Sec. II of a 1–2 percent volume fraction of V$_2$O$_3$ in this crystal. Our data therefore indicate that for the annealed triarc-grown crystal (an-2-50-c1), the anomalous features found above in the heat capacity and thermal expansion data at $T_{S1}$ arise mainly from this transition in the V$_2$O$_3$ impurity phase.

Furthermore, the temperature dependences of the linear thermal expansion coefficients at the transition $T_{S1} \approx 200$ K in Fig. 15 are significantly different than near the transitions $T_N \approx 70$ K and $T_S \approx 140$ K. There appears to be a discontinuity in the slopes of $\alpha_i(T)$ as the transition $T_{S1}$ is approached from above, whereas a continuous change in the slopes occurs as $T_S$ and $T_S$ are approached from above. The reason for this difference is evidently that the former transition is mainly due to the first order structural transition in the V$_2$O$_3$ coherently-grown impurity phase in this annealed crystal as investigated previously in Sec. II C 1, whereas the latter two transitions are second order.

However, we also found in Sec. II that for the annealed floating-zone crystal (an-3-074 OFZ), the structural transition of the V$_2$O$_3$ impurity phase was reduced by $\sim 60$ K from that of the V$_2$O$_3$ impurity phase in the annealed triarc grown crystal, and hence cannot be responsible for heat capacity anomaly at $T_{S1} \approx 200$ K for the annealed float-zone crystal in Fig. 15. Indeed, the relatively small heat capacity anomaly at $T_{S1} \approx 200$ K for the float-zone crystal appears to also be present at the same temperature for the annealed triarc-grown crystal, but rides on top of a broader anomaly that is evidently due to the structural transition of the V$_2$O$_3$ impurity phase in that crystal. Furthermore, the double peak structure in the heat capacity for the annealed triarc crystal at $T_S \approx 140$ K evidently arises due to the overlap of the onsets of the structural transitions in V$_2$O$_3$ and CaV$_2$O$_4$.

An issue of interest is the cause(s) of the variability in the structural rhombohedral-to-monoclinic transition temperature of the coherently grown V$_2$O$_3$ impurity phase in our annealed CaV$_2$O$_4$ crystals. Due to the first order nature of the transition, the transition is hysteresic. The transition temperature of bulk stoichiometric V$_2$O$_3$ has been reported to be at $\approx 170$ K on heating and $\approx 150$ K on cooling. The transition temperature decreases rapidly under pressure. A pressure of only 9 kbar lowers the transition temperature by 60 K, and the transition is completely suppressed at a pressure of $\approx 20$ Kbar. The transition temperature is also rapidly suppressed if the sample contains V vacancies; a crystal of composition V$_1$$_{98}$O$_3$ showed a transition temperature of $\approx 50$ K. Furthermore, it was found that when V$_2$O$_3$ is epitaxially grown on LiTaO$_3$, the transition temperature is enhanced from the bulk value by 20 K. Given the possibilities of compressive or tensile forces acting on the V$_2$O$_3$ due to the epitaxial relationship of the V$_2$O$_3$ impurity with the CaV$_2$O$_4$ host and the possibility of nonstoichiometry of the V$_2$O$_3$ impurity phase, one can see how the transition temperature of the V$_2$O$_3$ might be depressed or enhanced from the bulk value by $\approx 30$ K as we found for the coherently grown V$_2$O$_3$ impurity phases in our two annealed crystals in Sec. II C.

In summary, then, it appears that there is an intrinsic phase transition in the two annealed CaV$_2$O$_4$ crystals at about 200 K that has no obvious source. We speculate that this transition may be the long-sought chiral phase transition originally postulated by Villain, where there is long-range chiral order but no long-range spin order below the transition temperature, and the long-range chiral order is lost above the transition temperature.

B. Magnetic Susceptibility and Magnetic Heat Capacity

In separate experiments to be described elsewhere, we have carried out inelastic neutron scattering measurements of the magnetic excitation dispersion relations for CaV$_2$O$_4$ single crystals. We find that the dispersion along the c-axis (in the vanadium chain direction) is significantly larger than in the two perpendicular directions. Above the Néel temperature $T_N$, the magnetic susceptibility in Fig. 15 is nearly isotropic. Thus a quasi-one-dimensional Heisenberg model appears to be appropriate for the spin interactions in CaV$_2$O$_4$.

The crystal structure suggests the presence of spin $S = 1$ zigzag spin chains along the orthorhombic c-axis. We report here exact diagonalization (ED) calculations of the magnetic spin susceptibility versus temperature $\chi(T)$ and the magnetic heat capacity $C(T)$ of spin $S = 1$ Heisenberg chains containing $N = 30$, $10$, and $12$ spins for $J_2/J_1$ ratios from $-1$ to $5$, and containing 14 spins for $J_2/J_1 = 0$. We also report the results of quantum Monte Carlo (QMC) simulations of $\chi(T)$ and $C(T)$. These simulations were carried out with the ALPS directed loop application in the stochastic series expansion framework for chains with $N = 30$ and 60 spins and $J_2/J_1 = 0$. Here $J_1$ and $J_2$ are the nearest-neighbor and next-nearest-neighbor interactions on a linear chain, respectively. The spin Hamiltonian is the $\lambda = 1$ special case of Eq. (1), given by

$$\mathcal{H} = \sum_{i=1}^{N} (J_1 \mathbf{S}_i \cdot \mathbf{S}_{i+1} + J_2 \mathbf{S}_i \cdot \mathbf{S}_{i+2}),$$

where $\mathbf{S}$ is a spin-1 operator. Periodic boundary conditions are imposed, so the chains become rings. $J_1$ is always positive (antiferromagnetic) whereas $J_2$ was taken to be either positive or negative (ferromagnetic). This chain is topologically the same as a zigzag chain in which $J_1$ is the nearest-neighbor interaction between the two legs of the zigzag chain and $J_2$ is the nearest-neighbor interaction along either leg of the zigzag chain. For $J_2 = 0$, the $N$ spins are all part of the same nearest-neighbor exchange ($J_1$) chain. For $J_1 = 0$, two independent isolated equivalent chains are formed, each containing $N/2$ spins and with nearest-neighbor exchange $J_2$. This effect can be quantified using the $T = 0$ correlation length $\xi$ which
has been computed in Ref. [22]. We find that we can reach ratios \( N/\xi \) which are at least 2 for \( J_2/J_1 \lesssim 0.6 \) whereas \( \xi \) becomes comparable to or even bigger than the system sizes \( N \) which are accessible by ED for larger \( J_2/J_1 \). Accordingly, our finite chain data become a poorer approximation to the infinite \( J_1-J_2 \) chain for large \( J_2/J_1 \). This is exemplified below in Fig. 20 where the data for chains containing different numbers \( N \) of spins exhibit an increasing divergence from each other with increasing \( J_2/J_1 \).

We will compare the spin susceptibility calculations with the experimental magnetic susceptibility data to estimate the \( J_1 \) and \( J_2/J_1 \) values in the \( J_1-J_2 \) chain model for \( \text{CaV}_2\text{O}_4 \). These values will also be used as input to compare the calculated magnetic heat capacity versus temperature with the experimental heat capacity data.

1. Magnetic Susceptibility

The calculated magnetic spin susceptibility \( \chi(T) \) data for the spin \( S = 1 \) \( J_1-J_2 \) Heisenberg chain model are in the dimensionless form

\[
\frac{\chi J_1}{N g^2 \mu_B^2} \text{ versus } \frac{k_B T}{J_1}, \tag{4}
\]

where \( N \) is the number of spins, \( g \) is the spectroscopic splitting factor (\( g \)-factor) of the magnetic moments for a particular direction of the applied magnetic field with respect to the crystal axes, \( \mu_B \) is the Bohr magneton, and \( k_B \) is Boltzmann’s constant. Calculated \( \chi(T) \) data sets for \( N = 12 \) were obtained by exact diagonalization assuming periodic boundary conditions (ring geometry) for \( J_2/J_1 \) ratios of \(-1, -0.8, \ldots, 2.0, 2.5, \ldots, 5.0\). Examples of the calculations for a selection of \( J_2/J_1 \) values are shown in Fig. 17. Each chain has an energy gap (spin gap) from the nonmagnetic singlet ground state to the lowest magnetic excited states. No interchain (between adjacent zigzag chains) interactions are included in the calculations. These calculations are not expected to apply to our system at low temperatures where we see long-range antiferromagnetic ordering. However, we expect to be able to obtain approximate estimates of \( J_1 \) and \( J_2 \) by fitting the observed susceptibility data around the broad peak in the susceptibility at \( \approx 300 \text{ K} \).

At high temperatures \( k_B T \gg J_{\text{max}} \), where \( J_{\text{max}} = \text{max}(J_1, J_2) \), one expects that the calculated \( \chi_{J_{\text{max}}} \) versus \( k_B T/J_{\text{max}} \) should be nearly the same upon interchange of \( J_1 \) and \( J_2 \), i.e., the same for pairs of \( J_2/J_1 \) ratios that are reciprocals of each other. This is because all spins in the zigzag chain are equivalent, and at high temperatures the Curie-Weiss law is obtained. The Weiss temperature \( \theta \) only depends on the numbers of nearest neighbors \( z \) to a given spin and the corresponding interaction strengths \( J(\theta \sim z_1 J_1 + z_2 J_2 \text{ with } z_1 = z_2 = 2) \), which is invariant upon interchange of \( J_1 \) and \( J_2 \). This expectation is confirmed in Fig. 18, where such plots are shown for \( J_2/J_1 = 1/5 \) and \( 5 \); \( 1/2 \) and \( 2 \); and \( 1 \). The data for \( J_2/J_1 = 1/2 \) and \( 2 \), and for \( J_2/J_1 = 1/5 \) and \( 5 \), are seen to be about the same for temperatures \( k_B T/J_{\text{max}} \gtrsim 4 \), respectively.

The experimental magnetic susceptibility data of \( \text{CaV}_2\text{O}_4 \) will be fitted below by the calculated susceptibility \( \chi(T) \) of a single \( S = 1 \) chain \( \langle J_2/J_1 = 0 \rangle \). Such integer-spin chains are known as Haldane chains. We will therefore test here the sensitivity of the calculations to the number of spins \( N \) in the chain for this fixed \( J_2/J_1 \) value. Shown in Fig. 19 are exact diagonalization (ED) calculations of \( \chi(T) \) for \( J_2/J_1 = 0 \) and \( N = 12 \) and 14, and quantum Monte Carlo (QMC) simulations for \( J_2/J_1 = 0 \) and \( N = 60 \). On the scale of the fig-

FIG. 17: Calculated magnetic spin susceptibility \( \chi \) for spin \( S = 1 \) \( J_1-J_2 \) Heisenberg chains containing \( N = 12 \) spins versus temperature \( T \), where \( J_1 \) and \( J_2 \) are the nearest-neighbor and next-nearest-neighbor exchange interactions in the chain. The curves from top to bottom on the right are for \( J_2/J_1 = 0, 0.2, 0.4, \ldots, 2.0, 2.5, \ldots, 5.0 \).

FIG. 18: Magnetic susceptibility \( \chi \) versus temperature \( T \) for the spin \( S = 1 \) \( J_1-J_2 \) Heisenberg chain containing \( N = 12 \) spins. Here, \( J_{\text{max}} = \text{max}(J_1, J_2) \). Pairs of curves for \( J_2/J_1 \) ratios that are reciprocals of each other become the same at high temperatures.
magnetic susceptibility \( \chi \) distinguished. These data are fully consistent with previous values of 1.35 (Ref. 41) and 1.32(3).\(^{37}\) Probably the most accurate values for the susceptibility are those of Ref. 40, as listed in Table VI.

From the theoretical \( \chi(T) \) data, for each value of \( J_2/J_1 \) one can obtain the value of the normalized temperature \( k_B T_{\chi_{\text{max}}}^\text{max}/J_1 \) at which the maximum in the susceptibility occurs, and the normalized value of the susceptibility \( \chi_{\text{max}}^\text{max}/J_1/N g^2 \mu_B^2 \) at the maximum. For a given value of \( J_2/J_1 \), the product of these two values is a particular dimensionless number

\[
\frac{\chi_{\text{max}}^\text{max}/J_1}{N g^2 \mu_B^2/k_B} = \frac{\chi_{\text{max}} T_{\chi_{\text{max}}}^\text{max}}{N g^2 \mu_B^2/k_B}
\]

that does not contain either exchange constant.

The spectroscopic splitting tensor (\( g \)-tensor) for vanadium cations is found to not depend much on either the oxidation (spin) state of the V cation or on its detailed environment in insulating hosts. The physical origin of this insensitivity is the small magnitude of the spin-orbit coupling constant for the vanadyl atom. Typical values for the spherically-averaged \( g \)-factor (\( g \)) are between approximately 1.93 and 1.97, with the individual components of the diagonal \( g \)-tensor lying between 1.90 and 2.00. For example, for \( \text{V}^{4+} \) in single crystals of AgCl, one obtains \( g = 1.970(3) \) for \( \text{V}^{4+} \) in guanidinium vanadium sulfate hexahydrate, \( g = 1.94(1) \) for \( \text{V}^{4+} \) in TiO\(_2\), \( g = 1.973(4) \).

On the basis of the above discussion we set \( g = 1.97 \) for the \( \text{V}^{4+} \) spin \( S = 1 \) in Eq. 5. Then setting \( N = 2N_A \), where \( N_A \) is Avogadro’s number and the factor of 2 comes from two atoms of V per formula unit of CaV\(_2\)O\(_4\), the expression in Eq. 5 becomes

\[
\frac{\chi_{\text{max}}^\text{max}/J_1}{N g^2 \mu_B^2/k_B} = \frac{\chi_{\text{max}} T_{\chi_{\text{max}}}^\text{max}}{2.91 \text{ cm}^{-1} \text{K}^{-1} \text{mol}^{-1}}
\]

where a “mol” refers to a mole of CaV\(_2\)O\(_4\) formula units. Then from Eq. 6 and the calculated \( \chi(T) \) data for different values of \( J_2/J_1 \), the calculated \( \chi_{\text{max}}^\text{max}/J_1 \) versus \( J_2/J_1 \) for CaV\(_2\)O\(_4\) is shown in Fig. 20. From the figure, the dependence of \( \chi_{\text{max}}^\text{max}/J_1 \) on \( J_2/J_1 \) is about the same for \( N = 8, 10, 12 \) and 12 for \( J_2/J_1 \approx 0 \) which is consistent with a short correlation length \( \xi \approx 6 \) for \( 0 \leq J_2/J_1 \leq 0.6 \) (see Ref. 57). However, the curves for the different values of \( N \) are quite different at larger values of \( J_2/J_1 \); the behavior versus \( N \) even becomes nonmonotonic in this parameter region. The QMC results also shown in Fig. 20 nevertheless indicate that the ED calculations for \( N = 12 \) sites yield a good approximation to the infinite \( N \) limit also for \( J_2/J_1 \geq 1.8 \). Unfortunately, the QMC sign problems are so severe in the region 0.2 < \( J_2/J_1 < 1.8 \) that here we cannot resolve the maximum of \( \chi \) with our QMC simulations.

The experimental susceptibility \( \chi_{\text{exp}}(T) \) data for CaV\(_2\)O\(_4\) in Fig. 14 can be written as the sum \( \chi_{\text{exp}}(T) = \chi(T) + \chi_0 \), where \( \chi(T) \) is the spin susceptibility (which is

FIG. 19: Magnetic susceptibility \( \chi \) versus temperature \( T \) calculations for the spin \( S = 1 \) Heisenberg chain with nearest neighbor exchange interaction \( J_1 \) and next-nearest-neighbor interaction \( J_2 = 0 \). The calculations were carried out using exact diagonalization (ED) for \( N = 12 \) and 14, and by quantum Monte Carlo (QMC) for \( N = 60 \).

FIG. 20: The product \( \chi_{\text{max}}^\text{max}/J_1 \) versus \( J_2/J_1 \) for the spin \( S = 1 \) \( J_1-J_2 \) Heisenberg chain containing \( N = 8, 10, 12, 30 \) or 60 spins, where we have assumed \( N = 2N_A \) and \( g = 1.97 \). The data for \( N = 8, 10, 12 \) and 12 were obtained using exact diagonalization calculations. The data for \( N = 30 \) and 60 were obtained from quantum Monte Carlo simulations; most of these data were obtained for \( N = 60 \), except for \( J_2/J_1 = 0.2, 1.8 \) and 2 where we used \( N = 30 \). The horizontal dashed line is the experimental value of \( \chi_{\text{max}}^\text{max}/J_1 \) for CaV\(_2\)O\(_4\) from Eq. 7. Comparison of this experimental value with the calculations indicates that within the \( J_1-J_2 \) model, \( J_2/J_1 \approx 0 \) (or \( J_1/J_2 \approx 0 \)) in CaV\(_2\)O\(_4\).
The part calculated above) and \( \chi_0 \) is the temperature-independent orbital susceptibility. From the data in Ref. 40 for \( \text{V}_2\text{O}_3 \), we estimate \( \chi_0 \approx 0.4 \times 10^{-3} \text{ cm}^3/\text{mol} \) for \( \text{CaV}_2\text{O}_4 \). From Fig. 10 we then obtain the experimental value for the spin susceptibility at the maximum \( \chi_{\text{max}} \approx 2.2 \times 10^{-3} \text{ cm}^3/\text{mol} \) and for the temperature at the maximum \( T_{\chi} \approx 300 \text{ K} \), yielding for \( \text{CaV}_2\text{O}_4 \) \[ \chi_{\text{max}} T_{\chi} \approx 0.66 \text{ cm}^3 \text{ K}/\text{mol} . \] (7)



\[
\begin{array}{cccccc}
\hline
\text{method} & \chi_{\text{max}} / J_1 & k_B T_{\chi} / J_1 & \chi_{\text{max}} / k_B & k_B T_{\chi} / J_1 \\
\hline
\text{QMC} N = 60 & 0.174686(9) & 1.301(10) & 0.5431(4) & 0.857(10) \\
\text{ED} N = 12 & 0.174662 & 1.2992 & 0.5520 & 0.8295 \\
\text{ED} N = 14 & 0.174677 & 1.2980 & 0.5466 & 0.8398 \\
\text{Ref. 40} & 0.17496(2) & 1.2952(16) \\
\hline
\end{array}
\]

\( \chi_{\text{max}} \approx 300 \text{ K} \), combined with \( k_B T_{\chi} / J_1 \approx 1.30 \) from Table VI yields \( J_2/k_B = 230 \text{ K} \). Although the numerical results shown in Fig. 20 are the least accurate in the vicinity of \( J_2/J_1 \approx 1 \), it seems rather unlikely that the value of \( \chi_{\text{max}} T_{\chi} \) obtained from the \( J_1-J_2 \) chain model in the region \( 0.6 \lesssim J_2/J_1 \lesssim 1.8 \) could be consistent with the value in Eq. (7) expected for \( \text{CaV}_2\text{O}_4 \).

The calculated total susceptibility versus temperature for \( J_1/k_B = 230 \text{ K} \) and \( J_2 = 0 \) and \( \chi_0 = 0.4 \times 10^{-3} \text{ cm}^3/\text{mol} \) is shown in Fig. 21. Also shown are the experimental susceptibility data for annealed \( \text{CaV}_2\text{O}_4 \) crystal an-2-50-c1 from Fig. 10, where an excellent fit of the average anisotropic \( \chi(T) \) data near 300 K is seen.

Above the Néel temperature, one sees from Figs. 10 and 21 that the susceptibility is nearly isotropic. The relatively small anisotropy observed can come from anisotropy in the orbital Van Vleck paramagnetic susceptibility, from g-anisotropy arising from spin-orbit interactions, from single-ion anisotropy of the form \( DS_z^2 + E(S_z^2 - S_0^2) \), and from anisotropy in the spin exchange part of the spin Hamiltonian. The relative importance of these sources to the observed susceptibility anisotropies are not yet clear. The experimental data below 200 K in Fig. 21 increasingly deviate from the fit with decreasing temperature. This suggests that other interactions besides \( J_1 \) and \( J_2 \) and/or the presence of magnetic anisotropies may be important to determining the spin susceptibility above \( T_N \) in \( \text{CaV}_2\text{O}_4 \).

For collinear antiferromagnetic (AF) ordering, one nominally expects the spin susceptibility along the easy axis to go to zero as \( T \rightarrow 0 \). Comparison of the theoretical curve with the experimental easy axis (b-axis) data \( \chi_b(T) \) in Fig. 21 indicates that the zero-temperature b-axis spin susceptibility is not zero, but is instead a rather large value \( \chi_b^{\text{spin}}(T \rightarrow 0) \approx 0.9 \times 10^{-5} \text{ cm}^3/\text{mol} \). This finite spin susceptibility indicates either that the spin structure in the AF state is not collinear, that not all vanadium spins become part of the ordered magnetic structure below \( T_N \), and/or that quantum fluctuations are present that induce a nonzero spin susceptibility. Such quantum fluctuations can arise from the low-dimensionality of the spin lattice and/or from frustration effects. As discussed in the Introduction, our recent NMR and magnetic neutron diffraction experiments on single crystal \( \text{CaV}_2\text{O}_4 \) indicated that the magnetic structure at 4 K is noncollinear, which can at least partially explain the nonzero spin susceptibility along the (average) easy b-axis at low temperatures. In addition, the reduction in the local ordered moment 1.0–1.6 \( \mu_B/\text{(V atom)} \) of the ordered vanadium spins found in these studies from the expected value \( gS_B = 2 \mu_B/\text{(V atom)} \) suggests that quantum zero-point spin fluctuations could be strong and could contribute to the large finite \( \chi_b^{\text{spin}}(T \rightarrow 0) \).
FIG. 22: Magnetic heat capacity \( C \) versus temperature \( T \) for the spin \( S = 1 \) \( J_1,J_2 \) Heisenberg chain with \( J_2/J_1 \) values from \(-1 \) to \( 5 \), calculated using exact diagonalization with \( N = 12 \). Here \( N \) is the number of spins, \( k_B \) is Boltzmann’s constant, and \( J_1 > 0 \) and \( J_2 \) are the nearest-neighbor and next-nearest-neighbor exchange interactions, respectively.

FIG. 23: Magnetic heat capacity \( C \) versus temperature \( T \) for the \( S = 1 \) \( J_1,J_2 \) chain with \( J_2/J_1 = 0 \) ("Haldane chain"), calculated using exact diagonalization (ED) with \( N = 10 \) and 12, and quantum Monte Carlo (QMC) simulations for \( N = 60 \).

2. Magnetic Heat Capacity

The magnetic heat capacity \( C \) versus temperature \( T \) was calculated by exact diagonalization for \( N = 12 \) spins \( S = 1 \) over the range \(-1 \leq J_2/J_1 \leq 5 \). Representative results are plotted in Fig. 22. The variation in \( C(T) \) with \( N \) is illustrated in Fig. 23 for \( J_2/J_1 = 0 \) and \( N = 12 \) and 14 from exact diagonalization calculations, and for \( N = 60 \) from quantum Monte Carlo simulations. The data for the different \( N \) are seen to be nearly the same. The values of the maxima \( C_{\text{max}} \) in the magnetic heat capacity and the temperatures \( T_{C_{\text{max}}} \) at which they occur are listed above in Table VII. Our results for the specific heat are consistent with previous transfer-matrix renormalization-group computations.\(^{39,40}\) The two transfer-matrix renormalization-group results differ at high temperatures. Our QMC results for \( C \) obtained from rings with \( N = 60 \) sites are in better agreement with the older results which apply to the infinite \( N \) limit\(^{29}\) than the more recent results obtained for open chains with \( N = 64 \) sites.\(^{40}\) The \( C(T) \) data in Ref. 40 were calculated from a numerical derivative which resulted in systematic errors in the data at high temperatures.\(^{42}\)

We cannot confidently derive the exchange constants in \( \text{CaV}_2\text{O}_4 \) from fits of our heat capacity data by the theory. Extraction of the magnetic part of the experimental heat capacity is tenuous because of the presence of the orthorhombic to monoclinic structural transition at \( T_S \approx 150 \) K and the transition(s) at \( T_J \approx 200 \) K. Therefore the relationship of the heat capacities \( \Delta C(T) \) in Figs. 14a and 15 to the magnetic heat capacities of the samples is unclear. Here, we will just compare the theoretical magnetic heat capacity calculated for the exchange constants \( J_1 = 230 \) K and \( J_2 = 0 \), that were already deduced in the previous section, with the experimental \( \Delta C(T) \) data to see if theory and experiment are at least roughly in agreement. This comparison is shown in Fig. 24 for annealed \( \text{CaV}_2\text{O}_4 \) crystal an-2-50-c1 from Fig. 15. Overall, the theory and experimental data have roughly the same magnitude, but the data are systematically below the theoretical prediction. This is likely caused by the heat capacity of the nonmagnetic reference compound \( \text{CaSc}_2\text{O}_4 \) being somewhat different from the lattice heat capacity of \( \text{CaV}_2\text{O}_4 \). We note from Fig. 13 that a difference of 5 J/mol K between the theory and experiment in Fig. 24 is only about 5% of the total heat capacity of the samples at 200 K. In addition, we have not included in the theory interchain couplings that lead to long-range antiferromagnetic order, or the effect of the magnetic ordering on the heat capacity including the effect of the energy gap in the spin wave spectrum below...
Within the $S = 1 J_{1}-J_{2}$ Heisenberg spin chain model, we found above that $J_{2}/J_{1} \approx 0$ and $J_{1} \approx 230$ K in CaV$_{2}$O$_{4}$ near room temperature. Thus the crystallographic zigzag vanadium chains in CaV$_{2}$O$_{4}$ act like $S = 1$ linear spin chains with nearest-neighbor interaction $J_{1}$. This is a so-called Haldane chain with a nonmagnetic singlet ground state and an energy gap for spin excitations given by $\Delta J \approx 0.4105J_{1}$. An interchain coupling $J_{\perp}$ must be present in order to overcome this spin gap and induce long-range antiferromagnetic ordering at $T_{N}$. Pedrini et al.$^{42,50}$ have recently estimated the dependence of $T_{N}/J_{1}$ on $J_{\perp}/J_{1}$ using a random-phase approximation for the interchain coupling for $S = 1$ Haldane chains. Using our values $T_{N} = 68$ K, $J_{1} = 230$ K and $T_{\text{max}} = 300$ K, we obtain $J_{\perp}/J_{1} \approx 0.04$ and $J_{\perp} = 5–10$ K. However, it should be emphasized that the treatment of Refs. $^{42}$ and $^{50}$ assumes a nonfrustrated interchain coupling geometry such that the result $J_{\perp} \approx 10$ K should be considered as a lower bound. Still, the value of $J_{\perp}/J_{1}$ is sufficiently small that a redistribution of $J_{2}/J_{1}$ and $J_{1}$ from a $J_{1}-J_{2}-J_{\perp}$ model fitted to the observed susceptibility data for CaV$_{2}$O$_{4}$ near room temperature, would yield very similar values of $J_{2}/J_{1}$ and $J_{1}$ to those we have already estimated using the isolated chain $J_{1}-J_{2}$ model. Additional and more conclusive information about the interchain coupling strength(s) will become available from analysis of inelastic neutron scattering measurements of the magnetic excitation dispersion relations.$^{17,15}$

V. SUMMARY

We have synthesized the $S = 1$ spin chain compound CaV$_{2}$O$_{4}$ in high purity polycrystalline form and as single crystals. Our magnetic susceptibility $\chi(T)$ and ac magnetic susceptibility $\chi_{ac}(T)$ measurements do not show any signature of a spin glass-like transition around 20 K that was previously reported.$^{10,11}$ We instead observe long-range antiferromagnetic ordering at sample-dependent Néel temperatures $T_{N} \approx 50–70$ K as shown in Table IV. The Néel temperature and the orthorhombic-to-monoclinic structural transition temperature $T_{S}$ in Table IV both show a large systematic variation between different samples. Those temperatures for an unannealed crystal are each less than those for an annealed crystal which in turn are less than those for a sintered polycrystalline sample. The cause of these large temperature differences, especially between as-grown and annealed single crystals, is unclear. The transition temperature differences may arise from small changes in oxygen stoichiometry ($< 1$ at.$\%$, below the threshold of detection by TGA or XRD) and/or from structural strain, both of which may be reduced upon annealing the as-grown crystals at 1200 °C in 5% H$_{2}$/He. In addition, other small chemical differences and/or structural defects may be relevant.

Our heat capacity $C_{p}(T)$, linear thermal expansion $\alpha(T)$, and $\chi(T)$ measurements reveal distinct features at the orthorhombic-to-monoclinic structural transition temperature $T_{S}$ identified from our diffraction studies.$^{15}$ We inferred from a combination of structural studies and physical property measurements that the origin of the third transition at $T_{S1} \approx 200$ K in one of our annealed crystals was mostly due to the structural transition in the V$_{2}$O$_{3}$ impurity phase that grew coherently upon annealing the crystal. In the other annealed crystal, we ruled out this source and we are thus left with a transition at $T_{S1}$ with unknown origin. We speculate that this transition may be the long-sought chiral phase transition originally postulated by Villain in 1977.$^{2}$

The $\chi(T)$ shows a broad maximum at about 300 K indicating short-range antiferromagnetic (AF) ordering in a low-dimensional antiferromagnet as previously observed.$^{10,11}$ and the $\chi(T)$ above $T_{N}$ in single crystals is nearly isotropic. The anisotropic $\chi(T)$ below $T_{N}$ shows that the (average) easy axis of the antiferromagnetic structure is the orthorhombic $b$-axis. The magnetic spin susceptibility along this axis is found to be a large finite value for $T \to 0$, instead of being zero as expected for a classical collinear antiferromagnet. This result is consistent with our observed noncollinear magnetic structure below $T_{N}$.$^{14,15}$ In view of the fact that CaV$_{2}$O$_{4}$ is a low-dimensional spin system, quantum fluctuations could also contribute to both the observed reduced zero temperature ordered moment and the relatively large zero temperature spin susceptibility.

We analyzed the $\chi(T)$ data near room temperature in terms of theory for the $S = 1 J_{1}-J_{2}$ linear Heisenberg chain, where $J_{1}(J_{2})$ is the (next-)nearest-neighbor interaction along the chain. We obtain $J_{1}/k_{B} \approx 230$ K, but surprisingly $J_{2}/J_{1} \approx 0$ (or $J_{1}/J_{2} \approx 0$), so the exchange connectivity of the spin lattice appears to correspond to linear $S = 1$ Haldane chains instead of zigzag spin chains as expected from the crystal structure. This result is consistent with analysis of our high temperature (up to 1000 K) magnetic susceptibility measurements on single crystal CaV$_{2}$O$_{4}$.$^{15}$ We estimated here the coupling $J_{\perp}$ between these chains that leads to long-range AF order at $T_{N}$ to be $J_{\perp}/J_{1} \geq 0.04$, i.e., only slightly larger than the value $J_{\perp}/J_{1} \approx 0.02$ needed$^{12,50}$ to eliminate the energy gap (Haldane gap) for magnetic excitations.

From our $C_{p}(T)$ measurements, the estimated molar magnetic entropy at $T_{N}$ is only $\approx 8\%$ of its maximum value $2R\ln(2S + 1) = 2R\ln(3)$, where $R$ is the molar gas constant, and the heat capacity jump at $T_{N}$ is only a few percent of the value expected in mean field theory for $S = 1$. Both results indicate strong short range antiferromagnetic order above $T_{N}$ and large values $J_{1}$ and/or $J_{2} > 100$ K, consistent with the $\chi(T)$ data. We also compared the $C_{p}(T)$ data with the theoretical prediction for the magnetic heat capacity using the exchange constants found from the magnetic susceptibility analysis,
and rough agreement was found. However, this comparison is not very precise or useful because the structural transition at $T_S \sim 150$ K and the transition(s) at $T_{S1} \sim 200$ K for our two annealed single crystals, make large contributions to $C_p(T)$. In addition, the accuracy of the measured heat capacity of the nonmagnetic reference compound CaSc$_2$O$_4$ in representing the lattice heat capacity of CaV$_2$O$_4$ is unknown. Thus extracting the magnetic part of the heat capacity at high temperatures from the observed $C_p(T)$ data for comparison with theory is ambiguous.

In closing, we note the following additional issues that could usefully be addressed in future work. Our analyses of our $\chi(T)$ data for CaV$_2$O$_4$ to obtain the exchange constants $J_1$ and $J_2$ were based on fitting the experimental $\chi(T)$ data only near room temperature, since our calculations of $\chi(T)$ all showed nonmagnetic singlet ground states, contrary to observation, and could not reproduce the observed antiferromagnetic ordering at low temperatures. Calculations containing additional interactions (see also below) and/or anisotropies are needed for comparison with the lower temperature data.

The orthorhombic crystal structure of CaV$_2$O$_4$ at room temperature contains two crystallographically inequivalent but similar $V^{+3} S = 1$ zigzag chains. These chains may therefore have different exchange constants associated with each of them. For simplicity, our $\chi(T)$ data were analyzed assuming a single type of zigzag chain. Furthermore, the extent to which the transitions at $T_{S1}$ and $T_S$ affect the magnetic interactions is not yet clear.

From crystal structure considerations, one expects that $J_2/J_1 \approx 1$ in CaV$_2$O$_4$ instead of $J_2/J_1 \approx 0$ as found here. This suggests that additional magnetic interactions and/or anisotropy terms beyond the Heisenberg interactions $J_1$ and $J_2$ and interchain coupling $J_\perp$ considered here may be important. In addition to single ion anisotropy and other types of anisotropy, we mention as possibilities the Dzyaloshinskii-Moriya interaction, quadratic exchange, and cyclic exchange interactions within the zigzag chains. When such additional terms are included in the analysis, the fitted value of $J_2/J_1$ could turn out to be closer to unity. A four-spin cyclic exchange interaction has been found to be important to the magnetic susceptibility in cuprate spin ladders. In these spin ladders, there are exchange interactions $J$ and $J'$ between nearest-neighbor $Cu^{+2}$ spins 1/2 along the legs and across the rungs of the spin ladder, respectively. For the $S = 1/2$ two-leg ladder compound SrCu$_2$O$_3$, if only $J$ and $J'$ are included in fits to the data, one obtains $J'/J \approx 0.5$. However, by also including the theoretically derived cyclic four-spin exchange interaction, the ratio $J'/J$ increases from 0.5 to a value closer to unity, as expected from the crystal structure.

Pieper et al. have recently proposed a very different and very interesting model to explain the inference that $J_2/J_1 \approx 0$ around room temperature which involves partial orbital ordering of the two $d$-electrons of V among the three $t_{2g}$ orbitals. Furthermore, in order to explain the magnetic structure at low temperatures, they deduce that the nature of the orbital ordering changes below $T_S$ such that the effective spin lattice becomes a spin-1 two-leg ladder.

It has been well documented that fits of magnetic susceptibility data by theory tests only the consistency of a spin model with the data, and not the uniqueness of the model. A good example of this fact arose in the study of the antiferromagnetic alternating exchange chain compound vanadyl pyrophosphate, (VO)$_2$P$_2$O$_5$, the history of which is described in detail in the introduction of Ref. 51. The ultimate arbiter of the validity of a spin model is inelastic neutron scattering measurements of the magnetic excitation dispersion relations in single crystals. Theoretical calculations of the exchange interactions are much needed and would also be valuable in this regard.

Finally, the origin of the intrinsic heat capacity anomalies at $T_{S1} \approx 200$ K for the two annealed single crystals of CaV$_2$O$_4$ needs to be further studied. We speculate that this transition may be the long-sought chiral phase transition originally postulated by Villain in 1977.

Note added—After this work and this paper were nearly completed, Sakurai reported a very interesting and detailed study of the magnetic and electronic phase diagram of polycrystalline samples of the solid solution Ca$_{1-x}$Na$_x$V$_2$O$_4$ prepared under high pressure.

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