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Abstract
51V NMR studies on CaV2O4 single crystals and 17O NMR studies on 17O-enriched powder samples are reported. The temperature dependences of the 17O NMR linewidth and nuclear spin-lattice relaxation rate give strong evidence for a long-range antiferromagnetic transition at \( T_N = 78 \) K in the powder. Magnetic susceptibility measurements show that \( T_N = 69 \) K in the crystals. A zero-field 51V NMR signal was observed at low temperatures \( (f \approx 237 \text{ MHz at } 4.2 \text{ K}) \) in the crystals. The field-swept spectra with the field in different directions suggest the presence of two antiferromagnetic substructures. Each substructure is collinear, with the easy axes of the two substructures separated by an angle of \( 19(1)^\circ \), and with their average direction pointing approximately along the b axis of the crystal structure. The two spin substructures contain equal numbers of spins. The temperature dependence of the ordered moment, measured up to 45 K, shows the presence of an energy gap \( E_G \) in the antiferromagnetic spin wave excitation spectrum. Antiferromagnetic spin wave theory suggests that \( E_G/k_B \) lies between 64 and 98 K.

Keywords
Physics and Astronomy, Materials Science and Engineering

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I. INTRODUCTION

Frustrated magnetic systems have attracted a lot of research interest because such systems often exhibit interesting low temperature properties. The zigzag spin chain with antiferromagnetic interactions between nearest and next-nearest neighbors is about the most simple frustrated system. In a zigzag spin chain system with spin \( S = \frac{1}{2} \), the ground state phase diagram (at temperature \( T = 0 \)) as a function of XXZ anisotropy and ratio between nearest-neighbor (NN) and next-nearest-neighbor (NNN) interactions exhibits six different phases. In addition to two Néel ordered phases and two phases with a Haldane gap, there exists a gapless chiral phase where the chirality exhibits long-range order without accompanying spin order, and a small phase region where there is a gapped chiral phase. \( ^{17}\text{O} \) and \( ^{51}\text{V} \) NMR studies on \( \text{CaV}_2\text{O}_4 \) single crystals and \( ^{17}\text{O} \) NMR studies on \( ^{17}\text{O} \)-enriched powder samples are reported. The temperature dependences of the \( ^{17}\text{O} \) NMR linewidth and nuclear spin-lattice relaxation rate give strong evidence for a long-range antiferromagnetic transition at \( T_N = 78 \) K in the powder. Magnetic susceptibility measurements show that \( T_N = 69 \) K in the crystals. A zero-field \( ^{51}\text{V} \) NMR signal was observed at low temperatures (\( f \approx 237 \) MHz at 4.2 K) in the crystals. The field-swept spectra with the field in different directions suggest the presence of two antiferromagnetic substructures. Each substructure is collinear, with the easy axes of the two substructures separated by an angle of \( 19(1)\)°, and with their average direction pointing approximately along the \( b \) axis of the crystal structure. The two spin substructures contain equal numbers of spins. The temperature dependence of the ordered moment, measured up to 45 K, shows the presence of an energy gap \( E_G \) in the antiferromagnetic spin wave excitation spectrum. Antiferromagnetic spin wave theory suggests that \( E_G/\mu_B \) lies between 64 and 98 K.

FIG. 1. The orthorhombic crystal structure of \( \text{CaV}_2\text{O}_4 \) at room temperature. Large spheres, two inequivalent V sites; small dark spheres, Ca; and small light spheres, O. The crystallographic \( a \) and \( b \) axes are along the vertical and horizontal directions in the plane of the page, respectively. The \( c \) axis is perpendicular to the page. The cuboid denotes the size of a unit cell.
In order to obtain further evidence of the magnetic phase transition and to study the magnetic properties in the ordered state, we performed $^{17}$O and $^{51}$V NMR studies on $^{17}$O-enriched powder and single crystal samples, respectively. The $^{17}$O NMR spectrum and the nuclear spin-lattice relaxation rate measurements give strong evidence for a magnetic transition at $T_N=78$ K in the powder sample. In contrast to $^{51}$V NMR measurements, we could not detect a $^{51}$V NMR signal in the powder sample around the normal Larmor frequency in an applied field of 1.67 T in the temperature range of 4.2 K $< T < 296$ K. Instead, we observed a zero-field $^{51}$V NMR signal at $T < 45$ K ($f = 237$ MHz at 4.2 K).

The zero-field $^{51}$V NMR signal is observed because of a strong local field at $^{51}$V nuclear sites ($H_{loc}=21.2$ T at 4.2 K) in the ordered state. The local field arises mainly from interaction between nuclei and vanadium core electrons, which are polarized by the ordered 3$d$ electronic spins. This local field points antiparallel to the direction of the electronic spins. This local field also gives rise to a splitting between zero-field-cooled and field-cooled susceptibilities is observed below the magnetic transition temperature $T_N=78$ K.

$^{17}$O NMR measurements were performed utilizing a phase-coherent pulse spectrometer in applied fields of 3.0 and 4.7 T. The typical $\pi/2$ pulse length is 6 $\mu$s. The echo signal was produced by a sequence of a $\pi/2$ and a $\pi/3$ pulse, which produces the maximum echo signal intensity. The separation between these two echo-generating pulses was 40 $\mu$s. The $^{17}$O NMR spectra were measured by either Fourier transform of half the echo signal or by plotting the area of the echo as a function of the rf (frequency sweep). The nuclear spin-lattice relaxation rates were measured by monitoring the recovery of the echo intensity following a comb sequence of $\pi/2$ saturation pulses. Static magnetization versus temperature was measured in a Quantum Design superconducting quantum interference device magnetometer in a field of 1 T and in the temperature range of 5–100 K to confirm the low temperature magnetic behavior and the ordering temperature $T_N=78$ K. The magnetic susceptibility of the powdered $^{17}$O-enriched sample is shown in Fig. 2. The transition temperature is revealed by a small kink in the $\chi(T)$ data at $T_N$.

Two CaV$_2$O$_4$ crystals were used in $^{51}$V NMR measurements. Crystal 1 was grown in an optical floating zone furnace, while crystal 2 was grown using a tri-arc crystal pulling method. The sizes of crystals 1 and 2 are about 5 $\times$ 5 $\times$ 10 and 1 $\times$ 1 $\times$ 2 mm$^3$, respectively. Both crystals were annealed at 1200 $^\circ$C under 4.5% $H_2$-He flow, and the antiferromagnetic phase transition temperatures of the annealed crystals were found from magnetic susceptibility and heat capacity measurements to be 69 K. The difference in $T_N$ between the powder and single crystal samples may be related to different unit cell volumes of these samples. The unit cell volumes in the powder and single crystal CaV$_2$O$_4$ samples are 296.0(5) and 298.0(5) $\AA^3$, respectively. The reason for this difference is, however, unknown at present. A similar correlation between $T_N$ and the lattice volume was observed in EuCu$_2$Ge$_2$. The magnetic susceptibility of crystal 2 is shown in Fig. 3, with the field along $a$ and $b$ directions. The antiferromagnetic transition temperature $T_N$ is clearly seen as a bifurcation in the susceptibilities along the two directions. We note that, when the field is along the $b$ direction, a splitting between zero-field-cooled and field-cooled susceptibilities is observed below $T=20$ K.

![FIG. 2. Magnetic susceptibility $\chi$ versus temperature $T$ of the $^{17}$O-enriched CaV$_2$O$_4$ powder sample measured in a field of $H=1$ T. The vertical arrow indicates the position of the antiferromagnetic transition temperature $T_N=78$ K.](image-url)
spectra at T\text{\text{N}}=69 K were obtained via Fourier transform of half the echo signal, while the difference between the measured field and the field at the position of the sample (measured by the resonant frequency of protons in water) was less than 0.005 T over the whole field range. Individually, the crystals were placed inside copper solenoid coils with the crystal c axis parallel to the coil axis. Measurements of crystal 1 involved rotation of the field in the a-b and b-c planes. Measurements of crystal 2 involved rotation of the field in the a-b plane. The rotation of the field was achieved by rotating the cryostat together with the crystal about the crystallographic axes, perpendicular to the field plane. The misalignment between the rotation axis and the intended crystallographic axis is estimated to be less than 5°.

III. ^{17}\text{O} NMR IN POWDER SAMPLE OF CaV$_2$O$_4$

Figure 4 displays the ^{17}\text{O} NMR spectra for the ^{17}\text{O}-enriched powder sample of CaV$_2$O$_4$ at H=3 T at three different temperatures. The spectrum at T=296 K was obtained via Fourier transform of half the echo signal, while the spectra at T=80 and 77 K were obtained by frequency sweep. ^{17}\text{O} nuclei have spin 5/2 and, thus, possess a nonzero electric quadrupole moment. Since the local environments of all oxygen sites do not possess cubic symmetry (point group \text{m}1), one expects a quadrupole splitting of the ^{17}\text{O} resonance frequencies. We attribute the lack of a powder pattern of the first order quadrupole splitting in the observed spectra to a smaller quadrupole splitting compared to the magnetic broadening of the spectra. The positions of the spectrum peak position show negligible field dependence. The chemical shift K of the peak position is given by K=Å\text{hf}, where Å\text{hf} is the isotropic hyperfine coupling constant and \chi is the magnetic susceptibility. Using the data in Figs. 2 and 4 and additional \chi(T) data (not shown), we obtain the upper limit Å\text{hf} \leq 1.7 kg/\mu B.

The line gets broader below T\text{N} with decreasing temperature. As shown in Fig. 4, the absorption line at T=77 K is much broader than the lines at T=80 and 296 K. As will be further shown below, this broadening is a signature of an antiferromagnetic phase transition at T\text{N}=78 K, where the nuclear spin-lattice relaxation rate 1/T$_1$ exhibits a peak. As the temperature approaches the phase transition temperature, the electronic vanadium spins slow down dramatically and, thus, induce an inhomogeneous static (on the NMR time scale) dipolar or transferred hyperfine field on neighboring ^{17}\text{O} sites and broaden the ^{17}\text{O} NMR line. Due to the fast decrease of signal intensity below T\text{N} with decreasing temperature, detailed measurements of the temperature dependence of the line broadening in this temperature range were not pursued.

The recovery of the ^{17}\text{O} longitudinal nuclear magnetization M(t) following the saturation pulses is a single exponential function at T>100 K. This shows that all the ^{17}\text{O} NMR transitions are saturated and, thus, there are no satellite peaks located away from the main peaks displayed in Fig. 4, consistent with a small quadrupole splitting as discussed above. Below 100 K, deviation from single exponential behavior is observed, indicating a distribution of 1/T$_1$ values. In order to extract a characteristic relaxation rate at all temperatures, we fitted the recovery curves to a stretched exponential function

\[ 1 - \frac{M(t)}{M(\infty)} = \exp \left[ -\left( \frac{t}{T_1} \right)^\beta \right]. \]

The relation of the parameters 1/T$_1$ and \beta to the 1/T$_1$ distribution underlying a stretched exponential function has been discussed in a recent paper. Figure 5 shows the temperature dependence of 1/T$_1$ and \beta in H=3.0 and 4.7 T. At
T > 100 K, the relaxation rate is almost temperature independent. Below 100 K, 1/T1 exhibits a strong enhancement and reaches a peak at TN = 78 K. Combining the above NMR results with magnetization studies of powder and single crystals, we identify the 1/T1 peak temperature as the temperature of an antiferromagnetic phase transition TN. The peak in the nuclear spin-lattice relaxation rate at TN results from an enhancement and slowing down of the electronic spin fluctuations at wave vectors close to the antiferromagnetic ordering vector as the temperature approaches TN from either side.13

IV. 51V NMR BELOW TN IN SINGLE CRYSTALS OF CaV2O4

A. Spin structure at 4.2 K

In an external magnetic field $H$, the resonance frequency $f$ of the 51V nuclear spins is given by

$$f = A \langle S \rangle + |H| \gamma \nu/2\pi,$$

where $A$ is the hyperfine coupling constant between the nuclear spin and the vanadium electronic spins $S$, $\gamma$ is the gyromagnetic ratio of 51V nuclear spins, and $\langle S \rangle$ denotes the average electronic spin value in thermal equilibrium. In our experiments, the local field is much larger than the applied field: $A\langle S \rangle \gg H$. Depending on whether the applied field component along $\langle S \rangle$ is parallel or antiparallel to $\langle S \rangle$, the resonance frequency shifts to higher or lower values, respectively. If CaV2O4 is a collinear antiferromagnet at low temperatures, where opposite spin directions exist, upon application of an external field along the ordering axis, the zero-field spectrum should split into two peaks. These peaks should be symmetrically displaced above and below the zero-field peak frequency.

Figure 6 shows the field-swept spectra with the field at different angles in the $a$–$b$ plane, measured with rf both higher and lower than the zero-field peak frequency $f_0$ = 236.7 MHz. All measurements in this section were performed on CaV2O4 crystal 1. In contrast to a single peak above and a single peak below the zero-field peak frequency $f_0$ when an applied field is present, as expected for a collinear antiferromagnet, instead we see two peaks above $f_0$ and two peaks below $f_0$ in applied fields as shown by the vertical arrows in Fig. 6. Whether each set of two peaks is resolved depends on the angle of the applied field in the $a$–$b$ plane as shown. We infer below that the spectra in Fig. 6 (and Fig. 8) are consistent with a magnetic structure at 4.2 K that consists of two antiferromagnetic substructures, each of which is a collinear antiferromagnetic arrangement where the angle between the ordering axes of the two substructures is 19(1)°. The angle labeled in each panel of Fig. 6 is the angle between the applied field and the axis $S_m$, which is the average of the projections onto the $a$–$b$ plane of the two spin ordering directions (see Fig. 10 below). $S_m$ is approximately parallel to the $b$ axis and is determined by fitting the peak positions versus angle, as will be explained below.

In our discussions of the 51V NMR results, we assume that the applied magnetic field only shifts the NMR frequency without affecting the electronic spins. In fact, the ordered electronic moments can be tilted by the applied field due to the presence of a torque. However, we can show that the tilting angle is indeed negligibly small. From the magnetization measurements,6 at 4.2 K, the susceptibility $\chi$ of single crystal CaV2O4 with applied field in the $a$, $b$, or $c$ direction is $\chi \sim 0.003$ cm$^3$/mol, which corresponds to an induced moment of 0.005$\mu_B$ for each vanadium spin in a 2 T field. The tilting angle required to produce such a moment is only 0.3°, assuming an ordered moment of 1.06$\mu_B$.7 Both this angle and the induced moment are negligible to our studies.
The spectra in Fig. 6 exhibit a two-peak structure when the field points away from the $S_m'$ axis. When measured by a field swept at a fixed frequency $f$, each peak $i$ (=1,2) should appear at the field value

$$H_{\text{peak},i} = \frac{-f_0 \cos \alpha_i + \sqrt{f_0^2 - f_0^2 \sin^2 \alpha_i}}{(\gamma_i/2\pi)},$$

where $\alpha_i$ is the angle between the field and the respective electronic spin ordering direction of a magnetic substructure noted above. The observed two-peak structures for $f > f_0$ and $f < f_0$ strongly indicate the presence of these two different antiferromagnetic spin ordering directions in the system. The ability to resolve the two peaks at the larger angles in Fig. 6 (and Fig. 8) is related to the larger partial derivative $|\partial H_{\text{peak},i}/\partial \alpha_i|$ of Eq. (3) at the larger $\alpha_i$ values for $\alpha_i < \pi/2$ rad.

The two peaks in the same spectrum have different heights, as can be clearly seen in Figs. 6(b), 6(d), 6(g), and 6(i). The reason behind this difference is currently not understood. It may be due to the change of the nuclear spin-spin relaxation times at different field values, since we fix the separation between the two rf pulses for echo generation to be 18 $\mu$s. In fact, we observed a field-dependent oscillation of the spin echo intensity as a function of the separation between the two echo-generating pulses. Figure 7 displays two nuclear spin-spin relaxation curves measured under identical conditions except for different external magnetic fields of 1.346 and 1.86 T, respectively. The oscillation pattern shows a clear field dependence. However, without knowing the detailed functional form of the decay curves, we cannot extrapolate the signal intensity back to zero pulse separation to correct for the nuclear spin-spin relaxation effect.

We further note that the different heights of the two peaks cannot be attributed to the different percentages of spins in the two spin substructures. In such a scenario, the spins contributing to the left peaks in Figs. 6(b) and 6(g) should contribute to the right peaks in Figs. 6(d) and 6(i) (see Fig. 11), and the left peaks should be higher in one orientation while lower in the other in Figs. 6(b) and 6(d) and in Figs. 6(g) and 6(i), respectively. However, the spectra in Figs. 6(b) and 6(d) and in Figs. 6(g) and 6(i), are almost the same. The symmetry in the spectra with the field on opposite sides of $S_m'$, such as in Figs. 6(b) and 6(d) and in Figs. 6(g) and 6(i), indicates that the number of spins in the two substructures are the same.

Since the above two-peak structure is observed with the field in the $a$–$b$ plane, these measurements can only detect the difference of the spin projections of the two substructures onto the $a$–$b$ plane. In order to determine whether or not the projections onto the $b$–$c$ plane are also different, we also measured the spectra with the field in the $b$–$c$ plane. Some representative spectra with the field in different directions are displayed in Fig. 8, where the angles listed are described in the caption. As one can see, a two-peak structure is still observed when the field is at a large angle from the $S_m'$ axis. However, the separations between the two peaks are smaller than in Fig. 6, indicating a smaller angle between the two easy axis projections onto the $b$–$c$ plane than onto the $a$–$b$ plane.

In order to study whether there exists canting and/or an imbalance in the number of spins in opposite directions for each of the two ordered magnetic substructures, we compared the spectra with those measured with the field rotated by 180°. Figure 9 displays two spectra measured at $f = 222$ MHz, with the field parallel to the $a$–$b$ plane and $-31^\circ$ and 149° away from the $S_m'$ direction, respectively. These two spectra are identical within experimental error, indicat-
ing the absence of spin canting and the same number of spins in opposite directions within each magnetic substructure.

Thus, we propose a model of the spin structure as shown in Fig. 10. Various notations used in the model are explained in the caption of Fig. 10. There are equal numbers of spins in the two antiferromagnetic substructures, each of which consists of collinear antiparallel spins also with equal number. The plane defined by the two ordering directions is parallel neither to the $a$-$b$ nor the $b$-$c$ plane. The average ordered moment direction $S_m$ is approximately parallel to the $b$ axis. This is consistent with single crystal anisotropic magnetization measurements versus temperature which showed that below $T_N$, the average easy axis of the magnetic structure is approximately the $b$ axis.6 Note that in our NMR study, we cannot determine the location in the lattice of the two different magnetic substructures.

To extract the angle between the spin ordering directions of the two substructures, we measured the dependence of the peak positions versus the field directions at rf of 231 and 243 MHz. The results are shown in Fig. 11. For small angles between $H$ and $S_m$, or $S_m'$, only one peak is observed. At larger angles, the positions of two peaks can be resolved. Two different symbols are used to represent the two different spin substructures, while for spectra with single peaks, a third symbol is used. Since the angle between the spin direction and the $b$ axis is much less than 1 rad, the positions of two peaks can be observed. The error in $H_{\text{peak}}$ is comparable to the size of the symbols unless shown explicitly. The solid and dotted lines represent the fits by the theoretical prediction in Eq. (3).

![FIG. 10. The proposed ordered spin structure in CaV$_2$O$_4$. There are two different antiferromagnetic ordering substructures with equal numbers of spins, each of which has a collinear antiferromagnetic spin arrangement. $\Delta \theta$, $\Delta \theta'$, and $\Delta \theta''$ are the angles between these two directions, and their projections on $a$-$b$ and $b$-$c$ planes, respectively. $S_m$, $S_m'$, and $S_m''$ are the average of the two directions and their projections on $a$-$b$ and $b$-$c$ planes, respectively. $\theta_m$, $\theta_m'$, $\theta_m''$, $\Delta \theta_m$, $\Delta \theta_m'$, and $\Delta \theta_m''$ are the angles formed between a fixed arbitrary experimental reference direction in the $a$-$b$ ($b$-$c$) plane and the applied field $H$ and $S_m$ ($S_m'$), respectively.]

$$\cos \alpha_{1,2} = \cos(\theta_m' \pm \Delta \theta'/2 - \theta_m''),$$

where $\alpha_{1,2}$ are the angles between the field and the two spin directions $S_1$ and $S_2$, respectively. Similarly, for the field in the $b$-$c$ plane, one has

$$\cos \alpha_{1,2} = \cos(\theta_m'' \pm \Delta \theta''/2 - \theta_m).$$

We fitted Eq. (3) with $\cos \alpha_{1,2}$ given by Eqs. (4) and (5) to the data in Fig. 11. The free parameters in the fit were $f_0$, $\theta_m$, $\theta_m'$, $\theta_m''$, $\Delta \theta'$, and $\Delta \theta''$. The best fit results are $f_0=236.7(2)$ MHz, $\Delta \theta'=18(1)^\circ$, and $\Delta \theta''=6(1)^\circ$. The fits are shown in Fig. 11. Since the angles between the spins and the $b$ axis are much less than 1 rad, we have
The peak positions of the spectra can only be measured below 45 K. In order to more accurately determine the peak position of the spectra, we fitted the measurements were done on crystal 1 at 4.2 K.

\[
\sin \Delta \theta = \sqrt{\sin^2 \Delta \theta' + \sin^2 \Delta \theta''},
\]

from which one obtains the angle between the easy axes of the two magnetic substructures to be \(\Delta \theta = 19(1) ^\circ\).

In addition to the study of the angular dependence of the peak positions, we also measured their frequency dependences to further confirm the proposed spin structure. Figures 12(a) and 12(b) show the field-swept spectra with the field \(H\) pointing along the \(S''_m\) direction, at rf lower and higher than \(f_0 = 236.7\) MHz, respectively. Note that when \(H \parallel S''_m\), the two magnetic substructures have the same peak positions of the spectra (see the zero-angle data in Fig. 11). The peaks in Figs. 12(a) and 12(b) both shift to higher fields when the frequency shifts further away from \(f_0\), respectively. The peak positions \(H_{\text{peak}}\) versus rf are plotted in Fig. 12(c). The two sets of data points can be well fitted by two linear equations

\[
f = f_0 \pm H_{\text{peak}} \gamma / 2 \pi, \tag{7}
\]

where \(f_0\) is the peak frequency of the spectrum at zero applied field. A fit of Eq. (7) to the data gives \(\gamma / 2 \pi = 11.4(2)\) MHz/T and \(f_0 = 236.7(1)\) MHz. Assuming \(S_m\) to be parallel to the \(b\) axis, the value of \(\gamma\) should be \(\gamma / 2 \pi = (\gamma_c / 2 \pi) \cos(\Delta \theta / 2) = 11.07\) MHz/T, where \(\Delta \theta = 19^\circ\) is the angle between the ordering directions of the two magnetic substructures. This value of \(\gamma / 2 \pi\) is very close to the above fitting result.

B. Ordered moment and its temperature dependence

In this section, we will study the temperature dependence of the vanadium ordered moment, which provides evidence for an energy gap in the antiferromagnetic spin wave excitation spectrum, arising from anisotropy effects. Then we will discuss the value of the saturation vanadium spin moment at low temperatures. Measurements in this section were performed on crystal 2. The experiment was set up to allow field rotation in the \(a-b\) plane. By rotating the field in the \(a-b\) plane, the \(S'_m\) direction (see Fig. 10) is identified as the direction along which the peak position in the spectrum is a maximum at a fixed rf away from \(f_0\) (see Fig. 11). After identifying the \(S'_m\) direction, all subsequent measurements of the spectra were performed versus \(H\) at fixed rf with the field along the \(S'_m\) direction.

With the field along \(S'_m\), only a single peak is observed in the spectrum at each frequency (see Fig. 12). In Fig. 13, we display the frequency dependence of the peak position at 4.2 K. Similar to the case of crystal 1 (Fig. 12), the data points can be well fitted by two straight lines. A fit of Eq. (7) to the data gives \(f_0 = 236.98(8)\) MHz and \(\gamma / 2 \pi = 11.3(1)\) MHz/T. This value of \(\gamma\) is in agreement with the fitting value in crystal 1. However, the value of \(f_0\) is slightly larger than in crystal 1. This slight difference may be due to sample-dependent differences.

Figure 14 displays representative spectra measured at four different temperatures. For comparison between the different spectra, the \(x\) axis has been converted to the quantity \(f + H \gamma / 2 \pi\), with \(\gamma / 2 \pi = 11.3\) MHz/T. As the temperature increases, the signal intensity decreases rapidly and the spectra can only be measured below 45 K. In order to more accurately determine the peak position of the spectra, we fitted...
the original field-swept spectra (with the x axis being H) by a Gaussian function

$$I(H) = A + B \exp[-2(H - H_{peak})^2/W^2],$$

with A, B, H_{peak}, and W as fitting parameters. The zero-field peak frequency f_0 is then determined from

$$f_0 = f \pm H_{peak} \gamma/2 \pi,$$

where $\gamma/2 \pi = 11.3$ MHz/T, and the + and − signs correspond to the cases of $f < f_0$ and $f > f_0$, respectively. In order to determine whether $f < f_0$ or $f > f_0$, spectra were measured with at least two different frequencies at each temperature. With the correct choices of the + or − signs, the obtained $f_0$ values for different spectra as in Fig. 14 are the same within experimental error at each temperature. The final $f_0$ value is an average over all calculated $f_0$ values for various spectra at the same given temperature.

Figure 15 shows the temperature dependence of $f_0$. Since the temperature dependence of the hyperfine coupling constant can be ignored, $f_0(T)$ is directly proportional to the ordered local moment. The ordered moment is almost temperature independent at $T < 15$ K. In the spin wave theory of a three-dimensional antiferromagnet without anisotropy, the initial decrease of the ordered moment with temperature $T$ should follow a $T^2$ dependence. Fitting the data by a power law gives an exponent $\approx 3.5$, an unphysically large value (not shown). The temperature independence below $T < 15$ K, thus, indicates the presence of an anisotropy-induced energy gap for spin wave excitations.

Before estimating the gap energy, we will first estimate the value of the saturation moment at $T = 0$ K. The local moments reach their saturation value at $T < 15$ K. From the value of $f_0 = 237$ MHz at $T < 15$ K, one obtains a local field value of $H_{loc} = f_0/(\gamma/2 \pi) = 21.2$ T. In order to infer the value of local moment from the local field value, the hyperfine coupling constant $A$ and the $g$-factor have to be determined. With known values of $A$ and $g$, the ordered moment $\langle \mu_z \rangle = g \mu_B H_{loc}/A$. The local field is dominated by the contact interaction through the polarized core electrons, which is approximately proportional to the number of unpaired electronic spins in the 3d orbitals with a proportionality constant of 12.5 T per unpaired electron to within 20%. However, besides the contact interaction, orbital effects and transferred hyperfine coupling with the neighbor V$^{3+}$ ions may also contribute significantly to the local field at the $^{51}$V nuclear site.

In the absence of a knowledge of the orbital effects and transferred interactions, we will estimate a possible range of the $A/g \mu_B$ value in CaV$_2$O$_4$ using the known values of $A/g \mu_B$ in other V$^{3+}$ compounds. The values of $A/g \mu_B$ in LaVO$_3$, YVO$_3$, and V$_2$O$_3$ are 16.8, 20.8, and 15.5 T/\mu_B, respectively. The range of $A/g \mu_B$ in the above four compounds is between 13.3 and $20.8$ T/\mu_B. Assuming $A/g \mu_B$ in CaV$_2$O$_4$ lies in the same range, the low temperature ordered vanadium moment in CaV$_2$O$_4$ is, thus, in the range of 1.02–1.59 $\mu_B$. This $\langle \mu_z \rangle$ range is consistent with the value $1.06(6) \mu_B$ extracted from the previous neutron powder diffraction study.

Next we estimate the energy gap for the spin wave excitations. From the neutron diffraction studies, we know that the spins reverse their ordering direction upon moving along the c axis. Therefore, the spin structure in the ordered state within a zigzag chain should look as in Fig. 16, where we ignore the possible small misalignment of 19° between spins in the two magnetic substructures discussed above. Because each spin in one leg of the chain couples by the same exchange constant $J_1$ to two spins in the other leg that are ordered in opposite directions, we expect that the effective coupling between the two legs within a zigzag chain is greatly reduced in the ordered state. As a result, we will consider the nearest-neighbor interactions within the leg $J_2$ as the only dominant magnetic interaction and treat the effect of interleg interaction within a zigzag chain as a weak interchain interaction. For simplicity, we will use a single exchange constant $J'$ to characterize the effect of the interchain interactions. To include the effect of anisotropy, we assume a single ion anisotropy in the system with a single direction of easy axis. Then, the Hamiltonian can be written as

$$H = \sum_i \left( 2J_2 S_i \cdot S_{i+1} - \frac{1}{2} K S_i^2 \right) + 2 \sum_{(i,j)} J' S_i \cdot S_{j+1},$$

where $K$ is the anisotropy constant, the index $i$ runs through the spins in one leg of the chain, and the summation $(i,j)$ runs through all interleg and interchain nearest-neighbor pairs.

The Fourier transform of the exchange interactions is
\[ J(q) = \sum_j J(r_{ij}) \exp(-i q \cdot r_{ij}), \]

where \( r_{ij} \) connects two spins in opposite sublattices, \( J(r_{ij}) > 0 \) is the nearest-neighbor exchange constant, and the index \( j \) runs through all the nearest-neighbor spins of spin \( i \) in the opposite sublattice (each sublattice consists of spins in the same direction). The spin wave dispersion relation is given by

\[ E_q = [(2S J(0) + KS)^2 - (2S J(q))^2]^{1/2}, \]

where we ignored interactions between spins in the same sublattice. The spin wave gap value is given by the value of \( E_q \) at \( q=0 \). In the limit of small anisotropy \( K \ll 2 J(0) \approx 4 J_z \), the gap energy is given by

\[ E_G = 2S [J(0)K]^{1/2}. \]

In the spin wave theory, the decrease of sublattice magnetization is due to the thermal activation of spin wave excitations. In the above bipartite antiferromagnetic system, the dispersion relation in Eq. (10) depends on the spin lattice structure and the exchange interactions \( J(r) \). For a quasi-one-dimensional chain with interchain coupling \( J' \), at temperatures \( T > J'/k_B \), one can ignore the dispersion perpendicular to the chain direction. Then for small values of \( q_z \), which is the \( q \) vector component along the chain, one can perform a Taylor series expansion of \( |\mathcal{J}(q)|^2 \) as

\[ |\mathcal{J}(q)|^2 \approx |\mathcal{J}(0)|^2 [1 - iq_z^2]. \]

where \( l \) is the nearest-neighbor distance within the leg.

At \( T < J_z/k_B \), only spin waves at small \( q_z \) values have significant contributions to the integral in Eq. (12), so one can change the limits of integral for \( q_z \) in Eq. (12) to \( \pm \infty \). The small \( q \) approximation is valid only at temperatures where \( 1 - |\langle S_z(T) \rangle|/|\langle S_z(0) \rangle| < 0.1 \), which is satisfied within our experimental temperature range. Substituting Eq. (13) into Eq. (10), and changing the limits of integral for \( q_z \) in Eq. (12) to \( \pm \infty \), one obtains in the limit of small anisotropy \( K \ll 2 J(0) \) and \( T \ll E_G \),

\[ 1 - \frac{\langle S_z(T) \rangle}{\langle S_z(0) \rangle} = B e^{-E_G/k_B T} (E_G/k_B T)^{-1/2}, \]

where

\[ B = \frac{2}{\sqrt{2 \pi}} = 0.80. \]
\( j'J_z/k_B \approx 2 \, K \). However, this value of \( J' \) seems inconsistent with the initial assumption of \( T \ll j'J_z/k_B \) required for the three-dimensional model to be valid. Therefore, Eq. (19) of the 1D model might provide a better approximation to the \( f_0(T) \) data.

VI. SUMMARY AND CONCLUSIONS

We have presented \(^{17}\text{O}\) and \(^{51}\text{V}\) NMR results on the zigzag spin chain compound CaV\(_2\)O\(_4\). The strong inhomogeneous broadening and a peak in the nuclear spin-lattice relaxation rate versus temperature of \(^{17}\text{O}\) NMR confirm the presence of an antiferromagnetic phase transition at 78 K in a powder sample. The crystals we studied have \( T_N = 69 \, K \). \(^{51}\text{V}\) NMR in the ordered state of crystals reveals the presence of two antiferromagnetic substructures at 4.2 K, each of which is collinear and which form an angle of \( 19(1) \, ^\circ \) between them with the average direction approximately parallel to the \( b \) axis. The origin and location in the lattice of the different spin substructures remain unknown. However, we speculate that the two magnetic substructures are associated with the two inequivalent \( V^{3+} S=1 \) zigzag spin chains in the orthorhombic crystal structure, respectively. Magnetic neutron diffraction studies are required to further characterize the magnetic structure below \( T_N \). The temperature dependence of the zero-field resonance frequency at low temperatures suggests the presence of magnetic anisotropy and an energy gap in the spin wave excitation spectrum. The energy gap is estimated from spin wave theory to be between 64 and 98 K.

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