Magnetic phase diagrams of the Kagomé staircase compound Co$_3$V$_2$O$_8$

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Abstract

At zero magnetic field, a series of five phase transitions occur in Co$_3$V$_2$O$_8$. The Néel temperature, $T_N=11.4$ K, is followed by four additional phase changes at $T_1=8.9$ K, $T_2=7.0$ K, $T_3=6.9$ K, and $T_4=6.2$ K. The different phases are distinguished by the commensurability of the b-component of its spin density wave vector. We investigate the stability of these various phases under magnetic fields through dielectric constant and magnetic susceptibility anomalies. The field-temperature phase diagram of Co$_3$V$_2$O$_8$ is completely resolved. The complexity of the phase diagram results from the competition of different magnetic states with almost equal ground state energies due to competing exchange interactions and frustration.

Key words: Kagomé lattice; commensurate-incommensurate phase transitions; geometric frustration; magnetic anisotropy

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Co$_3$V$_2$O$_8$ is an interesting compound to be studied since multiferroic behavior was found recently in Ni$_3$V$_2$O$_8$ [1]. The inherent geometric frustration found in the Kagomé lattice in M$_3$V$_2$O$_8$ ($M=\text{Co, Ni, Cu}$) result in the very low temperature anti-ferromagnetic ordering of the M spins, $T_N=11.4$ K and $T_N=9.8$ K for Co$_3$V$_2$O$_8$ and Ni$_3$V$_2$O$_8$, respectively [2]. The presence of two different M sites along with competing interactions such as the single ion anisotropy, nearest neighbor, next nearest neighbor, dipolar, and Dzyaloshinskii-Moriya (DM) interactions allow fascinating magnetic behavior at low temperatures such as a cascade of magnetic phase transitions below $T_N$ [3], strong magnetic anisotropy [4], strong sensitivity of the phase transitions with respect to the orientation of an applied external magnetic field [1] and in the case for Ni$_3$V$_2$O$_8$, ferroelectricity.

In this report, we present the magnetic phase diagram of Co$_3$V$_2$O$_8$ with fields directed along the a-, b-, and c-axis. Due to the strong coupling between the magnetic orders and the lattice all phase transitions are clearly indicated by anomalies of the magnetization as well as of the dielectric constant. This enables us to uniquely define and trace the phase boundaries originating from $T_N$ to $T_4$ in the $H$ – $T$ phase diagram. At zero field, the 5 observed phase transitions are consistent with the results reported by Chen et al. [3]. Other recent reports on the magnetic phase diagram of Co$_3$V$_2$O$_8$ focus more on higher magnetic fields ($H \geq 0.5$ Tesla) [5-6] and they do not resolve all details of the phase diagram, particularly in the low-field range.

In the Kagomé staircase structure of Co$_3$V$_2$O$_8$ there are two Co$^{2+}$ sites, one located in the spines of the staircase and the other at the cross-tie site [3]. At $T_N=11.4$ K, only the

![Graph 1: Magnetization $M$ (left scale) and dielectric constant $\varepsilon$ (right scale) of Co$_3$V$_2$O$_8$ near H=0. The five phase transition temperatures are labeled as $T_N$ and $T_1$ to $T_4$. The critical temperatures are clearly defined by distinct anomalies in the $T$- and $H$-dependence of $M$ and $\varepsilon$.](image)
Co$^{2+}$ spins located in the spine site order antiferromagnetically (AFM) along the a-axis. The various phases observed in $Co_3V_2O_8$ at lower $T$ are distinguished by the commensurability of the spin density wave vector. The $b$-component of the magnetic modulation vector, $\delta$, decreases below $T_N$ continuously from $\delta = 0.55$ and it locks-in at a commensurate value of $\delta = 0.50$ at $T_1 = 8.9$ K. Below $T_2 = 7.0$ K, $\delta$ begins to decrease continuously again locking into another commensurate value, $\delta = 0.33$, at $T_3 = 6.6$ K. At $T_4 = 6.2$ K, $\delta$ becomes zero and the Co$^{2+}$ spins on both sites become ferromagnetically ordered with the spin alignment along the a-axis [3].

Single crystals of $Co_3V_2O_8$ were grown through the floating zone furnace method. The dielectric constant was measured using Andeen Hagerling’s AH2500 capacitance bridge at a frequency of 1 kHz. The magnetic susceptibility was measured with Quantum Design’s MPMS magnetometer.

The magnetic phase diagrams for $Co_3V_2O_8$ were constructed through temperature and field dependent dielectric constant and dc magnetization scans. The phase boundaries are well defined by distinct anomalies of the magnetization as well as the dielectric constant (Fig. 1). In order to determine precisely the stability range of the various phases measurements of $M(T)$ ($\varepsilon(T)$) as well as $M(H)$ ($\varepsilon(H)$) have been conducted. This enabled us to resolve the details of the phase diagram in the low-field range, for $H < 0.1$ T.

For magnetic fields applied along the a-axis (Fig. 2a), the two commensurate phases CM1 ($\delta = 1/2$) and CM2 ($\delta = 1/3$) are stable only to about 0.07 T. Cooling below this critical field results in a re-entrant behavior of the IC-AFM phase. Two tricritical points exist at $T_{C1} = 6.5$ K, $H_{C1} = 0.035$ T and at $T_{C2} = 9.8$ K, $H_{C2} = 0.36$ T where three phases coexist in a point of the $H - T$ phase diagram. This phase diagram is different from that derived recently from neutron scattering experiments [6]. The latter work resolves only three magnetic transitions at $H = 0$ due to the limited temperature and field resolution of the experiment. Our zero-field data, however, are consistent with the neutron work of Ref. [3] and the magnetic and heat capacity data of Ref. [2].

Similar behavior is found in the $H_b$ phase diagram (Fig. 2b) except that the stability range of the CM1 and CM2 phases extend to about 1.2 T. Similarly, the IC-AFM phase is stable towards higher fields ($H_b > 3$ T) and the transition temperature into the w-FM phase is nearly temperature independent. The first tricritical point (coexistence of CM2, IC-AFM, and w-FM phases) is located at $T_{C1} = 6.2$ K and $H_{C1} = 1$ T.

The $H_c$ phase diagram is shown in Fig. 2c. The main difference to the phase diagrams with $H || a$ and $H || b$ is the stability of the narrow CM2 phase (with $\delta = 1/3$) that extends to lower temperature at fields up to 1 T. The phase boundary at very low $T$ reported in Ref. [3] is shown in Fig. 2c as a dashed line.

The complex structure of the magnetic phase diagrams of $Co_3V_2O_8$ is a consequence of the existence of different magnetic states very close in ground state energy due to the competing exchange interactions in $Co_3V_2O_8$ and the inherent frustration. The magnetic anisotropy, the DM and the competing nearest and next nearest neighbor exchange interactions contribute to the richness of the magnetic phase diagram with various commensurate and incommensurate phases in a narrow temperature-field range. The strong spin lattice interaction in $Co_3V_2O_8$ is evident in subtle changes of the dielectric constant at the magnetic phase transitions. In the sister compound, $Ni_3V_2O_8$, the magnetoelastic coupling leads to ionic displacements and a ferroelectric polarization in a phase with an incommensurate transverse spiral (inversion symmetry breaking) magnetic modulation. This transverse spiral does not exist in $Co_3V_2O_8$ [6], hence all magnetic phases are paraelectric.

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