Field-induced spin-structural transition and giant magnetostriction in Ising chain $\alpha$-CoV$_2$O$_6$

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We have measured magnetization, specific heat ($C_p$), and sample length change ($\Delta L/L$) for understanding the field-induced spin-structural change in quasi-one-dimensional antiferromagnetic (AFM) spin chain $\alpha$-CoV$_2$O$_6$. Analysis of $C_p(T)$ shows that an effective $S=1/2$ Ising state is realized below 20 K, though the magnetic fluctuations persist well above $T_N$. Both $C_p$ and $\Delta L/L$ exhibit strong $H$ dependence in the AFM state. With increasing $H$, a sharp and symmetric peak emerges below $T_N$ due to the field-induced first order magnetic transition. The large magnetostriction and the emergence of new peak below $T_N$ suggest strong spin-lattice coupling in $\alpha$-CoV$_2$O$_6$.

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Several low-dimensional cobalt-based compounds and rare-earth-based pyrochlore oxides exhibit fascinating magnetic properties such as magnetic field ($H$) induced spin order-disorder transition, 1/3 magnetization plateau in the $M(H)$ curve, quantum phase transition spin-structural change. Geometrical frustration due to the triangular or tetrahedral arrangement of the magnetic moments, bond frustration as a result of competing ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions and large single ion anisotropy are the fundamental ingredients that eventually determines the complexity of the magnetic ground state and hence the new functionalities in these compounds. Often, the ground state of the frustrated materials is extremely sensitive to external perturbations such as magnetic field.

Recently, the quasi-one-dimensional (1D) spin-chain CoV$_2$O$_6$ has received attention to the scientific community due to the observation of 1/3 magnetization plateau similar to that reported in a regular triangular lattice. In monoclinic $\alpha$-CoV$_2$O$_6$ and triclinic $\gamma$-CoV$_2$O$_6$, the edge-shared CoO$_6$ octahedra form a 1D-like magnetic chain along the crystallographic axis $b$, and the edge-shared VO$_5$ square pyramids are located in between the magnetic chains. The much larger Co-Co interchain distance as compared to intrachain Co-Co distance and the presence of the nonmagnetic V$^{5+}$ ion in between the chains weaken the interchain magnetic coupling considerably. Both $\alpha$-CoV$_2$O$_6$ and $\gamma$-CoV$_2$O$_6$ show large single ion anisotropy and undergo long-range AFM transition below 15 and 6 K, respectively and multiple field-induced metamagnetic transitions. The values of magnetic moment determined from the saturation magnetization ($M_S$) in the field-induced FM state and susceptibility in the paramagnetic (PM) state are found to be significantly larger than that expected for spin only moment of high spin-state Co$^{2+}$ ion. In $\alpha$-CoV$_2$O$_6$, $M_S$ is as much as 1.5 $\mu_B$ larger than the spin only moment (3.0 $\mu_B$). This excess 1.5 $\mu_B$ moment is thought to come from the orbital magnetic moment due to strong spin-orbit or spin-lattice coupling.

Magnetic, electric, and structural properties have been studied extensively to disclose the underlying mechanism of step-like jumps in $M(H)$ of CoV$_2$O$_6$. Neutron diffraction studies have revealed that these jumps in $M(H)$ are coupled to the field-induced magnetic phase transitions from AFM to ferrimagnetic to FM. For complete understanding the field-induced magnetic phase transition and the thermodynamic properties of frustrated systems, measurement of specific heat ($C_p$) in applied field is important. For example, $C_p(T)$ of quasi-1D Ising spin chain BaCoV$_2$O$_6$ shows that a new magnetic phase emerges above a critical field as a result of the first order change in spin structure. In this work, we present specific heat of $\alpha$-CoV$_2$O$_6$ over a wide range of $H$ across the magnetic ordering at $T_N$. Strong spin-lattice coupling has also motivated us to investigate the magnetostriction effect ($\Delta L/L$). We observe that both $C_p(T)$ and the thermal expansion coefficient $\alpha=(1/L)\Delta L/dT$ exhibit a single $\lambda$-like peak at $T_N$ for $H=0$ but a sharp and symmetric peak appears below $T_N$ with applied field. Also, below $T \sim 20$ K, the system releases the Ising-like entropy (R$\ln$2) and exhibits very large magnetostriction effect. We believe that these results are useful for understanding the origin of metamagnetic transition in $\alpha$-CoV$_2$O$_6$.

Polycrystalline $\alpha$-CoV$_2$O$_6$ samples were prepared by standard solid-state reaction method using high purity cobalt(II) acetate tetrahydrate (Aldrich, 99.999%) and vanadium pentoxide (Alfa Aesar,
Stoichiometric quantities of these compounds were mixed properly and the mixture was heated in air for 16 h at 650 °C and then at 725 °C for 48 h. After the heat treatment, the material was quenched in liquid nitrogen to obtain single phase \( \alpha-\text{CoV}_2\text{O}_6 \). Phase purity was checked by powder x-ray diffraction (XRD) method with CuK\(\alpha\) radiation in a Rigaku TTRAX II diffractometer. No trace of impurity phases were detected within the resolution of XRD. All the peaks in the diffraction pattern were fitted well to a monoclinic structure of space group \( \text{C2/m} \) using the Rietveld method (Fig. 1). The observed lattice parameters \( a=9.2501 \) Å, \( b=3.5029 \) Å, \( c=6.6175 \) Å, and \( \beta = 111.61^\circ \) are in good agreement with reported values for \( \alpha-\text{CoV}_2\text{O}_6 \). The linear magnetothermal expansion measurements were done with field \( (H) \) parallel to sample length \( (H \parallel L) \) by capacitive method using miniature tilted plates dilatometer. The specific heat and magnetization were measured using a physical property measurement system (Quantum Design). The specific heat was measured by conventional relaxation time method.

Figure 2(a) displays the temperature dependence of dc magnetic susceptibility \( \chi (=M/H) \) of polycrystalline \( \alpha-\text{CoV}_2\text{O}_6 \) sample in an applied field 0.1 T. \( \chi(T) \) shows a sharp transition to an antiferromagnetically ordered state below \( T_N=15 \) K. No other anomaly is observed below \( T_N \), indicating that only one magnetic transition occurs in the measured temperature range. We observe that \( \chi^{-1}(T) \) can be fitted well to the Curie-Weiss law with an effective moment \( \mu_{\text{eff}}=5.4 \mu_B/\text{Co ion} \) and the Weiss temperature \( \theta=-9.2 \) K. The negative value of \( \theta \) implies that the predominant magnetic interaction is antiferromagnetic in nature. The observed value of \( \mu_{\text{eff}} \) is significantly larger than the expected spin-only moment of high spin Co\(^{2+} \) (3.87 \( \mu_B \)). This huge discrepancy has been attributed to the strong spin-orbit coupling \( 9 \)–\( 15 \).

The temperature dependence of zero-field specific heat is shown in Fig. 2(b). With decreasing \( T \),
$C_P$ decreases down to 20 K and then increases rapidly and exhibits a $\lambda$-like anomaly close to $T_N$. Similar to magnetic data, $C_P(T)$ supports single magnetic phase transition in $\alpha$-CoV$_2$O$_6$. For better understanding the nature of magnetic ground state, the magnetic contribution to the specific heat ($C_M$) in the vicinity of AFM transition and beyond has been estimated. After subtracting the lattice contribution from $C_P$, we have plotted $C_M(T)$ in Fig. 2(c). Figure clearly shows that $C_M$ does not decrease rapidly with increasing $T$ in the PM state. The magnetic entropy ($S_M$) obtained by integrating $(C_M/T)dT$ is shown in Fig. 2(c). $S_M$ does not saturate even at $T$ as high as $3T_N$, which reflects the highly anisotropic nature of the magnetic structure of $\alpha$-CoV$_2$O$_6$. We would like to mention that the observed value of $S_M (=8$ J mol$^{-1}$ K$^{-1}$ at $T=3T_N)$ for the present sample is about 1.5 times larger than that reported by Kim et al.[22]. The larger value of $S_M$ is an indication of superior ordering of spins because more number of spins are participating in the magnetic transition. However, the estimated value of $S_M$ is significantly smaller than the expected 11.5 J mol$^{-1}$ K$^{-1}$ for the high spin Co$^{2+}$ ($S=3/2$). It may be noted that $S_M$=5.6 J mol$^{-1}$ K$^{-1}$ at 20 K is almost in accord with the expected value (Rhn2) for the degree of freedom of the Ising moments. Thus, the entropy of the Ising-like spins is mostly released below 20 K. As the intrachain ferromagnetic interaction in CoV$_2$O$_6$ is much stronger than the interchain spin-flip interaction, the intrachain spin degree of freedom is effectively frozen and the spins would behave like the Ising spins and hence the huge reduction in magnetic entropy.

Typical specific heat data ($C_P/T$) in the vicinity of $T_N$ are shown in Fig. 3 as a function of $T$ for a wide range of $H$. The application of magnetic field suppresses and broadens the peak at $T_N$ and the peak position shifts slowly towards lower $T$. Apart from these usual changes, another important feature is emerging with increasing field strength. For $H=2$ T, a weak shoulder-like feature starts to appear in $C_P(T)$ curve just below 11 K. When $H$ exceeds 2 T, this weak anomaly transforms into a sharp and symmetric peak. The sharp nature of the peak suggests that the transition is first-order. As this phenomenon occurs in the neighborhood of strong AFM ordering transition, it is difficult to determine the exact position of the peak. Also, $C_P$ in the low temperature region is gradually enhanced with increasing $H$. We observe a slight decrease in $S_M$ with increasing $H$ above 2 T. This reduction of the entropy in the high-$H$ region corresponds to its transfer to the higher-$T$ region. In quasi-1D AFM Ising spin chain BaCo$_2$V$_2$O$_8$, the zero-field $C_P(T)$ exhibits a single peak at $T_N=4$ K. However, a field-induced first-order transition occurs below 1.8 K for $H>3.9$ T when $H$ is parallel to $c$ axis[8]. This behavior has been attributed to the formation of new magnetic phase which is observed to exist for applied field up to 10 T or above. Also, in Dy$_2$Ti$_2$O$_7$ pyrochlore, the zero-field $C_P(T)$ exhibits a single peak but a new and sharp peak appears at low $T$ ($\sim$0.5 K) for $H$ along the (111) direction due to the spin-flip transition[8].

In order to shed some light on the nature and origin of the field-induced peak in $C_P$, we have studied the linear expansion $[\Delta L/L]$ as functions of $T$ and $H$. Figure 4(a) presents $\Delta L(T)/L_{4K}$ plots up to 45 K for some selected fields, where $L_{4K}$ is the length of the sample at $T=4$ K in an applied field $H$. The inset of Fig. 4(a) shows $\Delta L(T)/L_{4K}$ plot up to 300 K in absence of field. For $H=0$, $\Delta L/L_{4K}$ decreases monotonically with decreasing $T$ and exhibits a strong anomaly at $T_N$. In the PM state, $\Delta L/L_{4K}$ is approximately linear in $T$ for $H\leq3$ T but it develops a broad maximum close to $T_N$ and an upward curvature above $T_N$ for higher fields. The anomaly at $T_N$ gets weakened but remains visible up to the highest applied field 8 T. For $H\geq1$ T, $\Delta L(T)/L_{4K}$ shows a step-like decrease below a critical temperature $T_S=8$ K. This decrease in $\Delta L/L_{4K}$ at $T_S$ is much sharper in nature than that at $T_N$. To keep track on the field-evolution of the anomalies at $T_N$ and $T_S$, we have determined $\alpha$ from the slope of the curves in Fig. 4(a). Figure 4(b) illustrates the temperature variation of the respective $\alpha$. At zero field, $\alpha(T)$ is positive over the whole temperature range. Similar to $C_P(T)$, $\alpha(T)$ exhibits a broad minimum around 20 K and a sharp $\lambda$-like peak close to $T_N$ and the peak shifts to lower $T$ and broadens with increasing field. $\alpha$ becomes small and negative over a narrow temperature range above $T_N$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(color online) $C_P/T$ versus $T$ plots for the $\alpha$-CoV$_2$O$_6$ sample for different $H$ in the vicinity of antiferromagnetic transition.}
\end{figure}
for $H \geq 7$ T. The field-induced peak in $\alpha(T)$ at $T_S$ is extremely sharp and symmetric and its position is almost insensitive to $H$. This peak is well separated from AFM transition and visible only below 5 T.

The magnetostriction $\Delta L(H)/L_0 = (L(H) - L_0)/L_0$, where $L_0$ is the length of the sample in absence of field, for some selected temperatures both below and above $T_N$ are depicted in Fig. 4(c). At high temperatures ($T > 9$ K), $\Delta L/L_0$ increases smoothly with $H$. However, at low temperatures ($T < 9$ K), the nature of $\Delta L(H)/L_0$ curve changes. $\Delta L(H)/L_0$ also increases with $H$ but exhibits weak anomalies at two critical fields correspond to field-induced metamagnetic transition in $M(H)$ curve\cite{9,10}. Similar to $M(H)$, these anomalies are clearly visible at low temperatures but become weak with increasing $T$ and disappears above $T > 9$ K\cite{9,10}. The disappearance of anomalies in $M(H)$ and $\Delta L(H)/L_0$ curves around 9 K may have a close correlation with the observed field-induced first order transition at $T_S$ as reflected in $C_P(T)$ and $\alpha(T)$. $\Delta L(H)/L_0$ approximately mimics the nature of $M(H)$ curve. At low temperatures, $\Delta L(H)/L_0$ develops a downward curvature with the increase of $H$ and it does not show any tendency of saturation up to the maximum applied field. The curvature decreases with increasing temperature and $\Delta L(H)/L_0$ becomes almost linear for $T$ close to or slightly above $T_N$. In the PM state, $\Delta L(H)/L_0$ decreases rapidly with decreasing $T$ and develops a very weak upward curvature. The magnetostriction effect is very small above 50 K. Note the unusually high value of the magnetostriction in the AFM state, which is comparable to that observed in frustrated spinels\cite{19,20}. The value of magnetostriction can be significantly larger in single crystal with field along $c$ axis. The appearance of the peak at $T_S$ in $C_P$ and $\alpha$ and the large magnetostriction effect in the AFM state suggest that the field-induced magnetostructural transition occurs due to the strong spin-lattice coupling. The reported neutron diffraction results also suggest strong spin-lattice interaction\cite{13}. We believe that measurements of $C_P(T)$ and $\Delta L/L$ on $\alpha$-CoV$_2$O$_6$ single crystal with $H$ along different crystallographic axes may reveal interesting physical properties and the exact ($T-H$) phase diagram.

In conclusion, $C_P(T)$ and $\alpha(T)$ of 1D spin chain $\alpha$-CoV$_2$O$_6$ exhibit a sharp $\lambda$-like peak around $T_N = 15$ K. The magnetic entropy calculated from $C_P(T)$ shows that the magnetic fluctuations persist well above $T_N$ but the system behaves like a spin-1/2 Ising chain below 20 K. In the AFM state, both $C_P$ and $\alpha$ exhibit strong $T$ and $H$ dependence. As in the case of pyrochlore oxides, a sharp and symmetric peak emerges well below $T_N$ with increasing $H$. The sharp nature of the peak indicates that the transition is first order.

FIG. 4. (color online) (a) The temperature dependence of the relative length change, $\Delta L/L_{4K}$, for the $\alpha$-CoV$_2$O$_6$ sample at different $H$. Inset: $\Delta L(T)/L_{4K}$ at 0 T in the temperature range 4-300 K. (b) Plots of the thermal expansion coefficient $\alpha(T)$ for different $H$. (c) Magnetostriiction, $\Delta L(H)/L_0$, of the $\alpha$-CoV$_2$O$_6$ sample at several temperatures both below and above $T_N$. Inset: field dependence of magnetization and $\Delta L/L_0$ at 5 K.
The huge magnetostriction effect and its strong $H$ dependence below $T_N$ along with the field-induced spin-structure transition at $T_S$ suggest that the spin-lattice coupling in this system is quite strong.

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