Rotating magnetocaloric effect in the ferromagnetic Weyl semi-metal Co$_3$Sn$_2$S$_2$

Anzar Ali*, Shama*, and Yogesh Singh$^1$

$^1$Department of Physical Sciences, Indian Institute of Science Education and Research, Knowledge City, Sector 81, SAS Nagar, Manauli PO 140306, Mohali, Punjab, India

The rotating magnetocaloric effect (RMCE) is a recent interest in magnetic refrigeration technique in which the cooling effect is attained by rotating the anisotropic magnetocaloric material from one orientation to the other in a fixed magnetic field. In this work, we report the anisotropic magnetocaloric properties of single crystals of the ferromagnetic Weyl semimetal Co$_3$Sn$_2$S$_2$ for magnetic field $H \parallel c$ axis and $H \parallel ab$ plane. We observed a significant (factor of 2) difference between the magnetocaloric effect measured in both orientations. The rotating magnetocaloric effect has been extracted by taking the difference of the magnetic entropy change ($\Delta S_M$) for fields applied in the two crystallographic orientations. In a scaling analysis of $\Delta S_M$, the rescaled $\Delta S_M(T,H)$ vs reduced temperature $\theta$ curves collapse onto a single universal curve, indicating that the transition from paramagnetic to ferromagnetic phase at 174 K is a second order transition. Furthermore, using the power law dependence of $\Delta S_M$ and relative cooling power RCP, the critical exponents $\beta$ and $\gamma$ are calculated, which are consistent with the recent critical behavior study on this compound.

I. INTRODUCTION

The magnetocaloric effect (MCE) has been a topic of sustained attention for the last two decades due to its potential application in magnetic refrigeration. Providing an environmental friendly alternative to conventional gases is one of the main advantages of this technique. MCE quantifies the thermal response of a magnetic material caused by a varying magnetic field. The rotating magnetocaloric effect (RMCE) is a new direction in magnetic refrigeration that has drawn strong interest recently in different crystallographic directions. In RMCE, advantage can be taken of the anisotropy in a material's magnetocaloric response for magnetic fields in different crystallographic orientations. In RMCE, the change in magnetic entropy ($-\Delta S_R$) is obtained by rotating the magnetic sample from one crystallographic orientation to another, in a fixed external magnetic field. RMCE is a potentially more favorable technique in comparison to MCE where cooling is achieved by changing the magnetic field. The other advantage of RMCE is the possible use of a permanent magnet or a fixed field which will lower the running cost.

There has been immense recent interest in the layered shandite-type half metallic ferromagnet Co$_3$Sn$_2$S$_2$ which shows a paramagnetic to ferromagnetic phase transition (PM-FM) at $T_c = 174$ K. Co$_3$Sn$_2$S$_2$ is also a Weyl semi-metal and shows strong intrinsic anomalous Hall effect due to the presence of Weyl fermions near the Fermi energy. Recently planar Hall effect has been reported on this material far below $T_c$, confirming the unconventional effects of the topological band structure. The crystal structure of Co$_3$Sn$_2$S$_2$ is built up of metallic hexagonal layers stacked along the crystallographic $c$-axis. Such a layered structure may lead to large magnetocrystalline anisotropy. Thus, the half metallic ferromagnet Co$_3$Sn$_2$S$_2$ is a suitable material to study the RMCE. There is also a push in the community to marry topological properties with other functionalities, and Co$_3$Sn$_2$S$_2$ would be a good candidate to look at MCE in a topological material. Recently, a critical behavior study of this half metallic ferromagnet Co$_3$Sn$_2$S$_2$ has been done by Yan et al. and Shi et al.

II. EXPERIMENTAL DETAILS

Single crystals of Co$_3$Sn$_2$S$_2$ were grown as described recently. All the magnetic measurement as a function of applied magnetic field and temperature have been performed using the vibrating sample magnetometer (VSM) option of a Quantum Design Physical Property Measurement System (PPMS). For the magnetocaloric study,
anisotropic isothermal magnetization data has been collected in the temperature range 155 to 195 K around the ferromagnetic $T_c \approx 175$ K and in magnetic fields up to 9 T for a Co$_3$Sn$_2$S$_2$ single crystal.

III. RESULTS AND DISCUSSION

Figures 1(a) and (b) show the zero field cooled (ZFC) and field cooled (FC) magnetization $M$ vs temperature $T$ measured in a magnetic field $H = 0.1$ T applied along the $c$-axis and within the $ab$-plane, respectively. The inset of Fig. 1(a) shows the $dM/dT$ vs $T$ plot with a minima at $T_c \approx 174$ K confirming the paramagnetic to ferromagnetic phase transition $^{24}$. The magnetization is strongly anisotropic, increasing to much larger values for $H \parallel c$ than for $H \parallel ab$. The ZFC and FC curve for $H \parallel ab$ show a large bifurcation below $T_c$ which most likely originates from ferromagnetic domains. Figures 1(c) and (d) show the field dependence of magnetization $M(H)$ at 2 K for $H \parallel c$ and $H \parallel ab$, respectively. For the case of $H \parallel c$ the magnetization increase abruptly and reaches saturation in a very low field with a narrow hysteresis loop, while for $H \parallel ab$ the magnetization, after an initial rapid increase, show a linear increase with field and does not saturate up to the highest fields measured 9 T. This indicates that the crystallographic $c$-axis is the magnetic easy axis. Inset of Figure 1(d) shows the hysteresis loop for small fields. The small hysteresis in both directions indicate that Co$_3$Sn$_2$S$_2$ is a soft ferromagnet.

We now turn to the magnetocaloric response of Co$_3$Sn$_2$S$_2$, which we obtain from isothermal magnetization. Figures 2(a) and (b) show a series of field dependent isothermal magnetization data recorded for temperatures around the critical temperature $T_c \approx 174$ K for the configurations $H \parallel c$ and $H \parallel ab$, respectively. The magnetization data was collected in the temperature range 155 K to 195 K at intervals of 2 K. The MCE (= negative magnetic entropy change $-\Delta S_M$) can be obtained using Maxwell’s relation $^5$:

$$\Delta S_M(T, H) = \mu_0 \int_0^H \left[ \frac{\partial S(T, H)}{\partial T} \right]_T dH. \quad (1)$$

Using thermodynamics relations, it can be further written as:

$$\Delta S_M(T, H) = \mu_0 \int_0^H \left[ \frac{\partial M(T, H)}{\partial T} \right]_H dH. \quad (2)$$

If magnetization data is available only at closely spaced discrete values of temperature, as is mostly the case in experiments, the integral in the above expression is replaced by a summation $^5$:

$$\Delta S_M(T, H) = \mu_0 \sum_i \frac{M(T_{i+1}, H) - M(T_i, H)}{T_{i+1} - T_i}. \quad (3)$$

Figures 3(a) and (b) display the calculated temperature dependence of $-\Delta S_M$ in various fields up to 9T applied in both $H \parallel c$ and $H \parallel ab$ geometries respectively.
Figure 3. Temperature dependence of magnetic entropy change (–ΔSM) at various magnetic fields applied (a) along the c-axis, and (b) in the ab-plane.

The -ΔSM vs T curves for both the cases show broad peaks around Tc = 174 K. The maximum value of –ΔSM at 9 T is 1.6 J/kg-K along the c-axis, while it is 0.8 J/kg-K in the ab plane. The large factor of 2 anisotropy in the magnetic entropy change –ΔSM between the two crystallographic orientations makes Co3Sn2S2 a good candidate for the RMCE. Additionally, –ΔSM is negative at low temperature and low field for H ∥ ab, while it is positive along c-axis, indicating a sign change anisotropy which can also be potentially exploited.

The temperature and field dependent rotating magnetocaloric entropy change ΔSR(T, H) can be calculated from the magnetic entropy change in the two crystallographic directions using the equation:

\[ \Delta S_R(T, H) = S_M(T, H∥c) - S_M(T, H∥ab) \]
\[ = [S_M(T, H∥c) - S_M(T, 0)] - [S_M(T, H∥ab) - S_M(T, 0)] \]
\[ = \Delta S_M(T, H∥c) - \Delta S_M(T, H∥ab) \]

Figure 4 shows the temperature dependence of the RMCE (–ΔSR) calculated using equation (4) in various applied magnetic fields as indicated in the plot. The maximum rotational entropy change (–ΔSR) at Tc increases with increasing field suggesting that the anisotropy of the magnetic entropy change between the two directions increases with field. Additionally, the width of the peak also becomes broader on increasing magnetic field and it becomes approximately constant below Tc for higher fields. Thus, for a broad temperature range near and below Tc, a significant magnetic entropy change can be achieved by rotating from the ab-plane to the c-axis in a fixed magnetic field. This is an advantage over the conventional MCE where an entropy change can only be achieved by changing the magnetic field.

In order to get further insight about the nature of the paramagnetic to ferromagnetic phase transition at 174 K, we have attempted a scaling of the magnetocaloric data at various temperatures and fields using the entropy scaling laws reported recently by Franco et al.25. They proposed a phenomenological universal curve for the magnetic entropy change near a second order phase transition in which all the ΔSM(T, H) data collapse onto a single universal curve when plotted as the normalized entropy (ΔSM/ΔSMmax) at each field vs a reduced temperature θ given by:

\[ \theta = \frac{T - T_c}{T_{r1} - T_c} \text{ for } T \leq T_c \]

![Figure 4. Temperature dependence of the RMCE: magnetic entropy change (–ΔSR) calculated by rotating the crystal from ab-plane to the c-axis in various magnetic fields.](image-url)
Figure 5. (a) Universal magnetocaloric curve when plotted as rescaled entropy $\Delta S_M/\Delta S_M^{\text{max}}$ vs reduced temperature $\theta$. (b) Power law fitting of $-\Delta S_M$ vs $H$ and $\text{RCP}$ vs $H$.

$$\theta = \frac{T - T_c}{T_{r2} - T_c} \quad \text{for} \quad T > T_c,$$

where $T_{r1}$ and $T_{r2}$ are the temperatures at the full width at half maximum of the anomaly in $\Delta S_M$ at $T_c$. Figure 5(a) show that all the $\Delta S_M$ curves for the different magnetic fields approximately collapse onto a single universal master curve. This is strong evidence of the second order nature of the ferromagnetic transition at $T_c = 174$ K in Co$_3$Sn$_2$S$_2$.

For materials having a second order magnetic phase transition, the field dependence of the maximum in $-\Delta S_M$ is expected to follow a power law field dependence:

$$-\Delta S_M^{\text{max}} = a H^n$$

Figure 5(b) shows results of such a power law fitting to the $-\Delta S_M^{\text{max}}$ vs $H$ data. The fit gave the value for the power law exponent $n = 0.603(5)$. The expected value for $n$ within a Mean field model is $2/3$.

The relative cooling power (RCP), which quantifies the usefulness of a magnetocaloric (MC) material, is defined as the product of the full width at half maximum $\Delta T_{\text{FWHM}}$ and $\Delta S_M^{\text{max}}$. RCP also depends on the magnetic field and is expected to have a power law field dependence $\text{RCP} = b H^m$, where $m$ can be related to the critical exponent $\delta$, obtained from the isothermal magnetization at $T_c$, by the relation:

$$m = 1 + \frac{1}{\delta}$$

Figure 5(b) show the RCP vs magnetic field. From the power law fitting, we obtain the value $m = 1.213$, which gives the value of $\delta = 4.695$, which is close to the value estimated from a previous Arrott plots analysis. So the construction of universal curve and power law fitting for maximum entropy change and RCP gives further insight about critical behavior of the ferromagnetic phase transition in Co$_3$Sn$_2$S$_2$.

IV. CONCLUSION

Co$_3$Sn$_2$S$_2$ is a half-metallic ferromagnet and a Weyl semi-metal candidate showing a paramagnetic to ferromagnetic phase transition at $T_c = 174$ K. Measurements on single crystals of Co$_3$Sn$_2$S$_2$ reveal a large anisotropy in magnetic properties which can be exploited for potential applications. In this work, we report the anisotropic magnetocaloric (MCE) response $-\Delta S_M$ of single crystals of Co$_3$Sn$_2$S$_2$ for $H \parallel c$ axis and $H \parallel ab$ plane near the PM-FM transition. The maximum entropy change ($-\Delta S_M$) is about 1.6 J/kg-K for $H \parallel c$ while the maximum entropy change for $H \parallel ab$ plane is 0.8 J/kg-K.
This factor of 2 anisotropy in $-\Delta S_M$ in the two crystallographic directions make Co$_3$Sn$_2$S$_2$ a good candidate to exploit the rotating MCE in which a large magnetic entropy change can be achieved at a fixed magnetic field by just rotating the crystal. To gain further insight into the nature of the ferromagnetic transition we have performed a scaling analysis of the magnetic entropy change at various temperature and fields. The successful construction of a universal magnetocaloric curve indicate that the PM-FM transition is a second order magnetic transition. Power law dependencies of the magnetic entropy change and RCP were found and yield the power law exponents $n = 0.603(5)$ and $m = 1.213(12)$, respectively. These values are consistent with values of the critical exponents reported in a previous critical behavior study on polycrystalline Co$_3$Sn$_2$S$_2$.

V. ACKNOWLEDGMENT

We acknowledge use of the x-ray facility and the SEM facility at IISER Mohali.

* These authors contributed equally to this work.

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