$B$-$T$ phase diagram of CoCr$_2$O$_4$ in magnetic fields up to 14 T

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We have measured the magnetization and specific heat of multiferroic CoCr$_2$O$_4$ in magnetic fields up to 14 T. The high-field magnetization measurements indicate a new phase transition at $T^\ast = 5 - 6$ K. The phase between $T^\ast$ and the lock-in transition at 15 K is characterized by magnetic irreversibility. At higher magnetic fields, the irreversibility increases. Specific-heat measurements confirm the transition at $T^\ast$, and also show irreversible behavior. We construct a field-temperature phase diagram of CoCr$_2$O$_4$.

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CoCr$_2$O$_4$ is a ferrimagnetic spinel with Curie temperature $T_C = 94$ K. At $T_S \approx 26$ K, a structural transition happens, below which a short-range-ordered spiral component develops in the spin system, resulting in a conical magnetic structure. The structural transition is also accompanied by the emergence of a spontaneous electric polarization, which direction can be reversed by applying a magnetic field. At $T_{\text{lock-in}} = 15$ K, the period of the spin spiral becomes commensurate ("locks") to the lattice parameter.

CoCr$_2$O$_4$ is believed to be the first example of a multiferroic, where both spontaneous magnetization and spontaneous polarization are of spin origin (cf. the spin-current model of Katsura et al., Ref. [3]). As multiferroics are appealing because of basic physical interest as well as their potential technological applications, the reported multiferroicity of CoCr$_2$O$_4$ has triggered a broad experimental research of the compound. So far the magnetic and thermal properties of CoCr$_2$O$_4$ have been investigated either in zero magnetic field or in relatively low fields. As the system is very rich for different types of phase transitions, measurements in high magnetic fields can shed more light on the nature of the different phases.

Here, we report results of a high-magnetic-field investigation (up to 14 T) of CoCr$_2$O$_4$. In the high-field magnetization data, we have found signs of a new transition at around $T^\ast = 5$ K. The phase between $T^\ast$ and $T_{\text{lock-in}}$ is characterized by magnetic irreversibility. Specific-heat measurements confirm the transition at $T^\ast$, and also show the irreversible behavior. We propose a field-temperature phase diagram of CoCr$_2$O$_4$.

The CoCr$_2$O$_4$ samples have been synthesized from Co$_3$O$_4$ and Cr$_2$O$_3$ powders at $T = 1400$°C. CoCr$_2$O$_4$ powder has been pressed into pellets of 10 mm diameter and 1 – 2 mm thickness. X-ray diffraction measurements have been performed at room temperature using a commercial diffractometer with a position-sensitive detector utilizing Cu-K$_\alpha$ radiation (Fig. 1 top panel).

FIG. 1: (Color online) Top panel: x-ray diffraction pattern of CoCr$_2$O$_4$ powder (peaks from a Ge reference are also marked). Bottom panel: specific heat of polycrystalline CoCr$_2$O$_4$. The line represents published single-crystal data (Ref. [3]). Insets: close-ups of the structural ($T_S$) and ferrimagnetic ($T_C$) transitions (note different vertical scales).

The data have been analyzed by standard Rietveld refinement. The diffraction pattern shows the cubic symmetry (space group $Fd\bar{3}m$) with no indication of spurious phases. The lattice constant, $a = 8.328(2)$ Å, is in good agreement with published results.

Magnetization measurements up to 14 T have been carried out in commercial SQUID and vibrating-sample-
magnetometry setups at temperatures between 1.8 and 300 K. Specific-heat measurements have been performed between 2 and 300 K in fields up to 14 T in a commercial $^4$He cryostat. At temperatures below 10 K, we also used a modified relaxation-calorimetry technique. For both, magnetization and specific-heat measurements, the sample was heated up to room temperature before each temperature sweep in order to avoid any influence of the sample history on our measurements.

To confirm the quality of our samples, specific-heat measurements have also been made in zero magnetic field. The outcome of these measurements is shown in the bottom panel of Fig. 1. At $T_C = 94.2$ K and $T_S = 26$ K, the specific heat demonstrates sharp anomalies, associated with the phase transitions. The first-order nature of the structural transition is evident. For comparison, data from single-crystal measurements of Ref. 3 are shown as well.

In Fig. 2 we show the results of temperature-dependent [(a) and (b)] and field-dependent [(c)] magnetization measurements. Above 2 T, the magnetization increases linearly with applied field. Hysteresis loops are shown in the inset of panel (c). The temperature-dependent data have been collected according to the standard zero-field-cooled (ZFC) and field-cooled (FC) measurement protocols. In order to show the low-temperature phase transitions more vividly, we plot the temperature derivative of the ZFC magnetization, $dM_{ZFC}/dT$, as a function of temperature in panel (d).

The FC data well reproduce the published magnetization data on polycrystalline and single-crystal samples.
The ferrimagnetic ($T_C$), structural ($T_S$), and lock-in transitions ($T_{\text{lock-in}}$) are clearly visible. Another anomaly is a kink around 50 K (marked as $T_{\text{lock}}$ in Fig. 2). This kink is most pronounced in the highest field curve (14 T). We believe the anomaly we observe at $T_{\text{lock}}$ should be related to the dielectric-constant anomaly reported by Lawes et al. at around 50 K, and attributed to the development of short-range spiral magnetic order.

At low fields, the ZFC data deviate from the FC curves below the Curie temperature $T_C$. This is in line with observations by Tomiyasu et al., who have interpreted this irreversibility as an indication of a possible spin-glass state. At higher fields (1 T and above), this irreversibility diminishes, which is consistent with the spin-glass picture.

In addition to the known transitions, a new transition appears at $T^* = 5–6$ K. This feature is most pronounced in fields above a few Tesla. In the ZFC magnetization curves a “bump” appears at temperatures between $T^*$ and $T_{\text{lock-in}}$. Below $T^*$ and above $T_{\text{lock-in}}$, the ZFC and FC curves merge. Remarkably, the bump becomes more pronounced as field increases. This is quite unusual and is in obvious contradiction with the simple spin-glass picture, where higher fields would suppress irreversibility.

Our specific-heat measurements confirm the transition at $T^*$, as well as the irreversible behavior related to this anomaly. In Fig. 3 we show the specific heat $C$, measured at temperatures around $T^*$ in ZFC and FC modes at 8 and 14 T. Overall, the specific heat decreases with increasing magnetic field, as the magnetic entropy at low temperature decreases in higher fields. As visible in the double-logarithmic scale in Fig. 3, at around $T^*$ the slope of all $C(T)$ curves changes. Most remarkably, around this temperature the ZFC curves deviate from the FC curves. The FC specific heat is always larger than the ZFC data. The deviation, $\Delta C = C_{\text{FC}} - C_{\text{ZFC}}$, increases with applied field. This fact is in line with our magnetization measurements: the irreversibility in magnetization increases with field.

As temperature approaches zero, $\Delta C$ vanishes (inset (a) of Fig. 3). Note, that the apparent divergence between the $C_{\text{FC}}$ and $C_{\text{ZFC}}$ curves, seen in the main frame of the figure at $T \to 0$, is an artifact due to the double-logarithmic scale.

This new transition at $T^*$ should be related to some changes in the spiral magnetic structure. Neutron-scattering measurements in magnetic fields should be able to clarify this issue.

We would like to note, that one should not expect the transition at $T^*$ to be visible as a sharp anomaly in the specific heat. Even a well-established (and sharper) lock-in transition at 15 – 16 K, is not seen in zero-field specific heat. Only in 14 T, a small peak appears (see inset (b) of Fig. 3).

Finally, based on the magnetization and specific-heat measurements, we plot a field-temperature phase diagram of CoCr$_2$O$_4$ (Fig. 4). As transition temperatures, we take the inflection points of the magnetization vs. temperature curves (except for $T_C$, which is taken equal to its zero-field value). In addition to the curves shown in Fig. 2 data collected at 0.3 and 0.7 T have been used for the phase diagram.

Summarizing, we have investigated thermodynamic properties of CoCr$_2$O$_4$ in magnetic fields up to 14 T. We have found signs of a new possible phase transition at $T^* = 5–6$ K. This transition is associated with an irreversibility in the magnetic system, as confirmed by
magnetization and specific-heat measurements. Remarkably, the magnetic field stimulates rather than suppresses the irreversibility effects. We believe, this can be related to the appearance of the spiral magnetic structure. Neutron-scattering measurements at high magnetic fields might give valuable information in clarifying the mechanisms of this transition.

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