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On the observation of negative magnetization under zero-field-cooled process

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ABSTRACT

We have addressed problems associated with the measurement of zero-field-cooled (ZFC) magnetization and its interpretation in the light of negative magnetization reported in certain ferrimagnetic materials such as $CoCr_2O_4$. We demonstrate that a small negative trapped field in the sample space as well as large coercive fields are responsible for the observed negative magnetization. The problem is commonly encountered while working with magnetometers and a superconducting magnet where the sign of the trapped field can be positive or negative depending on the way the field is reduced to zero.

The phenomenon of ferrimagnetism is well known since its discovery in spinel ferrites where the spontaneous magnetization arises due to uncompensated magnetic moment resulting from magnetic interactions among the magnetic ions at two different crystallographic sites. In 1948, Néel predicted [1] that certain ferrimagnetic materials will exhibit spontaneous magnetization that changes sign with temperature or magnetic field due to different temperature dependence of sublattice magnetization associated with the two different crystallographic sites. This phenomenon was indeed experimentally observed in mixed spinels, for example, in $Li_{0.5}Fe_{2.5-x}Cr_xO_4$ and Co_2VO_4 [2,3]. Later, many other ferrimagnetic systems such as garnets, molecular magnets and even antiferromagnetic [4–7] materials were shown to exhibit negative magnetization below a compensation temperature. In the case of orthovanadates RVO_3 (R = La, Nd, Sm, Gd, Er and Y), various models including antisymmetric Dzyaloshinsky–Moriya interactions have been proposed to account for the negative magnetization [8]. Experimentally, there are two ways of measuring magnetization as a function of temperature; these are field-cooled (FC) and zero-field-cooled (ZFC) processes which are based on whether the material is cooled under an applied magnetic field or not, respectively. The former represents the equilibrium magnetization and the latter the non-equilibrium time dependent magnetization.

Recently, there has been a lot of interest in the ferrimagnetic ($T_C \sim 93$ K) spinel $CoCr_2O_4$ because of its multiferroic properties with a magnetoelectric coupling below the spiral magnetic ordering at ∼26 K [9,10]. A few reports of magnetization studies on bulk and nanoparticles of $CoCr_2O_4$ have shown that these samples exhibit negative magnetization just below T_C under ZFC measurement condition with low applied field (∼100 Oe), while the magnetization remains positive in the case of FC measurement condition for the same applied field [11,12]. This behaviour is remarkably different from what is seen in the above mentioned materials where the magnetization changes sign at the compensation temperature which lies well below the magnetic ordering temperature. The observed negative magnetization in $CoCr_2O_4$ has been attributed to uncompensated spins at the grain boundaries [11]. But, it is difficult to conceive the negative magnetization based on the uncompensated spins. It is most likely arising from an artefact that there could be a small trapped field in the superconducting magnet during cooling that can affect the magnetization drastically under ZFC condition as observed in RVO_3 system [13,14]. However, if the origin of negative magnetization is intrinsic, such studies would be interesting from physics point of view as well as possibility of exploiting the phenomenon for device applications such as magnetic memory and switching. It is for these reasons that we have reinvestigated the magnetic properties of $CoCr_2O_4$ and demonstrate that the observed negative magnetization under ZFC condition is an artefact due to trapped field in the superconducting magnet. Although we have shown that the trapped fields can influence the magnetization behaviour of $CoCr_2O_4$, it is common for ferro- and ferrimagnetic materials, particularly with significant magnetic anisotropy and coercive field.

The sample $CoCr_2O_4$ was prepared by solid state reaction of thoroughly mixed powders of stoichiometric amount of Co_3O_4 and Cr_2O_3 at 1350 °C in air for several hours with intermittent grindings. Phase purity was checked by the analysis of powder

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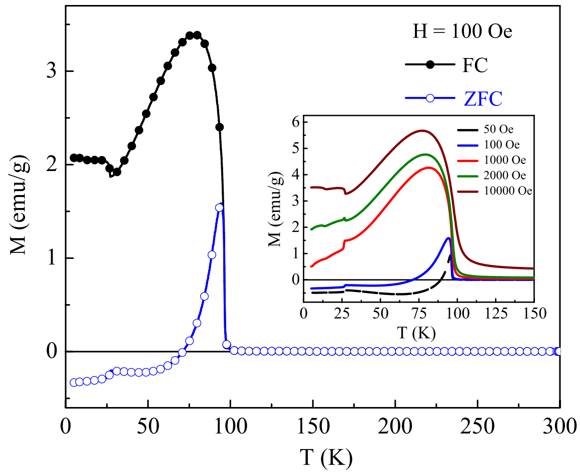

Fig. 1. ZFC and FC magnetization versus temperature curves of $CoCr_2O_4$ measured with an applied field of 100 Oe (See text). Inset shows ZFC curves at different applied fields.

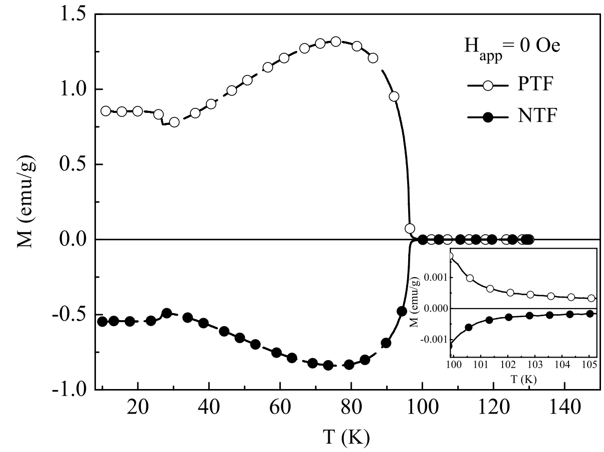

Fig. 2. Magnetization as a function of temperature measured under positive and negative trapped fields. Inset shows magnetization in the paramagnetic region in expanded scale.

X-ray diffraction (XRD) pattern recorded with a Bruker D8 Discover diffractometer. Magnetic measurements were carried out with Vibrating Sample Magnetometer (VSM) option in Physical Properties Measurement System (PPMS), Quantum Design, USA.

Analysis of XRD pattern of $CoCr_2O_4$ confirmed that the sample was single phase having the normal spinel structure (space group Fd3m) with lattice parameter, $a = 8.3343(1)$ Å. Shown in Fig. 1 is the magnetization as a function of temperature measured under ZFC and FC conditions with the same applied field (100 Oe) used in the literature and the observed magnetization behaviour is very similar to what is reported earlier [10,11]. There are two magnetic anomalies, one at 97 K which corresponds to ferrimagnetic ordering and the other at 27 K is due to noncollinear conical spiral ordering. More importantly, just below T_C, the ZFC curve shows a peak in magnetization below which it crosses zero magnetization and becomes negative at low temperatures. With increasing applied magnetic field, the peak in magnetization moves to low temperature and becomes broad. Further, the negative magnetization observed at lower fields become positive at large enough fields as shown in the inset of Fig. 1.

In order to understand this magnetization behaviour, it is important to rule out extrinsic origin of such unusual magnetism. In this respect, it is essential to look at the history of the superconducting magnet just before doing the magnetization measurement because the ZFC measurements are very sensitive to the remanent field present in most of the magnetometers. As our PPMS is not equipped with low-field option to reduce the magnitude of the remanent field below 0.1 Oe, we normally minimize the remanence down to a few Oersteds by setting the field to zero (from an initial field >1 T) in oscillation mode. This small field is the result of trapped magnetic flux inside the superconducting material. Consequently, in the ZFC measurement, the sample was cooled under the trapped field. The other important parameter is the sign of the trapped field that is opposite in sign when reducing the field to zero from a positive or negative field. In the present case, the field was reduced from a positive value and therefore the trapped field is negative. Thus, the sample was field cooled (FC) under negative trapped field (NTF) to the lowest temperature and then a positive field of 100 Oe was applied and the magnetization was measured while warming. During cooling, the NTF forces the moments to align in the negative direction and the applied positive field (100 Oe) cannot change the magnetization direction to positive presumably because of magnetic anisotropy and large coercive field. With increase of temperature, the magnetization changes its sign from negative to positive because of decrease in magnetic anisotropic constant and coercive field which results in rotation of spins towards applied field direction. This explains the observed negative magnetization in ZFC measurement. In order to confirm this, we measured magnetization under NTF *without applying* any external magnetic field and the results are shown in Fig. 2. It is seen that the magnetization in the entire temperature range including the paramagnetic state is negative. Similarly, we measured the magnetization under positive trapped field (PTF) after reducing the field to zero from a large negative field in oscillation mode. As expected, the magnetization in the entire temperature range is positive and mirror image of that measured under NTF. The positive and negative values of magnetization in the paramagnetic state are clearly seen in the inset of Fig. 2. The values of NTF and PTF obtained by equating the susceptibility values in the paramagnetic state are −2.1 Oe and 3.6 Oe, respectively. These results further confirm that the negative magnetization observed in $CoCr_2O_4$ under ZFC condition is an artefact arising from the trapped magnetic field in the superconducting magnet. Similar behaviour has been observed in $CoFe_2O_4$, $CoFeCrO_4$ and other intermediate compositions under ZFC condition with NTF which support the non-intrinsic characteristic of negative magnetization in some spinel systems. In fact, it was shown earlier that even earth's magnetic field can influence the magnetization behaviour of certain magnetic materials [15]. It is noteworthy that even in the case of materials which exhibit intrinsic negative magnetization, the ZFC magnetization measured under negative trapped field does not represent the intrinsic magnetic property of the material [7,16]. Therefore, we suggest that one has to be cautious while measuring and interpreting magnetization under ZFC condition. Unless the trapped field is removed completely by some means, the magnetization behaviour will be dominated by the trapped fields depending on the intrinsic magnetic properties of the material. In order to observe intrinsic negative magnetization under ZFC condition, the field should be reduced to zero from a negative field in oscillation mode so that the trapped field is positive [14]. Since this measurement condition is nothing but field cooling process under small positive trapped field, the ZFC magnetization will resemble the behaviour of FC magnetization as reported for YVO_3 [14]. We also suggest that the negative trapped field should be avoided for all magnetic measurements.

In conclusion, we have demonstrated various artefacts associated with ZFC magnetization measurement with magnetometers and a superconducting magnet. Furthermore, we have suggested magnetization measurement protocol to identify materials exhibiting intrinsic negative magnetization, particularly under ZFC process.

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