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A novel approach to determine blocking temperature in bulk materials

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A novel approach to determine blocking temperature in bulk materials

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Abstract: Blocking temperature (θ_B) holds utmost significance in magnetic devices. A novel approach to ascertain the θ_B for bulk materials has been propounded. The θ_B has been correlated with the magnetic entropy change (ΔS) during zero-field cooled (ZFC) and field cooled (FC) magnetization. The values of ΔS have been calculated in μ_B/f.u.K. The θ_B has been investigated for two distinct cases – (I) with ZFC magnetization reversal and (II) without ZFC magnetisation reversal. Based on the reported experimental approach, a novel definition of θ_B has been propounded for bulk materials. The combined analysis of ZFC and FC magnetization behaviour provides a better approximation of θ_B for bulk materials.

Keywords: Zero-field cooled magnetization, Field cooled magnetization, Blocking temperature, Magnetic entropy change.

1. Introduction

Blocking temperature (θ_B) in a cooling system is formally defined as the temperature at which all single-domain grains of a given shape and size change suddenly from the superparamagnetic state to a stable, permanently magnetized state [3]. The applied magnetic field controls θ_B for magnetite nanoparticles [4]. Magnetic anisotropy energy (MAE) dependence on particle's volume leads to superparamagnetic effect due to which magnetisation starts fluctuating. The temperature at which magnetisation fluctuation occurs is called blocking temperature [5]. Literatures do not provide any standard procedure to deduce blocking temperature for nanoparticles. Antoniak [5] referred inflection point temperature in ZFC as the θ_B. Presa et al. [6] represented temperature corresponding to maximum ZFC magnetization as θ_B for γ-Fe_2O_3 nanoparticles. Micha et al. [7] obtained θ_B for Co/SiO_2 discontinuous multilayers from temperature derivative of the difference between ZFC and FC magnetization curves while simultaneously relating it to the radius of the largest particle and the effective magnetic anisotropy constant. Mamiya et al. [8] theoretically justified the results of Micha et al. [7]. Bruvera et al. [9] further confirmed the results of Micha et al. [7] and termed ZFC maxima point as bad and ZFC inflection point as ugly approximation of blocking temperature. The past studies to ascertain θ_B, based on ZFC – FC magnetization values, are confined to nanoparticles.

Superparamagnetism is associated with nanomaterials only but magnetic anisotropy, i.e. the divergence between ZFC and FC curve, is exhibited by both nanomaterials as well as bulk materials. Moreover, the magnetic anisotropy is strongly dependent on the applied magnetic field and temperature. For bulk materials, temperature derivative of magnetization (dM/dT) is a useful approach to ascertain curie temperature (T_c) and the inflection point in dM/dT curve denotes T_c [10,11]. It is worth noting that temperature derivative of magnetization (dM/dT) is also an important tool to determine the magnetic entropy change [12]. The mathematical relation for ascertaining magnetic entropy change from M-T data has been proposed by Hussain et al. [13]. In magnetic devices such as spin valve, the coupling or exchange field depends on temperature and vanishes at θ_B. Also, the direction of coupling is strongly dependent on θ_B [14]. Hence, it becomes inevitable to determine the θ_B. Since blocking temperature is dependent on applied field and temperature for nanomaterials, a sincere effort, in this work, has been made to define blocking temperature based on the same concepts for bulk materials. The concept of entropy change, as suggested in [12,13] has been employed to determine the blocking temperature for samples having micron (µm) size particles. In this work, ZFC and FC magnetization data of $SmFe_{0.5}Co_{0.5}O_3$ [1] and $LnFe_{0.5}Co_{0.5}O_3$ (Ln = Eu & Dy) [2] has been used for experimental prediction of θ_B. Hereafter, $SmFe_{0.5}Co_{0.5}O_3$ will be denoted as SFCO while $EuFe_{0.5}Co_{0.5}O_3$ and $DyFe_{0.5}Co_{0.5}O_3$ will be denoted as EFCO and DFCO, respectively. The blocking temperature has been determined for two different cases – (I) with ZFC magnetization reversal and (II) without ZFC magnetization reversal. Case (I) refers to SFCO while Case (II) pertains to EFCO and DFCO. As far as knowledge from literatures is concerned, nobody has made an effort to define blocking temperature for bulk materials.

2. Results and Discussion

Magnetic entropy change (ΔS) can be correlated with magnetization and temperature as [13]:

$$\Delta S\,(T,H) = \sum_i \left(\frac{M_i - M_{i+1}}{T_{i+1} - T_i}\right)_{\Delta H} \quad (1)$$

where, M_i and M_{i+1} are the experimental data of the magnetization at T_i and T_{i+1}, respectively, under the same magnetic field (ΔH). Using equation (1), the values of ΔS_{ZFC} and ΔS_{FC} can be calculated.
The lowest applied field for which the ΔS_{ZFC} and ΔS_{FC} have been ascertained is 50 Oe. Fig. 1 illustrates the criticality of low field magnetic entropy change measurement as it gives an indication about the region of existence of θ_B. The magnetic entropy changes for ZFC and FC magnetization, viz. ΔS_{ZFC} and ΔS_{FC}, respectively, (at ΔH = 50 Oe) are shown in Fig. 1. The positive ΔS_{ZFC} peak just before the transition region is in the proximity to either the maxima or inflection point on M-T plot at low field.

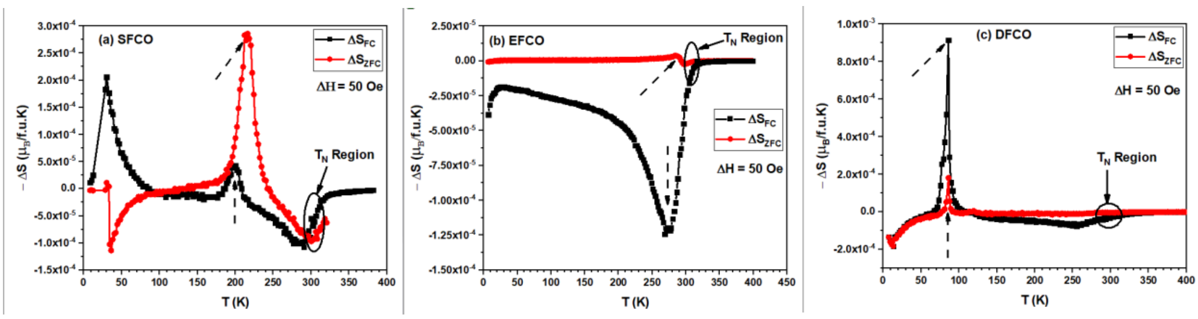

Fig. 1: Magnetic entropy change at ΔH = 50 Oe for (a) SFCO (b) EFCO and (c) DFCO.

In the vicinity of this ΔS_{ZFC} peak, ΔS_{FC} also has a peak either in positive or negative direction. Fig. 1 (a), (b) and (c) depict ΔS_{ZFC} and ΔS_{ZFC} peaks adjacent to each other (marked by dashed arrow). Visualising Fig.1 (a), (b) and (c), it is proposed that θ_B may correspond to peak temperature (of ΔS_{ZFC} or ΔS_{FC}) or any temperature between the peaks of ΔS_{ZFC} and ΔS_{FC}.
The sign of $-\Delta S$ Vs. T curve holds significance as it carries information regarding magnetic transition of the material. Under an applied magnetic field, an anti-ferromagnetic transition is represented by a negative sign while ferromagnetic ordering is represented by a positive sign [13]. This condition further confirms the anti-ferromagnetic transition of all the compounds, as indicated in Fig. 2. As the

applied field increases (ΔH = 1 kOe) (Fig. 2), ΔS_{ZFC} and ΔS_{FC} peaks almost overlap for all the compounds. The temperature (just before the transition temperature) at which the peaks of ΔS_{ZFC} and ΔS_{FC} overlap has been referred as the blocking temperature (θ_B) for a compound in this work. The position of the proposed θ_B is mentioned in Fig. 2 (a), (b) and (c).

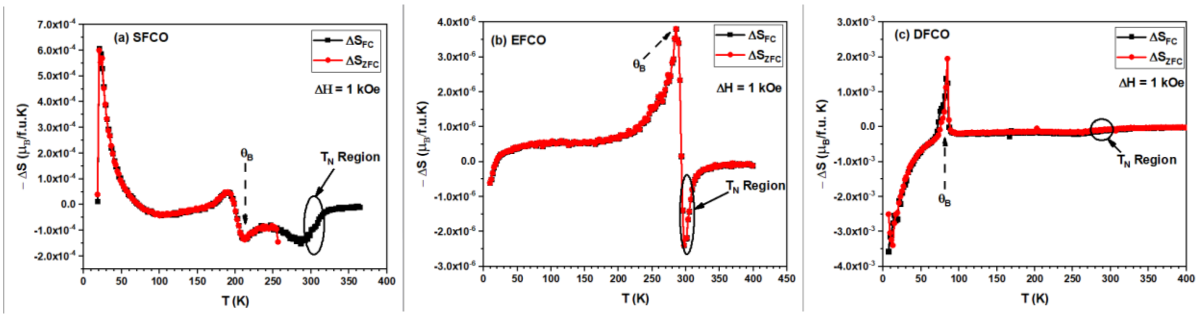

Fig. 2: Magnetic entropy change at ΔH = 1 kOe for (a) SFCO (b) EFCO and (c) DFCO.

The direction of overlapped peaks is influenced by the nature of M-T behaviour of a compound. For compounds showing significant negative ZFC magnetisation (SFCO), the ΔS_{ZFC} and ΔS_{FC} peaks signifying θ_B will overlap in negative direction whereas for compounds showing positive ZFC magnetisation (EFCO and DFCO), the ΔS_{ZFC} and ΔS_{FC} peaks signifying θ_B will overlap in positive direction. Table 1 shows the magnitude of θ_B and T_N for SFCO, EFCO and DFCO.

Table 1: Values of θ_B and T_N for SFCO, EFCO and DFCO.

Perovskite compound	**θ_B (K)**	**T_N (K)**
SFCO	212 ± 2	~ 310
EFCO	285 ± 2	~ 300
DFCO	83 ± 2	~ 300

From Table 1, it can be inferred that at low applied field the compounds depicting large magnetic anisotropy (SFCO and EFCO) have high magnitude of blocking temperature whereas those depicting small magnetic anisotropy (DFCO) will have low magnitude of blocking temperature. Also, a careful analysis of Fig. 1 and Fig. 2 stipulates that the variation of θ_B with applied filed is quite low as θ_B remains within the same range (indicated in Fig. 1) even at higher field value (Fig. 2). So, θ_B is nearly independent of the applied field for these bulk materials which is quite different from the concept reported by Goya et. al. [4] for nanomaterials. Hence, low field as well as high field magnetization study is needed to determine the magnitude of θ_B.
With all the results examined thoroughly, the θ_B has been defined in terms of magnetization as well as magnetic entropy change. The blocking temperature (θ_B) can be defined as "The temperature at which (i) the unblocking of magnetic moments (in M-T behaviour) occur as the applied field is increased, resulting in decrease in magnetic anisotropy and overall increase in magnetization values throughout the temperature range under consideration, and (ii) at high field, the peak of ΔS_{ZFC} and ΔS_{FC} occur simultaneously and the direction of two peaks is also same." It is noteworthy that (i) and (ii) must be satisfied simultaneously.

3. Conclusions
A sincere effort has been made to ascertain and define the blocking temperature (θ_B) for bulk materials based on their entropy change behaviour at different values of applied magnetic field. Influence of applied magnetic field on the magnitude of blocking temperature is quite low and θ_B is nearly independent of the applied field for theses bulk materials. The new definition of blocking temperature

(θ_B) has been proposed. The results obtained are consistent for all the three samples considered in this work. Further improvements/modifications to the proposed definition of θ_B are expected in future based on researches that will be carried out by other researchers.

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Conflict of Interest
There is no conflict of interest among authors of earlier work [1,2]. This manuscript is approved by all the authors.

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