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Low Temperature Study of Magnetism in Gd-system using SQUID magnetometry

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Abstract- The objective of this paper is to investigate the magnetic nature of Dilute Magnetic Dielectrics (DMD) at low temperature. SQUID-magnetometry is used to study the developed nano sized Gadolinium oxide and Gadolinium Sulfide as a DMD system. In this work magnetic moment is measured and magnetocalcaloric effect is also shown. The overall results obtained are good and encouraging.
Keywords – Magnetic properties of DMD, magnetization curve, Magnetocaloric effect

I. INTRODUCTION

It has been found that several experimental studies [1, 2] have been careied out at finite temperature on the nature of magnetism in the elemental ferromagnets. Rare earths provide apparently a simple case for these studies where the magnetism appears due to indirect exchange coupling between localized 4 f moments via the highly delocalized (5d 6s)-valence states [1]. Gd is the most investigated case, being a prototype Heisenberg ferromagnet with a large moment (S=7/2) in the half-filled 4f levels. Various investigations [2–4] report that the exchange splitting of the bulk valence bands vanishes at the Curie temperature (TCb =293 K) as also observed in other rare earths [5-6]. While most attention has been paid to the surface states magnetism, the bulk bands have been until now indisputably believed to follow a Stoner behavior. A comprehensive summary is also provided in a recent development [7].

Author performed SQUID-magnetometry for magnetic measurements. From the magnetic measurements observed magnetic ordering cannot be explained by conventional ferromagnetism. They concluded that the Gd is essential for the magnetic behavior but an additional contribution has to be considered. In their time and temperature dependent SQUID measurements, they deduced a metastable magnetism and memory effects, i.e., the magnetization loops depend on the history of the sample. These observations cannot be explained by common ferromagnetism, superparamagnetism, or spinglass behavior. In consideration the claim of ferromagnetism at room temperature has to be slightly put into perspective. The hysteresis in the SQUID magnetization loops might not point to common ferromagnetism but anyway to an interesting physical phenomenon.

In this work authors have investigated magnetic response for two specimens namely Gadolinium oxide, Gadolinium sulfide. In this paper magnetocalcaloric effect is also shown from SQUID-magnetometry. Magnetocaloric effect (MCE) is defined as the heating or cooling of the magnetic materials due to a varying magnetic field. It is due to the coupling of the magnetic sublattice with the magnetic field, which changes the magnetic part of the entropy of a solid. Magnetic refrigeration [8-9] is an environment-friendly technology based on a magnetic solid that acts as a refrigerant by magneto-caloric effect (MCE). In the case of ferromagnetic materials MCE is a warming as the magnetic moments of the atom are aligned by the application of a magnetic field, and the corresponding cooling upon removal of the magnetic field. Magnetic refrigeration is an emerging technology alternative to the conventional gas-compression refrigeration in food preservation and air conditioning applications. Importantly, solid state-cooling offers noise-free and energy efficient refrigeration suitable for room temperature cooling and cooling of microelectronic components [9-11]. Solid state cooling is essential for the growing needs of low temperature applications in space, particle detectors, and medical applications [8-9,12-14]. Liquefaction of H2 (20 K) by magnetocaloric method has been reported to be cost effective and could render hydrogen to be a competitive alternative fuel [8]. To achieve cooling below 1 K, the adiabatic demagnetization refrigeration is an attractive process compared to 3He/4He dilution refrigeration because of the growing cost of helium and scarcely available 3He isotope. For low temperature magnetic refrigerant materials, it is important to have: (i) large effective spin quantum number, (ii) low magnetic anisotropy and low magnetic ordering temperature, (iii) small specific heat (iv)large magnetization under magnetic field, and (v) weak magnetic exchange interactions [16]. In magnetic refrigeration technology, Gd and Gd based alloys [17, 18], large molecular materials [19] have continued to receive large attention because large magnetic moment of Gd. In this work authors have investigated magnetic response for two specimens namely Gadolinium oxide and Gadolinium sulfide. In this study we present the occurrence of large magnetic entropy change is~ 14.4 J Kg-1K-1 for the sample Gadolinium sulfide.

II. SAMPLE PREPARATION

The Gadolinium (III) acetate hydrate, analytical grade (Alfa Aesar) was heated (about 2000 C) for 8h to prepare Gadolinium oxide powder (namely S1). The developed powder was grinding and heated (about 300 C) for 20h. The Gadolinium (III) acetate hydrate, analytical grade (Alfa Aesar) was heated about 2000C for 8h with sodium sulfide to prepare Gadolinium Sulfide powder (namely S2).

III. EXPERIMENTAL DETAILS

Magnetic measurements were done with an Ever Cool Quantum Design SQUID-VSM magnetometer (USA). Temperature dependent magnetization, M (T) in field-cooled (FC) modes with 0.01 T DC field for both the samples are measured from 10K to 350K. Isothermal field-dependent magnetization i.e., M (H) of all samples at 10 K, 100K, 300K is measured up to 7 Tesla.

IV. RESULTS AND DISCUSSION

Isothermal field-dependent magnetization i.e., M (H) of specimen S1 and S2 samples at 10 K,100K, 300K up to 7 Tesla(70000 oe) is shown in the Fig1(a) and Fig 2(a). Both samples show no hysteresis and such kind of magnetic reversibility in M (H) is beneficial for the solid-state magnetic refrigeration. We have observed no bifurcation in between field-cooled cooling and field cooled warming modes of magnetization that suggests the absence of thermal hysteresis in both the samples. M vs. T (K) data in FC (open symbol) modes for 0.01 T field for the sample S1 and S2 is measured shown in the Fig1(b) and Fig 2(b).

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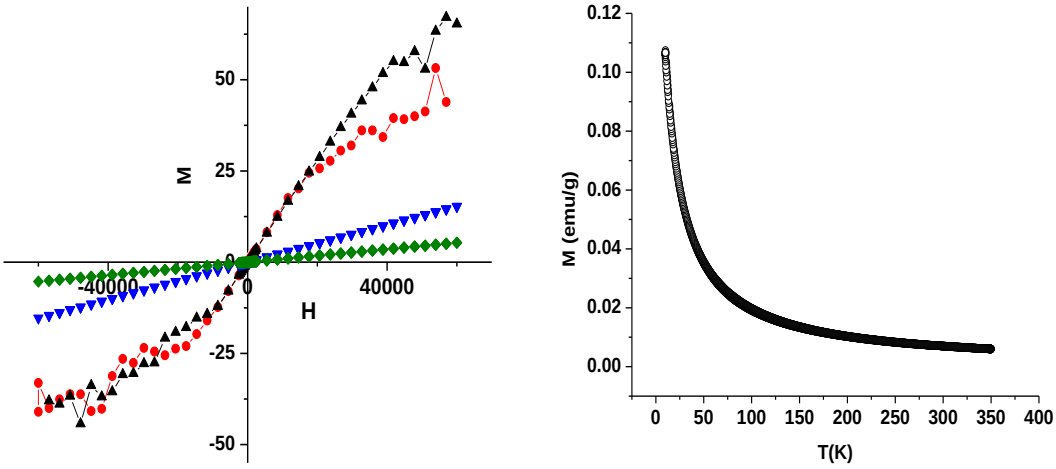
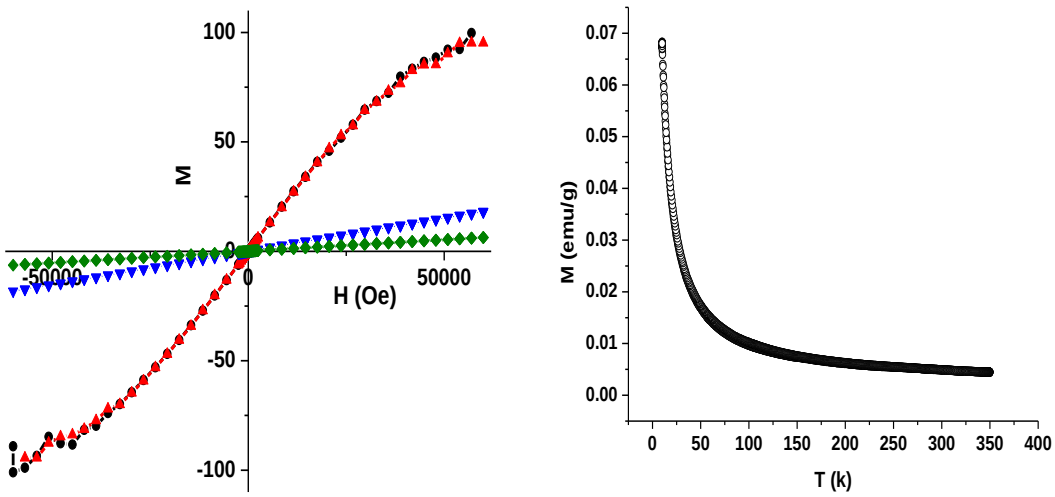
Gadolinium oxide is highly sensitive to its purity in environment. The most general form of Gd2O3 in general (Gd2+xO3-x), x varies in oxygen concentration; very small variation in x may change drastically. In this present experiment it is difficult to control x that causes apparent anomalous result.



(a) (d)

Figure 1. (a) M(μB/f.u.)--H (Oe) curve, Magnetization loops obtained for sample S1 at 10 K (black and red line),100K (blue line), and 300 K (green line). (b) Temperature dependence of magnetization at field-cooled (FC) conditions at a magnetic field of 100 Oe for sample S1.



(a) (d)

Figure2. (a) M(μB/f.u.)-H (Oe) curve, Magnetization loops obtained for sample S2 at 10 K (black and red line),100K (blue line), and 300 K (green line). (b) Temperature dependence of magnetization at field-cooled (FC) conditions at a magnetic field of 100 Oe for sample S2.

On the other hand Gadolinium oxide nanoparticles play a central role in multimodal imaging, targeting the cancer cells and drug delivery in medical science [20-21]. Magnetic Resonance (MR) images with higher resolution can be obtained with the help of contrast agents. Contrast agents are magnetic materials, either superparamagnetic or paramagnetic nanoparticles, which increases the MRI signal intensity. Among the various types of MRI contrast agents, gadolinium oxide nanoparticles are well suited for MR Imaging. Gadolinium oxide nanoparticles are positive contrast agents which can reduce the proton's spin-lattice (T1) relaxation time and increase the MR signal intensity. Incomplete saturation of magnetization in specimen can be related to the presence of significant 3d-4f negative AFM exchange correlations. With this data, we have calculated MCE using Maxwell's relation [13],

$$\Delta SM(T,M)=\int(\partial M/\partial T)H\ Dh \quad (1)$$

Since, isothermal M (H) curves are measured by discrete field changes, the following expression is used,

$$SM(T,M)= \sum (Mi\ -Mi+1\ /Ti+1\ –Ti\ )\ \Delta Hi \quad (2)$$

Here, Mi and Mi+1 are initial magnetization values at Ti and Ti+1 respectively for a field change of ΔHi. In this method, the magnetic entropy change corresponding to the average temperature T (= (T1+T2)/2) is given by the area enclosed by two consecutive isothermal M (H) curves at T1 and T2 divided by ΔT = T2-T1 (T2 > T1). We have calculated magnetic entropy change (-ΔSM) using Eqn. (2) and is plotted with temperature for different magnetic fields as shown in the Fig3. The value of -ΔSM is positive in the entire temperature region and increases with the magnetic field; this indicates that the magnetic field favors FM ordering. -ΔSM increases with the decrease of temperature and a maximum change of entropy of ~ 14.4 J Kg-1K-1 for the sample S2 is observed.

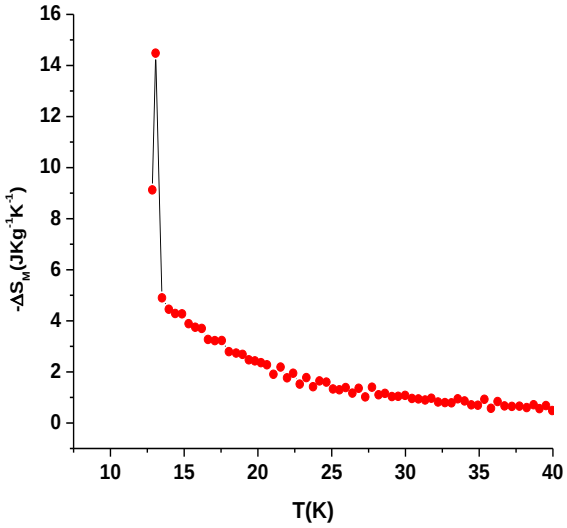


Figure 3. -ΔSM vs. T (K) curves measured from the isothermal magnetization curves of sample S2

We have measured the electrical resistivity in these samples [7], and it is of the order of 106 Ωm at room temperature. Particularly, for low temperature refrigeration, high electric resistivity is desirable as the low resistivity of the materials can induce significant eddy current loss that limits the cooling efficiency of magnetic refrigeration process [9, 14].

IV.CONCLUSION

In summary, we have prepared three DMD samples by simple solid-state reaction method and studied their magnetocaloric properties. Magnetic measurements on both sample has revealed a superior magnetocaloric performance and occurrence of large magnetic entropy change is of 14.4 J Kg-1K-1 for the sample S2. Further, simple synthesis, high chemical stability, absence of magnetic and thermal hysteresis and insulating nature suggest them as potential magnetic refrigerants below the liquid hydrogen temperatures.

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