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Magnetodielectric effect in CdS nanosheets grown within Na-4 mica

Amrita Mandal,[1,2] Sreemanta Mitra,[1,2] Anindya Datta,[3] Sourish Banerjee,[2] and Dipankar Chakravorty[1,a)]

[1]*MLS Professor's Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India*
[2]*Department of Physics, University of Calcutta, Kolkata 700 009, India*
[3]*University School of Basic and Applied Science (USBAS), Guru Gobind Singh Indraprastha University, New Delhi, India*

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CdS nanosheets of thickness 0.6 nm were grown within the interlayer spaces of Na-4 mica. Magnetization measurements carried out in the temperature range 2–300 K showed the composites to have weak ferromagnetic-like properties even at room temperature. The saturation magnetization (M_S) at room temperature was found to be higher than that reported for CdS nanoparticles. The higher value of M_S may be ascribed to the presence of a large number defects in the present CdS system, due to a large surface to volume ratio in the nanosheets as compared to that of CdS nanoparticles. The nanocomposites exhibited a magnetodielectric effect with a dielectric constant change of 5.3% for a magnetic field of 0.5 T. This occurred due to a combination of magnetoresistance and Maxwell-Wagner effect as delineated in the model developed by Catalan. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3698501]

I. INTRODUCTION

Materials exhibiting d^0 ferromagnetism have attracted considerable attention in recent years.[1,2] These are characterized by the absence of any magnetic ion. Mainly, defects play the key role to induce magnetism in such materials. In oxide nanoparticles it has been proposed that oxygen vacancies at the surfaces contribute to room temperature ferromagnetism (RTFM) because of exchange interactions between the electron spin moments associated with them.[3–5] Although, CaO, MgO, HfO_2 and ZnO have been reported to exhibit RTFM due to cation vacancies.[6–9] Room temperature ferromagnetism has also been reported in the case of undoped GaN and CdS nanoparticles, respectively.[10] This property has been explained as arising due to the presence of surface defects in these nanoparticles. GaN nanosheets of thickness ~0.6 nm and grown within the interlayer spaces of Na-4 mica have been found to exhibit ferromagnetic behavior at room temperature.[11] Gallium vacancies have been shown to introduce magnetic moments which lie on the nitrogen atoms at the neighboring sites.[12,13] In the case of ZnS nanostructures, sulfur/zinc vacancies were suggested to cause room temperature ferromagnetism.[1,14] It is apparent from the above discussion that a morphology of CdS which has a large surface to volume ratio could show a ferromagnetic-like behavior at room temperature. With this aim, we have grown CdS sheets within the interlayer spaces of nanoscale dimension of Na-4 mica. These nanosheets exhibit magnetization at room temperature which is much higher than that reported for CdS nanoparticles. Also, the nanocomposites show a large magnetodielectric effect which has been explained on the basis of an inhomogeneous conductor model. The details are reported in this paper.

a)Author to whom correspondence should be addressed. Electronic mail: mlsdc@iacs.res.in.

II. EXPERIMENTAL

The Na-4 mica ($Na_4Mg_6Al_4Si_4O_{20}F_4.xH_2O$) was synthesized by the sol gel method. The details were reported earlier.[15,16] 2 g Na-4 mica powder was immersed in 20 ml aqueous solution of $CdCl_2$. The solution was kept inside an autoclave at 373 K for 1 week to bring about the ion exchange reaction $Cd^{2+} \leftrightarrow 2\ Na^+$ between Cd^{2+} ions in the solution and Na^+ ions within Na-4 mica. The ion exchanged powder was filtered and washed thoroughly with de-ionized water several times. The powder was dried and then subjected to a sulfidation treatment in H_2S gas flow at 873 K for 1 h. CdS was formed within the interlayer spaces of Na-4 mica.

X-ray diffractogram of the nanocomposites was taken in a BRUKER D8 XRD SWAX diffractometer using CuK_α radiation to identify the crystalline phase synthesized. The microstructure of the sample was investigated by a JEOL Model JEM 2010 transmission electron microscope (TEM) operated at 200 kV. To examine the CdS nanosheets, the nanocomposite sample was dispersed in 10% HF aqueous solution for 15 min and then centrifuged in SORVALL RC 90 ultracentrifuge at 30 000 rpm for 30 min for etching the Na-4 mica phase. The resulting powder was subjected to washing in distilled water several times. After drying the powder the latter was dispersed in acetone. A drop of the latter containing the nanostructured CdS entities was placed on the carbon coated grid which was mounted on the TEM for microstructural studies. Elemental analysis of the sample was carried out by the EDAX analyzer attached to the field emission scanning electron microscope (FESEM) (JEOL JSM-6700 F). Magnetic properties were investigated using an MPMS superconducting quantum interference device (SQUID) magnetometer (supplied by Quantum Design, USA) over the temperature range 2–300 K. For studying the magnetodielectric effect pellet of 1 cm diameter and 1 mm thickness was prepared by compacting the sample powder at room temperature with a pressure of 5 tons/cm^2. The change

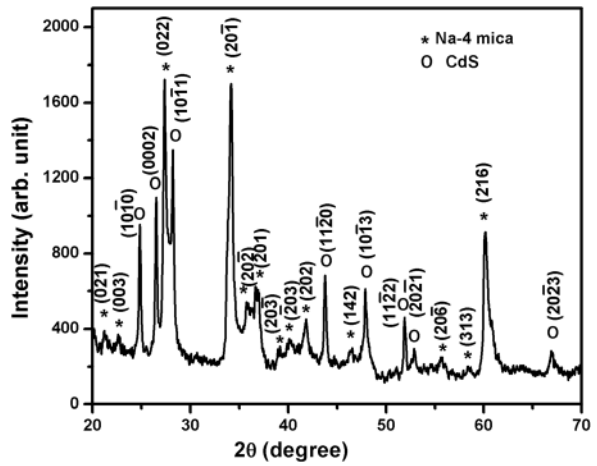

FIG. 1. X-ray diffactrogram of CdS-mica nanocomposite. The Na-4 mica and CdS phases are marked with stars (*) and open circles, respectively.

of dielectric constant as a function of magnetic field was measured using an electromagnet supplied by M/S Control Systems & Devices, Mumbai, India and an Agilent E4890 A precision LCR meter.

III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffractogram of the nanocomposite specimen. All the diffraction peaks have been identified with the phases CdS (JCPDS file No. 41-1049) and Na-4 mica,[17] respectively. It is evident that both CdS and Na-4 mica phases are present in our sample. The peaks have been marked with stars and open circles for Na-4 mica and CdS phases, respectively, in the figure. CdS crystallizes in the hexagonal phase. The hexagonal phase of the CdS crystal is known as the wurtzite phase. Figure 2(a) shows a transmission electron micrograph of the nanocomposite specimen. It is evident that CdS nanosheets are comprised of several nanodiscs with an average diameter ~100 nm. Figure 2(b) shows an electron diffraction pattern of CdS nanosheets. Hexagonal symmetry of the diffraction spots is clearly visible and confirms the presence of wurtzite CdS crystal. The interplanar spacings of the CdS crystal are calculated and are summarized in Table I. For a comparison, the standard JCPDS interplanar spacings data for CdS and the reported interplanar spacings values for Na-4 mica[17] are also given in the table. The observed values of interplanar spacings in the present study are in a good agreement with the reported values. A high resolution lattice image is shown in Fig. 2(c) which corresponds to the plane $(10\bar{1}1)$ of hexagonal CdS

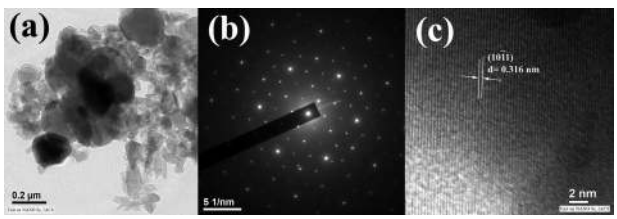

FIG. 2. (a) Transmission electron micrograph of CdS nanosheets. (b) Selected area electron diffraction pattern of nanosheets. (c) High resolution lattice image of a portion of CdS nanosheets.

TABLE I. Comparison of interplanar spacing (d_{hkl}) values, obtained from electron diffraction with standard data for CdS and Na-4 mica.

	Standard data (nm) with corresponding planes	
Observed d_{hkl} (nm)	CdS[a]	Na-4 mica[b]
0.46		0.459 (020)
0.26		0.263 $(20\bar{1})$
0.24	0.245 $(10\bar{1}2)$	
0.18	0.179 $(20\bar{2}0)$	
0.17	0.173 $(20\bar{2}1)$	
0.16	0.158 $(20\bar{2}2)$	
0.14	0.139 $(20\bar{2}3)$	

[a]JCPDS file No. 41-1049.
[b]Reference 17.

crystal with interplanar spacing of 0.31 nm. Figure 3 gives the data obtained from EDAX measurements of our sample. It is evident that the atoms present are only those associated with Na-4 mica and CdS. Thus no impurity phase has been detected in our system.

Figure 4 shows the variation of magnetization (M) as a function of magnetic field (H) at different temperatures (2, 10, 35, 150, and 300 K). The $M(H)$ curve of pure Na-4 mica phase is also given in the figure (solid line). The negative value of the magnetization confirms that Na-4 mica is diamagnetic in nature. It is to be noted that the M-H curves for the nanocomposite were drawn after subtracting the contribution from Na-4 mica. All the curves show hysteresis. The inset of Fig. 4 shows an enlarged view of the M-H curve measured at 300 K over a low field region. At the room temperature, coercivity and saturation magnetization (M_S) are found to be 47 Oe and 0.065 emu/g, respectively. The observed M_S value is one order of magnitude higher than that reported for CdS nanoparticles (0.004 emu/g).[10] This is ascribed to a large surface to volume ratio in our nanodisc samples as compared to that for the reported nanoparticles. As discussed earlier the average diameter of the nanodiscs is ~100 nm. The thickness of these nanodiscs is 0.6 nm as they are grown within the interlayer spaces of Na-4 mica with thickness ~0.6 nm.[18,19] The surface to volume ratio for these entities is calculated to be ~3.35 nm^{-1}. In the case of a

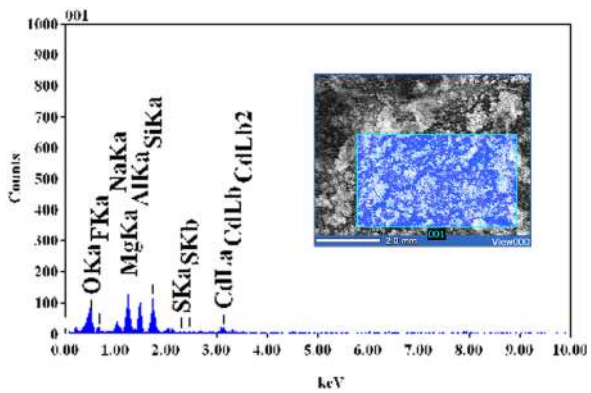

FIG. 3. EDAX analysis of CdS-mica nanocomposite.

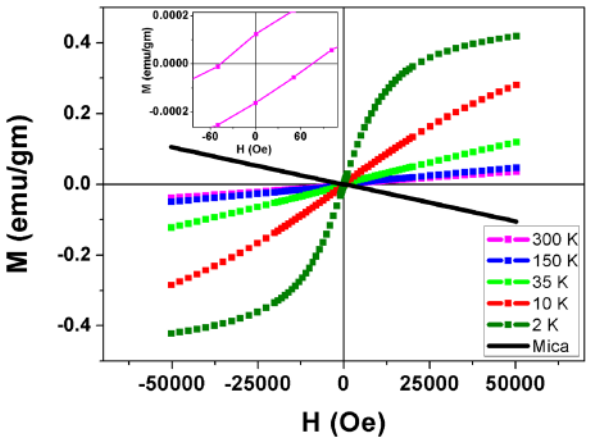

FIG. 4. Magnetization vs magnetic field at different temperatures (2, 10, 35, 150, and 300 K). (Inset) An enlarged view of the *M-H* curve over the low field region at 300 K.

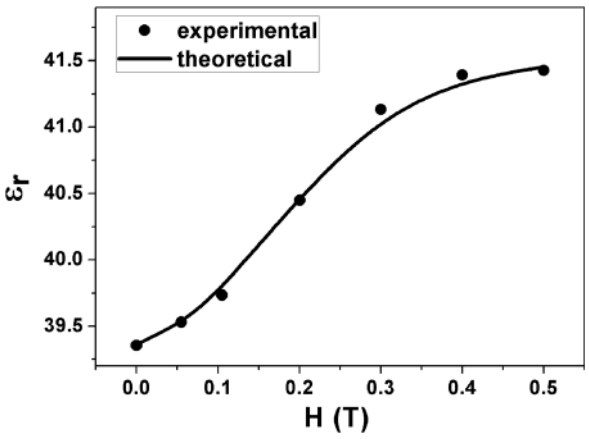

FIG. 6. Variation of dielectric constant with magnetic field for the CdS-mica nanocomposite at room temperature.

spherical particle having identical volume the concerned ratio is estimated to be $\sim 0.18\,\mathrm{nm}^{-1}$only.

Ferromagnetism in sulfide nanomaterials was shown to owe its origin to defects / vacancies.[1,14,20] A theoretical study by Shidpour *et al.* showed that sulfur vacancies could give rise to a local magnetism in MoS_2 nanoribbons.[20] Gao *et al.* reported a d^0 ferromagnetism in the case of undoped ZnS nanoparticles due to presence of sulfur vacancies.[1] A recent work, done by Zhu's group, showed that Zn vacancies can induce ferromagnetism in ZnS nanowires.[14] Rao *et al.* reported a RTFM in CdS nanoparticles experimentally.[10] The origin of ferromagnetism was explained in terms of surface defects. In the present work, the weak ferromagnetic-like behavior may be attributed to the presence of defects/ vacancies in the two-dimensional CdS nanosheets..

Figure 5 shows the variation of magnetic susceptibility with temperature measured at 100 Oe magnetic field under zero field cooled (ZFC) condition. The curve has a sharp rise at low temperature. This type of susceptibility variation is consistent with that shown by a two-dimensional Heisenberg ferromagnetic system.[21]

Figure 6 shows the variation of dielectric constant ε' as a function of magnetic field at frequency 100 kHz. It is evident

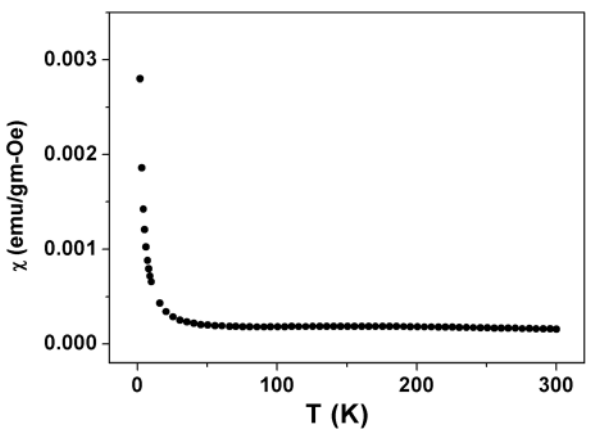

FIG. 5. Variation in magnetic susceptibility (χ) as a function of temperature for the CdS-mica nanocomposite under a magnetic field of 100 Oe in the zero field cooled condition.

that ε' increases with the increasing magnetic field. This can be explained on the basis of Maxwell-Wagner capacitor model.[22] In the present case, the conducting nanodimensional CdS layers sandwiched between the insulating blocks containing Si, Al, Mg, O atoms of the Na-4 mica structure make an ideal Maxwell-Wagner dielectric.[23] The impedance of this composite system can be described as contributed by two lossy capacitors in a series. The real part of dielectric permittivity $\varepsilon'(\omega)$ is given by[22]

$$\varepsilon'(\omega) = \frac{1}{C_0(R_i + R_b)} \frac{\tau_i + \tau_b - \tau + \omega^2 \tau_i \tau_b \tau}{1 + \omega^2 \tau^2}, \qquad (1)$$

where, $C_0 = \varepsilon_0(A/t)$, A is area of the capacitor, t is the thickness, ε_0 is free space permittivity, R_i is the resistance of interfacial like layer between Na-4 mica and CdS, R_b is the resistance of CdS layer, C_i is the capacitance of Na-4 mica, C_b is the capacitance of the CdS layer, $\tau_i = C_i R_i$, $\tau_b = C_b R_b$, and $\tau = (\tau_i R_b + \tau_b R_i)/(R_i + R_b)$. The experimental results shown in Fig. 6 were fitted to Eq. (1) using C_0, C_i, and C_b as parameters. We have assumed a negative magnetoresistance (MR) of the CdS layer with the change of resistance as a function of magnetic field given by, $R_b = R_0 + A' \exp(-H/H_s)$, where, R_0, A', and H_s are the parameters. It must be pointed out that our experimental results could not be fitted to the above model by assuming a positive magnetoresistance. Also, magnetodielectric effect arising due to a negative magnetoresistance has been reported in the case of γ-Fe_2O_3 (Ref. 24) $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ (Ref. 25), and $BaTiO_3/\gamma$-Fe_2O_3 core/shell nanoparticles.[26] The results on γ-Fe_2O_3 have been explained by Boneady *et al.* using the Catalan model.[24] The theoretically calculated curve is shown in Fig. 6 with the experimental data, represented by the points. There is satisfactory agreement between the two. The extracted parameters are reasonable. We have found from the analysis that the R_b decreases with the increase of H as shown in Fig. 7. Evidently, there is about 78% negative change of resistance of CdS layer as the magnetic field is increased to 0.5 T. This is a substantial reduction of resistance and may be associated with the conduction by spin-polarized electrons.[27,28] The magnetodielectric (MD) parameter is defined as $\text{M.D.} = \varepsilon(H) - \varepsilon(0)/\varepsilon(0)$, where,

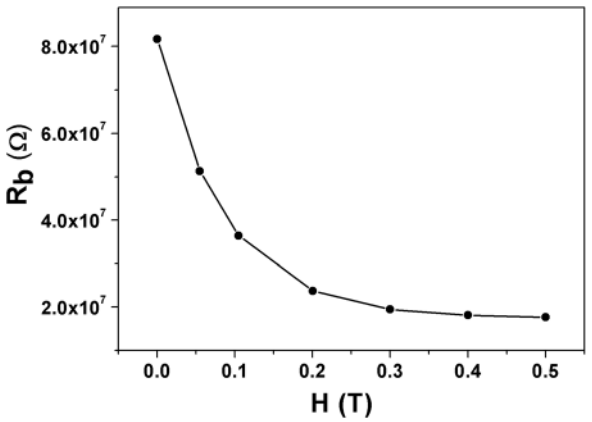

FIG. 7. Variation of resistance (extracted from analysis) of the CdS layer with magnetic field.

$\varepsilon(H)$ and $\varepsilon(0)$ are dielectric constants at a magnetic field H and zero magnetic field, respectively, is found to be 5.3%. It may be noted that no magnetodielectric effect has been reported in the case of CdS only. To our knowledge, this is the first report on the magnetodielectric behavior observed in the case of a nanocomposite consisting of CdS nanosheets embedded in Na-4 mica.

IV. SUMMARY AND CONCLUSIONS

In summary, we have synthesized CdS nanosheets of thickness 0.6 nm within the interlayer spaces of Na-4 mica. These composites showed weak ferromagnetic-like behavior even at room temperature. The saturation magnetization obtained was higher than that reported for CdS nanoparticles due to a larger number of defects present in the two-dimensional CdS sheets. A magnetodielectric effect was observed in this nanocomposite with a change of 5.3% in the dielectric constant for a magnetic field of 0.5 T, which has been explained on the basis of a combination of Maxwell-Wagner effect and magnetoresistance as developed by the Catalan model. These nanocomposites will be suitable for spintronic applications.

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