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Magnetic and photomagnetic studies in nanocrystalline $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.7}\text{Co}_{0.3}\text{O}_4$

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This work presents magnetic and photomagnetic studies on the nanocrystalline form of the spinel $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.7}\text{Co}_{0.3}\text{O}_4$. Field cooled, zero field cooled, and hysteresis have been recorded for this compound with and without irradiation. Kinetics of relaxation of the magnetization in the dark and after irradiation has also been studied. An explanation of these results is given in the framework of freezing/melting of cluster glass behavior. © 2008 American Institute of Physics. [DOI: 10.1063/1.2831389]

I. INTRODUCTION

The photoinduced magnetic studies in magnetic oxides, such as manganites, cobaltites, diluted magnetic semiconductors, and ferrites, have gained great importance in recent past.^{1,2} Seki *et al.*³ have investigated the photomagnetic response of the thin films of Zn- and Ti-substituted NiFe_2O_4 , and Al-substituted Fe_3O_4 , and the results have been interpreted in terms of a photoinduced intervalence charge transfer (IVCT) between the ions. Muraoka *et al.* have investigated the effect of light irradiation on $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ $\text{Mg}_{1.4}\text{Fe}_{1.2}\text{Ti}_{0.4}\text{O}_4$ ⁵ ferrite thin films and discussed the results on the basis of spin glass state.

The present work deals with the magnetic and photomagnetic investigations on the compound $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.7}\text{Co}_{0.3}\text{O}_4$ in nanocrystalline form. The base compound $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ is well known for its soft magnetic properties. It may be noted that Zn^{2+} and Ni^{2+} ions in the spinel structure have a very strong preference for tetrahedral and octahedral sites, respectively. Fe^{3+} ions do not exhibit any strong preference for either the tetrahedral A or the octahedral B sites. Co is likely to be there in the structure in either Co^{2+} or Co^{3+} , both of which have a strong preference for octahedral site. These preferences, however, may significantly change in the nanocrystalline form. An additional degree of freedom with cobalt ion is the possibility of variable spin states, besides the variable valency. The systems which possess multivalent ions at the equivalent energy sites as in the present case may undergo charge transfer phenomena by light irradiation. For the present compound, both the cobalt (Co^{2+} and Co^{3+}) and iron (Fe^{2+} and Fe^{3+}) ions may exist at the octahedral site and can easily undergo charge transfer due to their abilities to exist in variable valence states. Nickel is also known to exist in 2+ and 3+ states particularly in relation to charge transfer in ferrites. This eventually may impart different properties on light irradiation, such as reported on molecular-based materials.⁶

II. EXPERIMENTAL SECTION

For the synthesis of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.7}\text{Co}_{0.3}\text{O}_4$, the stoichiometric proportion of metal nitrates are dissolved in distilled water. Citric acid as a fuel was added, the metal nitrates to citrates ratio and pH of the solution were maintained at 1:1 and 7 respectively. After slow dehydration of the nitrate-fuel complexes, the temperature was raised to 150 °C. The gel got autoignited and dry foam formed, which is ground and heat treated at 850 °C for 2 h.

Phase formation has been conformed using PANalytical XRERT-PRO diffractometer. Particles size has been conformed by FEI make transmission electron microscopy (TEM). We have carried out a detailed magnetization, relaxation, and photomagnetic studies via a coupled optical fiber to a Kr^+ laser (multiline of 647.1–676.4 nm) or to the cavity of a MPMS-55 Quantum Design superconducting quantum interference device magnetometer.⁷

III. RESULTS AND DISCUSSIONS

X-ray diffraction of the sample $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.7}\text{Co}_{0.3}\text{O}_4$ exhibits essentially a monophasic structure. A few very weak extra lines are due to $\alpha\text{-Fe}_2\text{O}_3$. Transmission electron micrograph (Fig. 1) exhibits variation of particle size and morphol-

FIG. 1. TEM of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.7}\text{Co}_{0.3}\text{O}_4$ nanocrystalline powder.^{a)}Tel.: +91-22-25767632. Electronic mail: dhiren@iitb.ac.in.^{b)}Electronic mail: letard@icmcb-bordeaux.cnrs.fr.

FIG. 2. Hysteresis loop on $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.7}\text{Co}_{0.3}\text{O}_4$ nanocrystalline powder.

ogy. While the particle size varies between 20 and 90 nm, the morphology exhibits irregular shape as well as regular shape such as cuboid or square.

Figure 2 shows the hysteresis for the sample measured at 10 K up to a field of 5 T after the sample is zero field cooled from ambient before and after irradiation. The magnified demagnetization part is shown in the inset. A simultaneous observation of the absence of complete saturation as well as a large coercivity and remanance are indications of variation in particle size, which gets support from TEM data also suggesting a mixture of superparamagnetic and ferrimagnetic particles. The large coercivity of around 1600 Oe is essentially due to substitution of Co ions in the lattice, which introduces a large anisotropy in the spinel structure. This increases to 2700 Oe after irradiation. Similarly, M_r (remnant magnetization) increases from 13 to 25 emu/g after irradiation. The specific magnetization value measured at 10 K and 5 T is 43 emu/g which is equivalent to 1.85 bohr magneton/f.u. This reduced to 35 emu/g after the irradiation. These values are less compared to the bulk $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. The reduced magnetization in the nanocrystalline form is now well documented and it arises due to several reasons. Surface effects leading to noncolinearity of magnetic moments, swapping of sites, and weakening of superexchange interaction are among several reasons for the reduction of magnetic moments.⁸

Figure 3 shows the temperature dependence of magnetization in zero field cooled (ZFC) and field cooled (FC) con-

FIG. 3. ZFC and FC at 200, 5000, and 10000 Oe.

FIG. 4. M vs time off and on condition. Inset: M vs T with and without irradiation in a field of 200 Oe (experimental points: square; liner fit: red line).

ditions measured at three different fields of 200, 5000, and 10 000 Oe. A large bifurcation is seen between ZFC and FC data even up to a field of 10 000 Oe. This is one of the characteristics of spin/cluster glass system and nanoparticles. However, spin glass, generally, exhibits a cusp and a sharp decrease in ZFC plot, characteristic of spin freezing temperature. The absence of such features would rather suggest a cluster glass type of behavior possibly originating from the nanosized structure. Some other noteworthy features of Fig. 3 are the shift of the bifurcation point to lower temperatures as the strength of the applied dc magnetic field increases. These are also characteristics of the cluster glass behavior. We carried out kinetic studies in a field of 200 Oe when the irradiation is switched on and off. A large rise of approximately 12% is seen in the initial 1800 s of irradiation, as shown in Fig. 4. This result is characteristic of the population of a magnetic state. Then, magnetization continues to rise with much smaller time dependence. At that point, when the light is switched off for a period of nearly 1 h, no further change is noticed and further irradiation does not anymore affect the magnetic response. This kind of long relaxation is characteristic of metastable magnetic state. Interestingly, a similar observation has been made by Seki *et al.* while studying the photoinduced effects in the thin films of $\text{Al}_{0.5}\text{Fe}_{2.5}\text{O}_4$ thin films.⁹ They attribute this behavior to the melting of the cluster glass state.

We further studied the evolution of the magnetization as a function of time, both in dark and after illumination at different temperatures. We show data obtained in the dark before and postirradiation at 200 Oe and at 100 K in the inset of Fig. 4. An increase in the magnetization as a function of the time is clearly seen. We have carried out this measurement also at 50 and 150 K and similar results are obtained. We have fitted the data to an empirical stretched exponential, which has been commonly used to analyze this long time relaxation.¹⁰ Hence, the time evolution of the magnetization is analyzed using a combination of a stretched exponential and a constant term,

$$M(t) = M_0 - M_r \exp[-(t/\Gamma)^\beta]. \quad (1)$$

Here, Γ is the characteristic time constant, M_0 represents

TABLE I. Fitting parameters for the evolution of magnetization with time in the dark and after irradiation at different temperatures ($H=200$ Oe) from Eq. (1) (see text).

T/K	$M_0/\text{emu g}^{-1}$		$M_r/\text{emu g}^{-1}$		β		Γ/min	
	Dark	After irradiation	Dark	After irradiation	Dark	After irradiation	Dark	After irradiation
50	0.9307	1.168 41	0.0143	0.004 64	0.5821	0.827 28	92.35	45.396 01
100	1.0432	1.280 25	0.0152	0.016 56	0.6742	1.010 27	93.40	76.366 05
150	1.2167	1.436 87	0.0117	0.008 94	0.6869	0.722 78	68.92	34.783 47

an intrinsic ferromagnetic component, and M_r is related to a glassy component contributing to the relaxation. The parameters derived from the above fit of the plots corresponding to the measurements at different temperatures are summarized in Table I.

Since the light irradiation has a significant influence on the magnetic behavior and also we observe large bifurcation of FC and ZFC data recorded at different fields, we considered it worthwhile to compare the FC and ZFC measurements in dark and after illumination. Figure 5 compares one such typical data recorded in a field of 200 Oe. It is noteworthy that while the FC data do not change on irradiation, the ZFC plot, however, exhibits significant enhancement in magnetization on irradiation at low temperatures up to about 100 K. Similar results are reported for the spinel $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_{1.7}\text{Ti}_{0.3}\text{O}_4$ by Seki *et al.*³ These authors also reported no such divergence in ZFC data with and without irradiation for $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$. The same group has earlier reported photoinduced enhancement of magnetization for Ti-substituted $(\text{Mg}, \text{Fe})_3\text{O}_4$ film.⁵ In both the cases, the enhancement in magnetization is attributed to Ti^{4+} ion, which undergoes photoinduced charge transfer with Fe^{2+} ions at B site in the spinel structure. This behavior is an indication of the melting of the cluster glass state on light irradiation.

The distribution of cations in the bulk form may be represented as

Assuming that Fe and Co exist only in 3+ state, whereas Zn and Ni exist in 2+ state, which is also necessary for

charge balance, if $\delta=0$. In practical situation, however, δ is often nonzero and therefore a trace amount of Fe^{2+} and Co^{2+} may also be expected in the compound, which eventually triggers charge transfer among Co and Fe ions. Besides the possibility of Fe and Co existing in the variable valence state, Co has additional degree of freedom and can exist in variable spin states. These variable valence and spin states, particularly, on photoirradiation, may exhibit interesting changes in the magnetic properties. For example, Co^{3+} in the low spin state with configuration $t_{2g}^6e_g^0$ ($S=0$) is a diamagnetic, while the high spin state $t_{2g}^4e_g^2$ ($S=2$) is paramagnetic.

We believe that IVCT, which may occur between cations at equivalent energy sites by photon irradiation, gives different valence states of cations and hence variation in properties. In addition, spin transition, which is seen on photoirradiation in cobalt containing oxides, also plays a significant role.¹¹

We propose a core-shell type of structure due to large surface effects in nanoparticles. The surface spins, which are rather disordered, interact strongly with the core spins and may cause frustration giving cluster glass type of behavior. The extent of frustration and hence the size of the clusters depend on the different conditions of measurement such as temperature, field, and photoirradiation. The magnetic clusters may gradually reorient the freezing spins/melting of cluster glass as the measuring conditions vary. In addition, the charge transfer and spin transition also manifest themselves on the different magnetic and photomagnetic properties.

FIG. 5. ZFC and FC before and after irradiation in 200 Oe field.

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