Comparison of the irreversible thermomagnetic behaviour of some ferro- and ferrimagnetic systems

P S ANIL KUMAR[†], P A JOY* and S K DATE

Physical and Materials Chemistry Division, National Chemical Laboratory, Pune 411 008, India
[†]Present Address: Information Storage Technology Group, MESA Research Institute, University of Twente, 7500 AE Enschede, The Netherlands

Abstract. The magnetic behaviour of two ferromagnetic oxides and two ferrimagnetic oxides (ferrites) are compared to study the effect of magnetocrystalline anisotropy on thermal-history-dependence of magnetization of these ordered magnetic systems. All four compounds show thermomagnetic irreversibility ($M_{FC} > M_{ZFC}$) below a certain temperature, T_{irr}. The highly anisotropic ferromagnetic oxide, $SrRuO_3$ and the hard ferrite, $SrFe_{12}O_{19}$ show sharp peaks below T_c in their $M_{ZFC}(T)$ curves, whereas for the soft ferrite $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and the low anisotropic ferromagnetic oxide $La_{0.7}Ca_{0.3}MnO_3$ only a broad maximum is observed in M_{ZFC}, when measured in small magnetic fields. The shapes of the $M_{ZFC}(T)$ curves are inversely-related to the magnitude of the coercivities (H_c) of the compounds in relation to the applied field, and the temperature dependence of H_c. M_{FC} and M_{ZFC} are related through the coercivity for all four magnetic systems.

Keywords. Ferromagnet; ferrimagnet; thermomagnetic irreversibility; magnetocrystalline anisotropy; coercivity.

1. Introduction

Spin glasses are frustrated magnetic systems characterized by their peculiar time and thermal-history-dependent magnetic behaviour. The spins are frozen in random directions due to lack of long-range magnetic interactions, when the system is cooled through its freezing temperature, T_f, to a temperature $T < T_f$. Thermal irreversibility between field-cooled (FC) and zero-field-cooled (ZFC) susceptibilities below T_f, with a cusp in the low-field c_{ZFC} as well as in the ac susceptibility, long time relaxation of magnetization, etc are the characteristic properties of a spin glass (Mydosh 1993). Nishigori *et al* (1998) have recently reported that for the ferrimagnetic compounds, TbPdIn and DyPdIn, the field-cooled (FC) and zero-field-cooled (ZFC) magnetizations show thermal irreversibility below the ferrimagnetic ordering temperature concluding that the irreversibility is due to the appearance of spin-glass state. The origin of this spin-glass state is attributed to spin frustrations, due to the rare earth ions forming a deformed Kagome lattice. Similarly, while Maignan *et al* (1997) have reported the spin-glass-like behaviour of $Pr_{0.7}Ca_{0.3}MnO_3$ from low-field susceptibility studies, neutron-diffraction data of the compound evidence a ferromagnetic component. Itoh *et al* (1994) have concluded that there is no true long-range ferromagnetic order in Sr-rich compositions in the $La_{1-x}Sr_xCoO_3$ system, and that they are cluster glasses. Long-time relaxation of M_{ZFC}, large difference between M_{FC} and M_{ZFC} below a characteristic temperature, and the absence of magnetic saturation are indicated as evidences for the cluster glass behaviour of compositions with $x > 0.18$. Similar spin-glass-like properties have been reported recently for other magnetic systems also (Greedan *et al* 1996; Pecher *et al* 1999) for which neutron diffraction studies indicate long-range magnetic ordering. The origin of the spin-glass-like nature of these magnetic systems is generally attributed to the competing ferromagnetic and antiferromagnetic exchange interactions, structural disorder, etc.
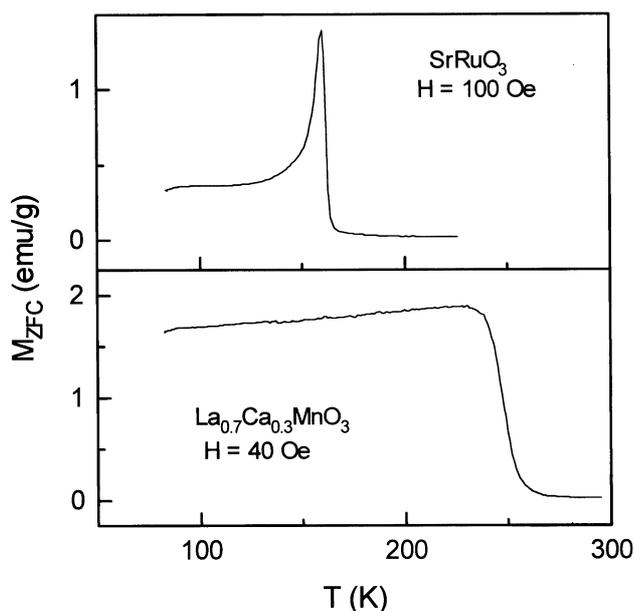
Our results from a comparison of the low field magnetic behaviours of the ferromagnetic oxides $La_{0.7}Ca_{0.3}MnO_3$ and $Pr_{0.7}Ca_{0.3}MnO_3$ have indicated that the properties similar to that of a spin glass, observed for $Pr_{0.7}Ca_{0.3}MnO_3$, are due to its relatively larger magnetocrystalline anisotropy compared to that of $La_{0.7}Ca_{0.3}MnO_3$ (Anil Kumar *et al* 1998a). The magnetic behaviour of $La_{0.5}Sr_{0.5}CoO_3$ similar to that of a cluster glass as reported (Itoh *et al* 1994), could also be explained based on the high anisotropy of the compound (Anil Kumar *et al* 1998b). Roy *et al* (1994, 1997) reported the thermomagnetic irreversibility of different ordered magnetic systems, and concluded that the features of these ordered systems which are similar to those of spin glasses are due to a combination of intrinsic disorder along with inherent anisotropy. In this paper we have compared the low-field FC

---

*Author for correspondence

and ZFC magnetic behaviours of the ferromagnetic oxides, $SrRuO_3$ and $La_{0.7}Ca_{0.3}MnO_3$, and the ferrimagnetic oxides, $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and $SrFe_{12}O_{19}$, having widely differing magnetocrystalline anisotropies. $SrRuO_3$ is a well-known ferromagnetic oxide with very high magnetocrystalline anisotropy (Kabayasi 1976) and there is no magnetic saturation even at very high magnetic fields and low temperatures, whereas $La_{0.7}Ca_{0.3}MnO_3$ easily saturates in low magnetic fields and its calculated ferromagnetic moment is comparable to the expected value (Hwang *et al* 1995). Similarly, the magnetocrystalline anisotropy of the hexagonal ferrite $SrFe_{12}O_{19}$ (hard ferrite) is very high (Smit and Wijn 1959; Goldman 1990) compared to that of the cubic ferrite $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (soft ferrite).

2. Experimental

The methods of synthesis and characterization of polycrystalline samples of $SrRuO_3$ (SRH), $La_{0.7}Ca_{0.3}MnO_3$ (LCM), $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZF) and $SrFe_{12}O_{19}$ (SRF) have been reported previously (Kulkarni *et al* 1989; Anil Kumar *et al* 1996, 1998c; Joy *et al* 1997). Magnetic measurements (field-cooled (FC) and zero-field-cooled (ZFC) magnetizations and magnetic hysteresis) were performed using a EG&G PAR model 4500 vibrating sample magnetometer. Magnetic hysteresis measurements (maximum field = 15 kOe) were performed after cooling the sample through its T_c to the required temperature in zero magnetic field.
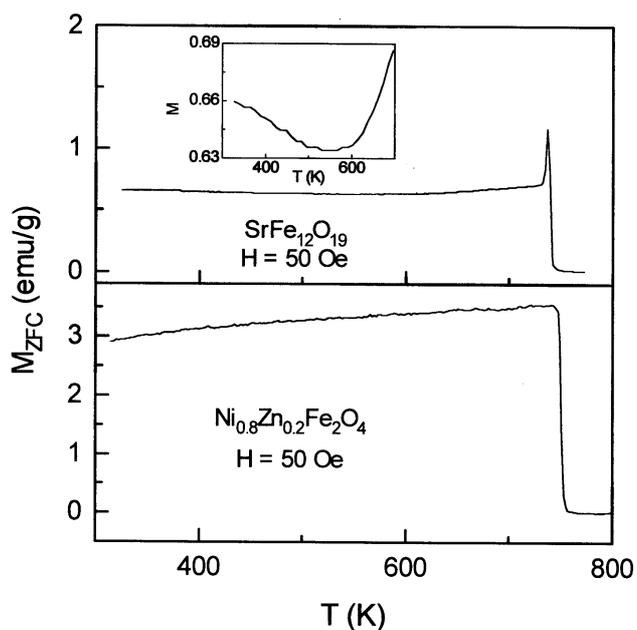
3. Results and discussion

Temperature variation of the zero-field-cooled magnetizations (M_{ZFC}) of $SrRuO_3$ (SRH), $La_{0.7}Ca_{0.3}MnO_3$ (LCM), $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZF) and $SrFe_{12}O_{19}$ (SRF), measured at low magnetic fields, are shown in figures 1 and 2. For LCM and NZF, M_{ZFC} increases slowly with increasing temperature and shows a broad maximum below the Curie temperature. M_{ZFC} of SRF decreases slowly as the temperature is increased, a broad minimum is observed between 523 and 623 K (see inset of figure 2) and again slowly increases up to ~ 730 K above which a drastic increase in the magnetization is observed. A sharp peak is obtained at 737 K followed by the transition to paramagnetic state at $T_c = 740$ K. Similar sharp peak is observed for SRH also at 160 K close to its $T_c = 161$ K.
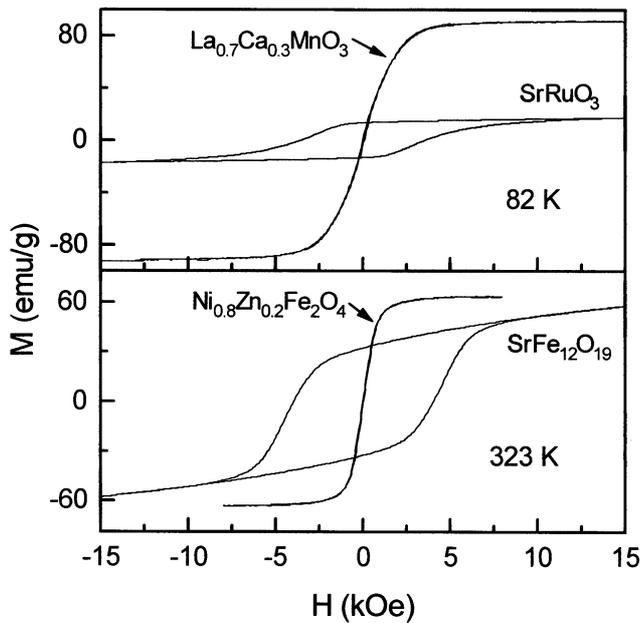
The magnetic hysteresis behaviour of the ferro- and ferrimagnetic compounds are shown in figure 3. The coercivities of the low anisotropy compounds, LCM and NZF, are very small compared to the coercivities of SRH and SRF with very large magnetocrystalline anisotropies ($H_c \approx 2K_1/M_s$, where K_1 is the anisotropy constant and M_s is saturation magnetization (Brown 1962)). Temperature dependence of coercivities (H_c) of the ferromagnetic and ferrimagnetic compounds are compared in figures 4 and 5, respectively. The coercivity of LCM decreases linearly from a value of 35 Oe at 82 K ($T_c = 245$ K), as the temperature is increased, whereas for SRH, the coercivity is very high (~ 3500 Oe) at low temperatures. Similarly, for NZF the coercivity decreases from 21 Oe at 323 K ($T_c = 750$ K) compared to the high coercivity of SRF at
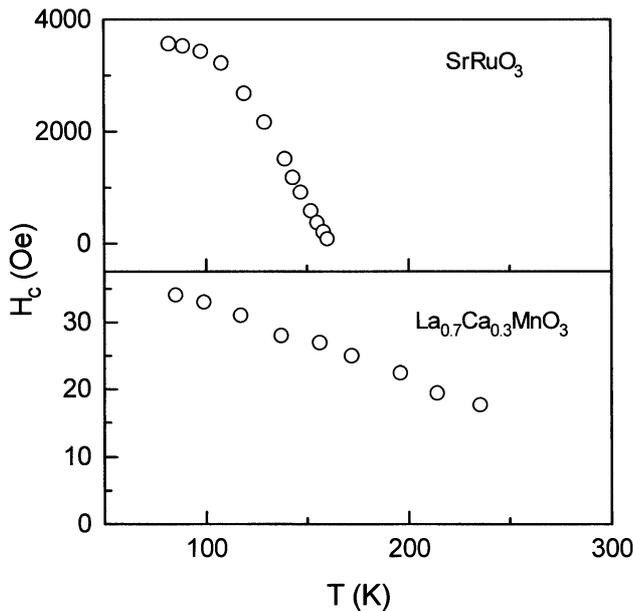

Figure 1. Temperature dependence of M_{ZFC} of $SrRuO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ measured at the low magnetic fields indicated.

Figure 2. Temperature dependence of M_{ZFC} of $SrFe_{12}O_{19}$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ measured at the low magnetic fields indicated. Inset: expanded M_{ZFC} (T) curve of $SrFe_{12}O_{19}$.

room temperature (Jahn and Muller 1969). H_c of SRF increases from ~ 4000 Oe at 323 K to ~ 5500 Oe at 473 K and decreases further to ~ 4000 Oe at 673 K, as the temperature is increased.

A comparison of figures 1 and 4 and 2 and 5 shows that for all the four compounds, the temperature dependence of the low-field $M_{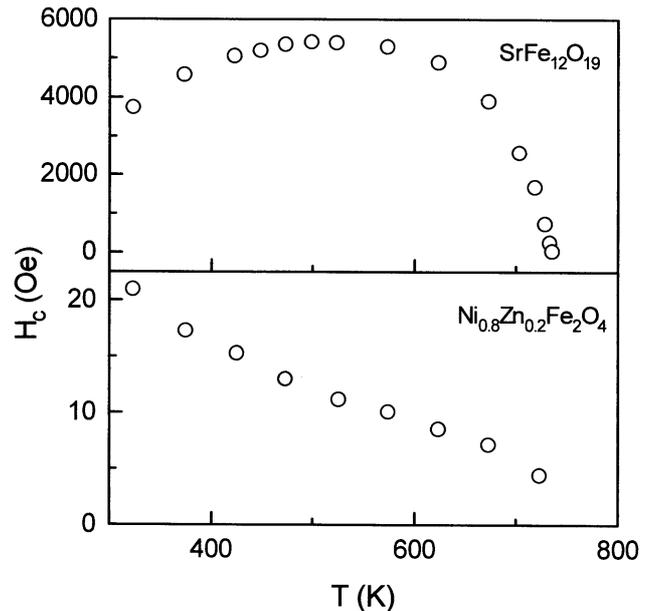ZFC}$ is inversely related to the magnitude of the coercivities of the compounds in relation to the applied field, and the temperature dependence of the coercivity. For NZF and LCM the coercivity decreases very slowly with increasing temperature and M_{ZFC} increases slowly as the temperature is increased. For SRF, M_{ZFC} decreases up to about 473 K and again increases up to 730 K as the temperature is increased. A reverse trend is observed for H_c in this temperature region, showing maximum H_c at ~ 473K. This relation between the temperature variations of H_c and M_{ZFC} of SRF may be clearly seen in figure 2 where the expanded M_{ZFC} curve measured at 50 Oe is shown as inset. Above 723 K, the coercivity decreases very fast up to the T_c and the M_{ZFC} curve shows a drastic increase up to 737 K. A sharp peak is observed in M_{ZFC} at this temperature. For SRH also, a similar trend is observed between M_{ZFC} and H_c. As the applied magnetic field is increased, the peak in the M_{ZFC} curves becomes broader and the peak temperature is shifted to lower temperatures, as shown for SRF and SRH in figure 6. The difference between T_c and temperature at which a maximum is observed in $M_{ZFC}(T)$ is related to the magnitude of the applied field and the coercivity at that temperature. The peak in M_{ZFC} is observed at a temperature where the coercivity is larger than the applied field and a broad maximum is observed when H_c is comparable or smaller than the applied field. This observation shows the influence of the coercivity on the shape of the M_{ZFC} curves.

FC and ZFC magnetization curves of LCM at H_{app} = 100 Oe and SRH at H_{app} = 2000 Oe are shown in figure 7 and that of NZF at H_{app} = 50 Oe and SRF at H_{app} = 2000 Oe are shown in figure 8. All the compounds

Figure 3. Magnetic hysteresis curves of SrRuO$_3$, La$_{0.7}$Ca$_{0.3}$MnO$_3$, SrFe$_{12}$O$_{19}$ and Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ recorded at the temperatures indicated.

Figure 4. Temperature dependence of H_c of SrRuO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$.

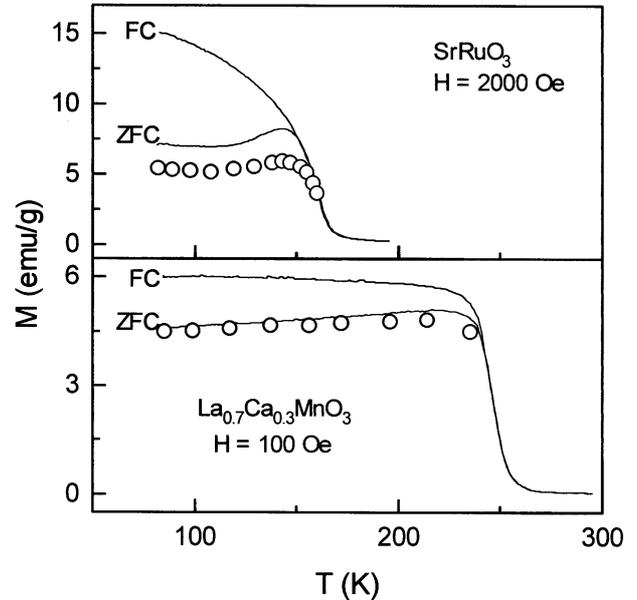**Figure 5.** Temperature dependence of H_c of SrFe$_{12}$O$_{19}$ and Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$.

show thermomagnetic irreversibility ($M_{FC} > M_{ZFC}$) below a certain temperature, T_{irr}. Furthermore, with increasing applied field, there is a corresponding decrease in the value of T_{irr}, as observed for La$_{0.5}$Sr$_{0.5}$CoO$_3$ (Anil Kumar *et al* 1998b). M_{FC} and M_{ZFC} of different magnetic systems were found to be related through the expression (Joy *et al* 1998)

$$M_{ZFC} \approx M_{FC} \frac{H_{app}}{H_{app} + H_c},$$

where H_{app} is the applied field and H_c the coercivity. M_{ZFC} values calculated using the above expression from the measured M_{FC} at different temperatures are shown in figures 7 and 8. It may be seen that the magnitudes of the calculated M_{ZFC} at different temperatures are comparable to that of the measured M_{ZFC} for LCM and NZF. For SRH and SRF also, the shapes of the calculated M_{ZFC} curves are identical to those of the measured M_{ZFC}, though there are slight differences in their magnitudes. This difference between the calculated and measured M_{ZFC}s may be attributed to the presence of a small residual net magnetic field during the process of zero field cooling (Joy *et al* 1998). A small net magnetic field present during the zero field cooling will greatly affect the M_{ZFC} of the highly anisotropic compounds than that of the low anisotropy compounds because the magnitude of the measured M_{ZFC} at low temperatures is determined by the magnetic anisotropy.

The results show that M_{ZFC} is related to M_{FC} through the coercivity, and the difference between M_{FC} and M_{ZFC} (i.e.

thermomagnetic irreversibility) is due to the magnetocrystalline anisotropy since coercivity is a measure of the anisotropy. Because of the large magnetocrystalline anisotropy of SrRuO$_3$ and SrFe$_{12}$O$_{19}$, their thermomagnetic irreversibility is much larger and sharp peaks are observed in the M_{ZFC} curves, whereas the low anisotropy

Figure 7. Temperature dependence of M_{FC} and M_{ZFC} of SrRuO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ measured at the magnetic fields indicated. The circles represent the calculated M_{ZFC} from the measured M_{FC} using the expression given in the text.
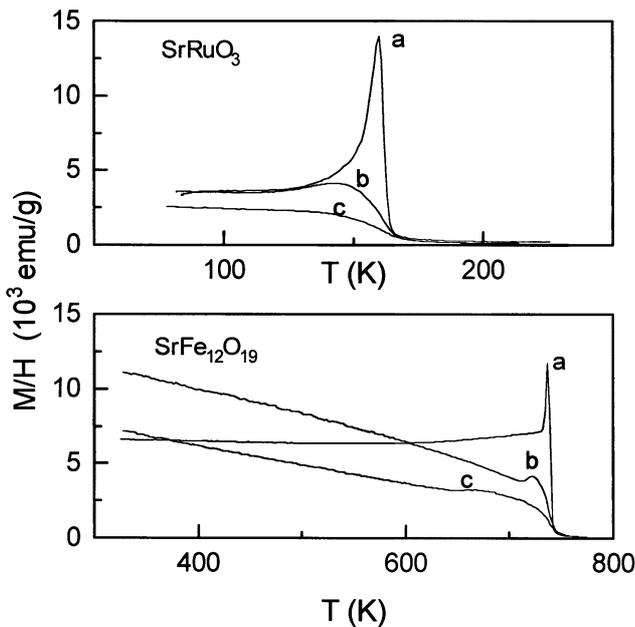
Figure 6. Temperature dependence of M_{ZFC}/H of SrFe$_{12}$O$_{19}$ and SrRuO$_3$, measured at different applied fields; 50 Oe (**a**); 2000 Oe (**b**); 5000 Oe (**c**).
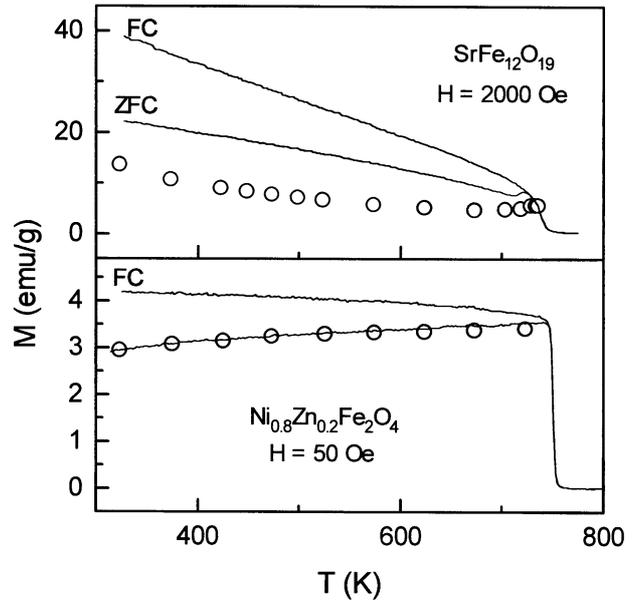
Figure 8. Temperature dependence of M_{FC} and M_{ZFC} of SrFe$_{12}$O$_{19}$ and Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ measured at the magnetic fields indicated. The circles represent the calculated M_{ZFC} from the measured M_{FC} using the expression given in the text.

compounds $La_{0.7}Ca_{0.3}MnO_3$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ show broad maximum in their M_{ZFC} curves and relatively small irreversibility. The shape of the M_{ZFC} curve is determined by the applied magnetic field strength in relation to the coercive field at a given temperature.

The thermomagnetic irreversibility arises from the magnetic anisotropy due to the difference in the way in which the FC and ZFC measurements are performed on the polycrystalline samples, the sample is either cooled in a magnetic field (FC) or in zero magnetic field (ZFC) through the magnetic ordering temperature. The response of the spins to the external magnetic field depends on the competition between magnetocrystalline anisotropy energy and the applied magnetic field strength. At low measuring fields, compared to the anisotropy field, all the spins will not be oriented in the direction of the applied magnetic field. The magnitude of M_{ZFC} at low temperatures below the T_c of the compounds will depend on the anisotropy, and therefore the difference between M_{FC} and M_{ZFC} will be larger for the highly anisotropic compounds. Hence, the irreversibility between M_{FC} and M_{ZFC} and a maximum (cusp or peak) in the ZFC magnetizations of the ferro- and ferrimagnetic systems are due to their magnetic anisotropy and not due to any spin-glass-like behaviour as reported for many ordered magnetic systems.

4. Conclusions

The field-cooled and the zero-field-cooled magnetizations of two ferromagnetic compounds, $La_{0.7}Ca_{0.3}MnO_3$ and $SrRuO_3$, and two ferrimagnetic compounds, $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and $SrFe_{12}O_{19}$, having widely differing magnetocrystalline anisotropies, are compared. All four compounds show thermal irreversibility between M_{FC} and M_{ZFC}. M_{FC} and M_{ZFC} are related to each other through the coercivity and applied magnetic field. The extent of irreversibility and the shape of $M_{ZFC}(T)$ curve at a given applied field are directly related to the coercivity in relation to the magnitude of the applied magnetic field. The magnetic behaviour of $La_{0.7}Ca_{0.3}MnO_3$ is similar to that of $Ni_{0.8}Zn_{0.2}Fe_2O_4$ which are low anisotropy materials and the properties of the highly anisotropic compounds, $SrFe_{12}O_{19}$ and $SrRuO_3$, are comparable to each other.

References

Anil Kumar P S, Shrotri J J, Kulkarni S D, Deshpande C E and Date S K 1996 *Mater. Lett.* **27** 293

Anil Kumar P S, Joy P A and Date S K 1998a *Solid State Commun.* **108** 67

Anil Kumar P S, Joy P A and Date S K 1998b *J. Phys.: Condens. Matter* **10** L487

Anil Kumar P S, Joy P A and Date S K 1998c *J. Mater. Chem.* **8** 1219

Brown Jr W F 1962 *Magnetostatic principles in ferromagnetism* (Amsterdam: North-Holland)

Goldman A 1990 *Modern ferrite technology* (New York: van Nostrand)

Greedan J E, Raju N P, Maignan A, Simon Ch, Pederson J S, Niraimathi A M, Gmelin E and Subramanian M A 1996 *Phys. Rev.* **B54** 7189

Hwang H Y, Cheong S-W, Radaelli P G, Marezio M and Batlogg B 1995 *Phys. Rev. Lett.* **75** 914

Itoh M, Natori I, Kubota S and Motoya K 1994 *J. Phys. Soc. Jpn.* **63** 1486

Jahn L and Muller H G 1969 *Phys. Status Solidi* **35** 723

Joy P A, Date S K and Anil Kumar P S 1997 *Phys. Rev.* **B56** 2324

Joy P A, Anil Kumar P S and Date S K 1998 *J. Phys.: Condens. Matter* **10** 11049

Kabayasi A 1976 *J. Phys. Soc. Jpn.* **41** 1876

Kulkarni S D, Shrotri J J, Deshpande C E and Date S K 1989 *J. Mater. Sci.* **24** 3739

Maignan A, Varadaraju U V, Millange F and Raveau B 1997 *J. Magn. Magn. Mater.* **168** 237

Mydosh J A 1993 *Spin glasses—an experimental introduction* (London: Taylor & Francis)

Nishigori S, Hirooka Y and Ito T 1998 *J. Magn. Magn. Mater.* **177–181** 137

Pecher S, Chevalier B, Laffargne D, Darriet B, Roisnel T and Etourneau J 1999 *J. Magn. Magn. Mater.* **191** 282

Roy S B, Pradhan A K and Chaddah P 1994 *J. Phys.: Condens. Matter* **6** 5155

Roy S B, Pradhan A K, Chaddah P and Sampathkumaran E V 1997 *J. Phys.: Condens. Matter* **9** 2465

Smit J and Wijn H P J 1959 *Ferrites* (Eindhoven: Philips Technical Library)