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## Role of the rare-earth ion on the strength of the ferromagnetic exchange interactions in $\text{RMn}_{0.5}\text{M}_{0.5}\text{O}_3$ ( $\text{M} = \text{Co}, \text{Ni}$ )

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### Abstract

The role of the trivalent rare-earth ion on the paramagnetic to ferromagnetic transition temperature ( $T_c$ ) of the substituted perovskite-type rare-earth (R) manganese oxides,  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$  ( $\text{R} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}$  and  $\text{Yb}$ ), is compared. For a particular  $\text{R}^{3+}$  with larger ionic size, the  $T_c$  of  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$  is larger than that of  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and vice versa for smaller ionic size, though the ionic sizes of trivalent low-spin Co and Ni ions are comparable.  $T_c$  values of both Co and Ni containing compositions decrease with the decrease in the ionic size of  $\text{R}^{3+}$ , showing a faster decrease for heavier rare-earth ions beyond  $\text{Gd}^{3+}$ . Though the decreasing size of the rare-earth ion is responsible for the decrease in the magnetic transition temperature, due to structural distortions, an anomalous change in the rate of decrease of  $T_c$  beyond  $\text{Gd}^{3+}$  is due to contributions from the single-ion anisotropy of the heavier rare-earth ions.

### 1. Introduction

In the perovskite-type manganites,  $\text{RMnO}_3$  ( $\text{R} =$  trivalent rare-earth ion or  $\text{La}^{3+}$ ), which are insulating and antiferromagnetic, when a divalent ion is substituted at the R site, a corresponding number of  $\text{Mn}^{4+}$  ions are formed, which reduces orthorhombic distortion of  $\text{RMnO}_3$  and induces ferromagnetism and conductivity through  $\text{Mn}^{3+}\text{--O--Mn}^{4+}$  double exchange interactions [1]. Such R-site substituted manganites have been studied extensively in the recent past after the discovery of colossal magnetoresistance in this class of materials [2, 3]. On the other hand, if Mn in  $\text{RMnO}_3$  is substituted by other transition metal ions like Co, Ni, etc, the compounds become ferromagnetic but remain insulating [4–7]. Most of these behaviours can be explained in terms of the removal of co-operative Jahn–Teller (JT) distortion of the  $\text{Mn}^{3+}$

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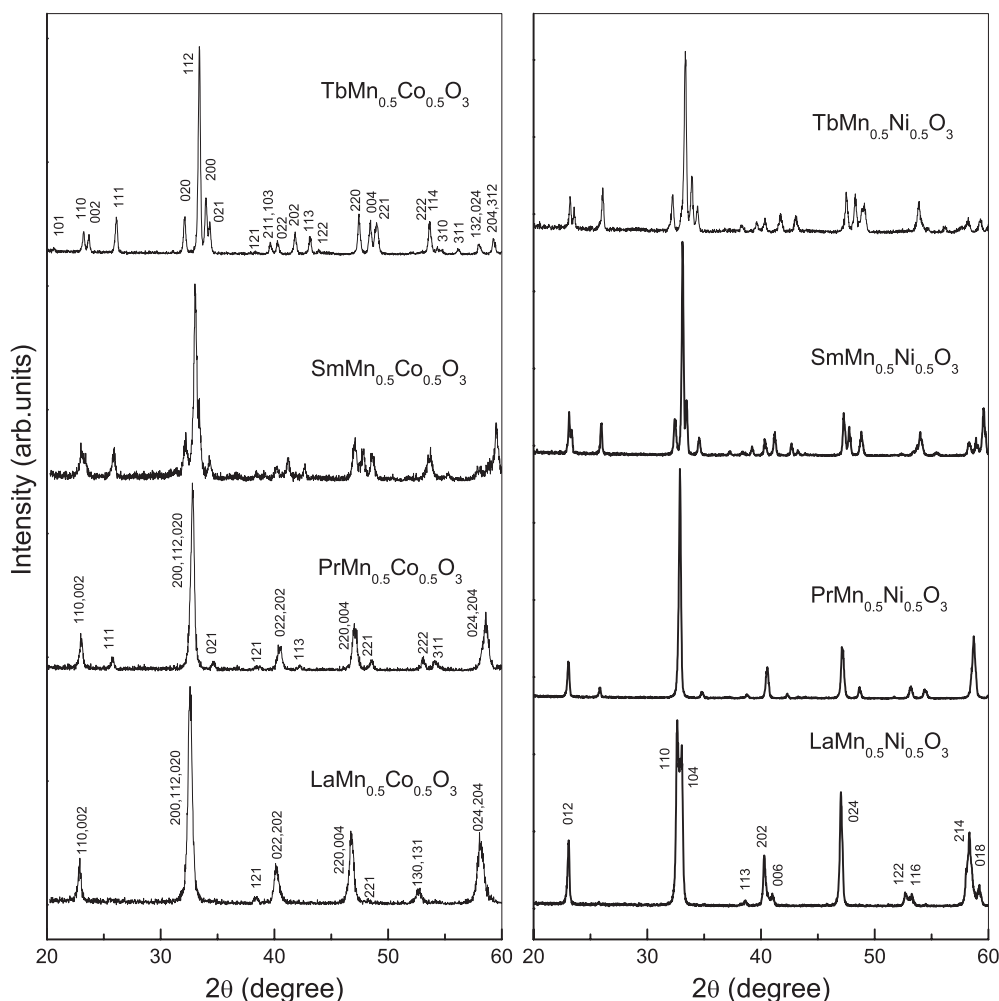
ion and the structural distortions associated with the ionic size mismatches in the perovskite lattice. In the case of substitution at the Mn site, such as  $\text{RMn}_{1-x}\text{M}_x\text{O}_3$ ,  $\text{Mn}^{4+}\text{--O--Mn}^{2+}$  and/or  $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ , ferromagnetic superexchange interactions, in addition to  $\text{Mn}^{3+}\text{--O--M}^{3+}$  exchange, cause ferromagnetism, apart from the reduction in JT distortion.

Recent reports indicate that, for  $\text{LaMn}_{0.5}\text{M}_{0.5}\text{O}_3$  with  $\text{M} = \text{Co}$  [8, 9] or  $\text{Ni}$  [10], two ferromagnetic phases are possible with different spin states of Mn and M. In one of these phases of  $\text{LaMn}_{0.5}\text{M}_{0.5}\text{O}_3$ , which show higher  $T_c$  values (high- $T_c$  phase), Mn is present in the trivalent state and Co or Ni is present in the low-spin trivalent state. Though the ionic sizes of low-spin Co and Ni ions are almost comparable (0.545 and 0.56 Å, respectively [11], for six coordination), the  $T_c$  of the Ni compound is higher than that of the corresponding Co compound by 50 K. This is probably due to the contribution from additional  $\text{Mn}^{3+}\text{--O--Ni}^{3+}$  ferromagnetic exchange interactions in  $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ , because low-spin  $\text{Co}^{3+}$  is a diamagnetic ion ( $t_{2g}^6 e_g^0$ ,  $S = 0$ ) whereas low-spin  $\text{Ni}^{3+}$  contains one unpaired electron in the  $e_g$  orbital ( $t_{2g}^6 e_g^1$ ,  $S = 1/2$ ) which can take part in the superexchange process.

The extent of overlap between O 2p and Mn 3d orbitals, which determines the strength of the Mn–O–Mn superexchange interactions, in the perovskites, is maximum if the Mn ions are in a cubic crystal structure so that the Mn–O–Mn bond angle is at the ideal value of  $180^\circ$  [12]. As the ionic sizes of the R- and Mn-site ions in the perovskite  $\text{RMnO}_3$  deviate from the ideal size required for the formation of a cubic perovskite unit cell, an internal pressure develops in the crystal lattice and to relieve this pressure the Mn–O–Mn bond puckers, resulting in a lower symmetric crystal structure such as rhombohedral, orthorhombic, etc. The puckering of the Mn–O–Mn bond lessens the overlap between O 2p and Mn 3d orbitals which in turn weakens the ferromagnetic exchange interaction and ultimately reduces the ferromagnetic ordering temperature. In the perovskite oxides,  $\text{ABO}_3$ , the tolerance factor,  $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ , where  $r_A$ ,  $r_B$  and  $r_O$  are the coordination dependent ionic radii of A, B and O, respectively, gives an account of the degree of distortion of the unit cell structure from cubic symmetry for which  $t = 1$ . So, a decrease in the ferromagnetic transition temperature is expected as the tolerance factor is decreased. The tolerance factor can be decreased by decreasing the ionic radius of A for a given B ion. We have studied and compared how the size of the rare-earth ion ( $\text{R} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}$  and  $\text{Yb}$ ) affects the ferromagnetic exchange interactions, and therefore the  $T_c$ , of the high- $T_c$  phases of  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ .

## 2. Experimental details

Previous studies on  $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$  showed that the high- $T_c$  phases of these compounds, in single-phase forms, were formed on annealing the powders obtained from a combustion method of synthesis, at 700 and 1350 °C, respectively [8, 10]. Hence, all the  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  (RMC) and  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$  (RMN) compositions were prepared by this low-temperature method. In this method of synthesis, a mixture of the nitrate solutions of R (obtained by dissolving the corresponding amount of the rare-earth oxide in nitric acid), Mn and Co, taken in the required stoichiometric ratio, was mixed with a water solution of glycine (2 mol glycine/mol metal cation). The solution was evaporated slowly, on a hot plate, until it formed a thick mass, which subsequently underwent auto-combustion to give a fine powder. The extremely fine powders thus obtained were initially heated in air for 12 h each at 700 °C. Single-phase compounds were obtained after this heating for Co containing compositions up to  $\text{R} = \text{Dy}^{3+}$ , whereas heating at 1000 °C was required for the formation of single-phase compounds of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ . Similarly, all the Ni containing compositions up to  $\text{R} = \text{Gd}^{3+}$  were heated at 1350 °C for 24 h to obtain single-phase materials, whereas for the corresponding heavier rare-earth based compounds the samples were heated at 1200 °C for

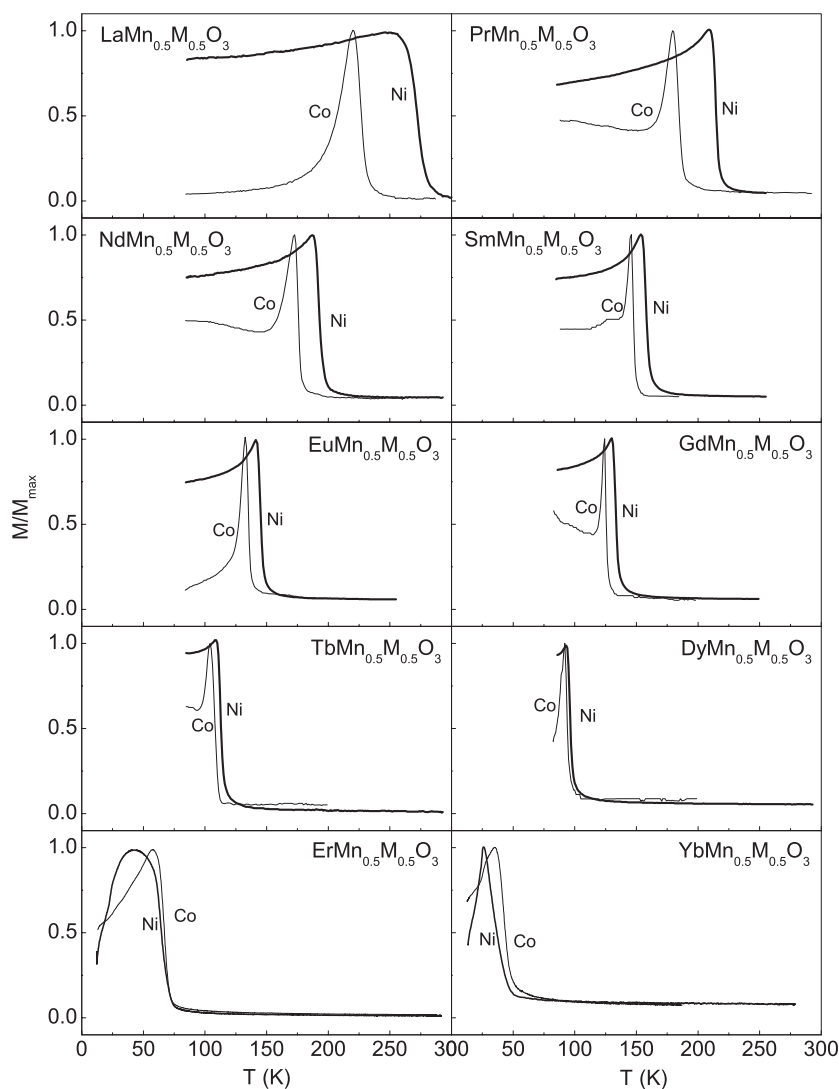


**Figure 1.** The powder x-ray diffraction patterns of  $R = \text{Pr, Sm}$  and  $\text{Tb}$  based compounds in  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ . The patterns of the  $\text{La}$  based compounds are also shown for comparison.

24 h. The heavier rare-earth based compounds were found to be partially transformed from their orthorhombic phase to hexagonal phase when heated above this temperature. However, the magnetic transition temperatures were not affected with increasing fraction of the hexagonal phase. The compounds were characterized by powder x-ray diffraction (XRD) and magnetic measurements. As zero-field cooled (ZFC) magnetization measurements, using low magnetic fields, can give sufficient information on the phase purity and transition temperature of magnetic compositions [8], ZFC measurements were made at a magnetic field of 50 Oe, using a vibrating sample magnetometer, in the temperature range 10–300 K.

### 3. Results and discussion

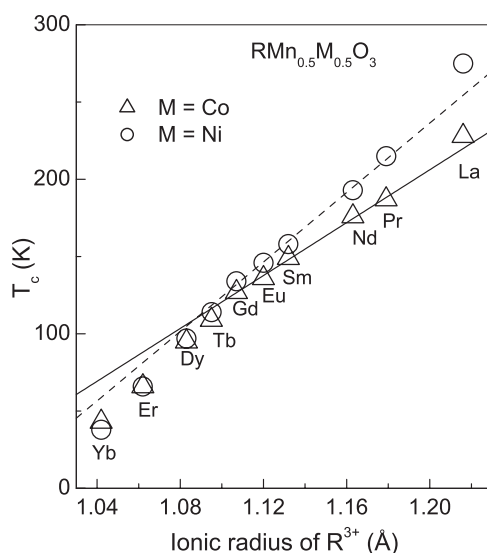
The powder XRD patterns of all the compositions showed the formation of phases with perovskite structure. Figure 1 shows the typical XRD patterns of some  $\text{Co}$  and  $\text{Ni}$  containing compositions ( $R = \text{Pr, Sm, Tb}$ ). The patterns of the corresponding  $\text{La}$  compounds are also



**Figure 2.** The zero-field cooled (ZFC) magnetization curves of  $\text{RMn}_{0.5}\text{M}_{0.5}\text{O}_3$  ( $\text{M} = \text{Co}, \text{Ni}$ ),  $H = 50$  Oe. The magnetization curves of the corresponding La based compounds are also shown for comparison.

shown for comparison. All the  $\text{RMn}_{0.5}\text{M}_{0.5}\text{O}_3$  compounds are found to be orthorhombic and the orthorhombic distortion increases for heavier rare-earth ion based compositions, as evidenced by the increased degree of splitting of the corresponding reflections. The XRD patterns could be indexed on the  $\text{GdFeO}_3$ -type orthorhombic perovskite structure with  $Pbnm$  space group.  $\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  shows relatively less orthorhombic distortion whereas  $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$  is rhombohedral [10]. For heavier rare-earth based compositions, the extent of orthorhombic distortion is found to be comparable for both the Co and Ni compounds.

The zero-field cooled (ZFC) magnetization curves of  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$  ( $\text{R} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}$  and  $\text{Yb}$ ), and those of the La based compounds, measured using a low applied field of 50 Oe, are shown in figure 2. All the magnetization curves

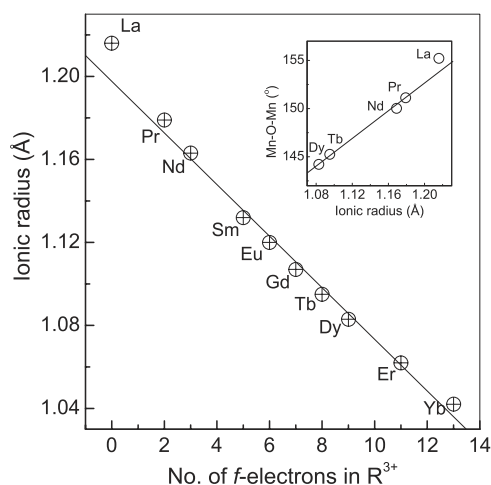


**Figure 3.** The variation of the  $T_c$  values of  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ , with the ionic radius of the rare-earth ions [11]. The straight lines are linear fits to the data. The  $T_c$  values of the La compounds are also included for comparison.

show sharp magnetic transitions, indicating the formation of single phase compositions. The transition temperatures of the Ni compounds are larger than those of the corresponding Co compounds, except for the Er and Yb based compositions, and there is a gradual decrease in the  $T_c$  values of both Co and Ni compounds as the rare-earth ion is changed from  $\text{Pr}^{3+}$  to  $\text{Yb}^{3+}$ . Almost identical  $T_c$  values are observed when  $R = \text{Er}$  and the magnetic transition temperature of the Co compound is larger than that of the corresponding Ni compound for  $R = \text{Yb}$ . Also, there is a significant difference in the shapes of the curves below  $T_c$  for the Co and Ni compounds due to the contribution from magnetocrystalline anisotropy from Co [13, 14]. Similarly, the contribution from the magnetocrystalline anisotropy of the rare-earth ions is visible in the magnetization curves of  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ ; the broad maximum observed for the La compound becomes sharper with the change in R from Pr to Yb, as observed in the case of  $\text{R}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  [15].

The changes in the ferromagnetic transition temperatures of  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$  as a function of the ionic size of  $\text{R}^{3+}$  (the effective ionic radius of  $\text{R}^{3+}$ , for ninefold coordination [11]) are shown in figure 3.  $T_c$  values decrease almost linearly from  $R = \text{Pr}^{3+}$  to  $\text{Gd}^{3+}$ , except for relatively large  $T_c$  values for the La based compounds. There is a change in the rate of decrease of  $T_c$  with decreasing ionic size of R, after  $\text{Gd}^{3+}$ , and again a much faster linear decrease is observed for the heavier rare-earth based compounds, for both  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ . Another important observation is that the  $T_c$  of the Ni compounds falls relatively fast with decrease in the ionic radius of  $\text{R}^{3+}$ , when compared to the variation for the Co compounds.

The higher  $T_c$  values for  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$  when compared to those of  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ , including the La based compositions, are possible if there is an additional contribution to ferromagnetism from  $\text{Mn}^{3+}-\text{O}-\text{Ni}^{3+}$  superexchange interactions through the single  $e_g$  electron in low-spin  $\text{Ni}^{3+}$ . Similarly, the relatively large  $T_c$  values for the La based compositions can be understood in terms of the relatively large size of  $\text{La}^{3+}$ . As shown in figure 4, the ionic size of trivalent rare-earth ions decreases linearly with number of f electrons, from  $\text{Pr}^{3+}$  to

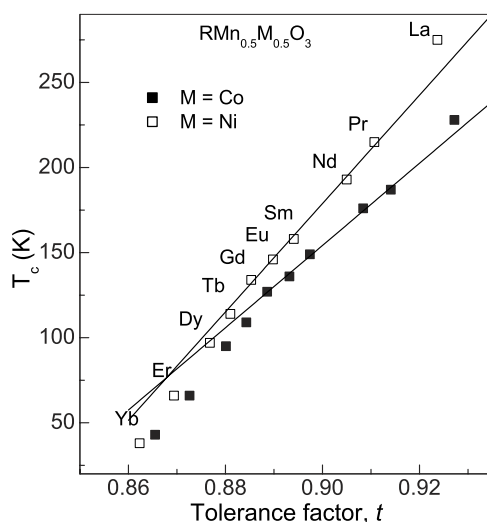


**Figure 4.** Variation of the ionic radius of  $R^{3+}$ , for ninefold coordination [11], with number of  $f$  electrons. The inset shows the variation of the average Mn–O–Mn angle in  $RMnO_3$  [16] with the ionic radius of  $R^{3+}$ . The parameters for  $La^{3+}$  and  $LaMnO_3$  are also included for comparison.

$Yb^{3+}$ . In fact, in the case of  $RMnO_3$ , the average Mn–O–Mn angle [16] decreases linearly with the radius of the rare-earth ion, as shown in the inset of figure 4, and the same trend is also expected in the case of the  $RMn_{0.5}M_{0.5}O_3$  series. Therefore, a linear decrease in the  $T_c$  with ionic size of  $R^{3+}$  is expected, based on the linear change in the Mn–O–Mn angle. The ionic size of  $La^{3+}$  and the Mn–O–Mn angle in  $LaMnO_3$  are relatively large and the less distorted orthorhombic or rhombohedral structures observed for the La compounds may be due to the relatively large size of  $La^{3+}$  ion. The lesser structural distortion and relatively large Mn–O–Mn angle for  $LaMn_{0.5}Co_{0.5}O_3$  and  $LaMn_{0.5}Ni_{0.5}O_3$  can give rise to relatively large ferromagnetic transition temperatures, as observed. However, the deviation from linearity, in the decrease of  $T_c$  with decreasing ionic size, after  $Gd^{3+}$ , and the much faster drop in  $T_c$  for the heavier rare-earth based compounds, are not expected since the rare-earth ionic size decreases almost linearly from  $Pr^{3+}$  to  $Yb^{3+}$ , as shown in figure 4.

The decrease in  $T_c$  with the ionic size of  $R^{3+}$  is in good agreement with the fact that the size of the A-site ion in the perovskite  $ABO_3$  affects the strength of the  $180^\circ$  B–O–B ferromagnetic superexchange interactions. For a given crystal structure and B-site ion, the strength of this superexchange interaction is determined by the extent of overlap between the oxygen and B-site ion orbitals. The difference between the  $T_c$  values of  $RMn_{0.5}Co_{0.5}O_3$  and  $RMn_{0.5}Ni_{0.5}O_3$ , for a given R, decreases with the size of  $R^{3+}$  and becomes almost constant for smaller R ions, indicating that the R ionic size effect overrules the contribution from additional ferromagnetic exchange interactions due to the  $Ni^{3+}$  ion for the Ni compounds. Moreover, the higher  $T_c$  of the Co compound when compared to that of the Ni compound, for  $R = Yb$ , indicates that the Mn–O–Ni superexchange interactions are greatly affected by the smaller size of  $R^{3+}$ .

Since the magnetic transition temperature is determined by the extent of superexchange due to the variation of the Mn–O–Mn angle associated with structural distortions, this can be better understood in terms of the tolerance factor which is a direct measure of the structural distortion. Figure 5 shows the variation of the  $T_c$  of the Co and Ni compounds with tolerance factor. Tolerance factor is calculated using the effective ionic radius of  $R^{3+}$  for ninefold coordination, sixfold coordination for the trivalent transition metal ions and sixfold coordination of  $O^{2-}$  [11]. The tolerance factors are slightly different for the Co and Ni compounds due to the slight



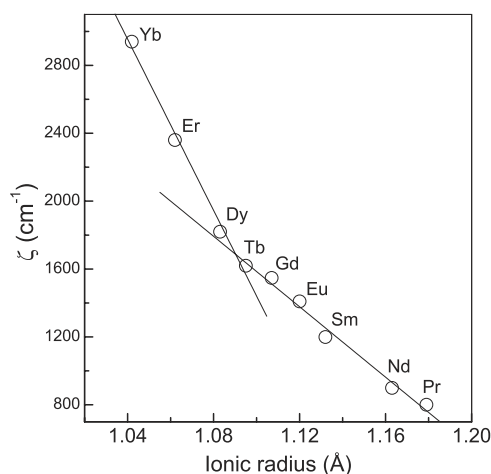
**Figure 5.** The variation of  $T_c$  values of  $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{RMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$  with tolerance factor. The corresponding data of the La based compounds are shown for comparison. The straight lines are linear fits to the data.

difference in the sixfold coordination ionic radii of  $\text{Co}^{3+}$  and  $\text{Ni}^{3+}$ . The  $T_c$  values decrease with decreasing tolerance factor and this decrease in  $T_c$  with the decrease in tolerance factor is in good agreement with the theoretical predictions based on structural distortions.  $T_c$  values of  $\text{RMn}_{0.5}\text{M}_{0.5}\text{O}_3$  compositions decreases linearly with  $t$  from  $\text{Pr}^{3+}$  to  $\text{Gd}^{3+}$  and a larger linear rate of decrease is observed for R beyond  $\text{Gd}^{3+}$ , indicating another contribution to the strength of the magnetic exchange interactions after  $\text{Gd}^{3+}$ .

The possibility that the unusually lower  $T_c$  values for the heavier rare-earth based compounds, beyond  $\text{Gd}^{3+}$ , is due to any anomaly in their ionic sizes can be ruled out. Another possibility for the anomaly is the magnetocrystalline anisotropy of the rare-earth ions. The variation of one-electron spin-orbit coupling constant, which leads to single-ion anisotropy, of the rare-earth ions, as a function of the ionic radius, is shown in figure 6. The spin-orbit coupling constant increases almost linearly from  $\text{Pr}^{3+}$  to  $\text{Gd}^{3+}$  and then increases much faster, linearly, beyond  $\text{Tb}^{3+}$ , showing a slope change after  $\text{Tb}^{3+}$ . The change in the slope of the variation of  $T_c$  with ionic size is exactly in accordance with the variation of the spin-orbit coupling constant, indicating that single-ion anisotropy of the heavier rare-earth ions may be responsible for the anomaly (relatively low  $T_c$  values for the heavier rare-earth ions after  $\text{Gd}^{3+}$ ) observed.

It has been shown that the increasing magnetocrystalline anisotropy of the heavier rare earth ions does not contribute any associated magnetic interactions with the Mn lattice, as evidenced from neutron diffraction studies on  $\text{TbMnO}_3$  [18]. However, Cheng *et al* [19] have reported unusually large shifts in the magneto-optical Kerr rotation in thin films of  $\text{CoFe}_2\text{O}_4$  doped with  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$ . Similarly, Kahn and Zhang [20] found unusually large blocking temperatures and coercivities for  $\text{CoFe}_2\text{O}_4$  spinel ferrite nanoparticles doped with  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  ions when compared to the effect of other lanthanide ions. The authors concluded that the single-ion anisotropy of the lanthanide ions may be the controlling factor, but found that the effect of the lanthanide ion on the modulation of the magnetic properties of the system is very complex. The present studies demonstrate that single-ion anisotropy of the heavier rare-earth ions marginally affects the magnetic exchange interactions in the ferromagnetic compositions





**Figure 6.** The variation of the one-electron spin-orbit coupling coefficient [17],  $\zeta$ , with the ionic radius of  $R^{3+}$  [11]. The straight lines are linear fits to the data.

in  $RMn_{0.5}Co_{0.5}O_3$  and  $RMn_{0.5}Ni_{0.5}O_3$ , apart from the contributions from structural distortions associated with the decreasing ionic size of the rare-earth ions.

#### 4. Conclusions

Studies on the rare-earth manganites,  $RMn_{0.5}Co_{0.5}O_3$  and  $RMn_{0.5}Ni_{0.5}O_3$ , show that  $T_c$  decreases as the size of R decreases.  $T_c$  values of the Ni compounds decrease more rapidly than that of the Co compositions, indicating either that the  $Mn^{3+}-O-Mn^{3+}$  exchange in the Ni samples is more sensitive to structural distortion than that in the Co counterparts or that the additional  $Mn^{3+}-O-Ni^{3+}$  exchange present in the Ni compositions is more prone to structural distortion. So, it appears that the ionic size of R has a double impact on the magnetic exchange interactions in  $RMn_{0.5}Ni_{0.5}O_3$ . An anomalous change in the rate of decrease of the magnetic transition temperature with ionic radius, though marginal, is attributable to the contribution from single-ion anisotropy of the heavier rare-earth ions.

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#### References

- [1] Zener C 1951 *Phys. Rev.* **82** 403
- [2] Coey J M D, Viret M and Von Molnar S 1999 *Adv. Phys.* **48** 167
- [3] Cheong S W and Hwang H Y 2000 *Colossal Magnetoresistive Oxides* ed Y Tokura (Singapore: Gordon and Breach) p 237
- [4] Goodenough J B, Wold A, Arnott R J and Menyuk N 1961 *Phys. Rev.* **124** 373
- [5] Blasse G 1965 *J. Phys. Chem. Solids* **26** 1969
- [6] Havinga E E 1966 *Philips Res. Rep.* **21** 435
- [7] Jonker G H 1966 *J. Appl. Phys.* **37** 1424
- [8] Joy P A, Kholam Y B and Date S K 2000 *Phys. Rev. B* **62** 8608
- [9] Joly V L J, Joy P A, Date S K and Gopinath C S 2001 *J. Phys.: Condens. Matter* **13** 649

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- [10] Joly V L J, Joy P A, Date S K and Gopinath C S 2002 *Phys. Rev. B* **65** 184416
- [11] Shannon R D 1976 *Acta Crystallogr. A* **32** 751
- [12] Egami T 2001 *Structure and Bonding* vol 98, ed J B Goodenough (Berlin: Springer) p 115
- [13] Kumar P S A, Joy P A and Date S K 1998 *J. Phys.: Condens. Matter* **10** L487
- [14] Joy P A and Date S K 2000 *J. Magn. Mater.* **218** 229
- [15] Kumar P S A, Joy P A and Date S K 1998 *Solid State Commun.* **108** 67
- [16] Alonso J A, Martinez-Lope M J and Casais M T 2000 *Inorg. Chem.* **39** 917
- [17] Boudreaux E A and Mulay L N 1976 *Theory and Applications of Molecular Paramagnetism* (New York: Wiley-Interscience)
- [18] Blasco J, Ritter C, Garcia J, de Teresa J M, Perez-Cacho J and Ibarra M R 2000 *Phys. Rev. B* **62** 5609
- [19] Cheng F, Liao C, Kuang J, Xu Z, Yan C, Chen L, Zhao H and Liu Z 1999 *J. Appl. Phys.* **85** 2782
- [20] Kahn M L and Zhang Z J 2001 *Appl. Phys. Lett.* **78** 3651