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Investigation of Lattice Effects in Rare Earth Manganites by ¹⁸O-isotope Exchange*

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Abstract

The strong coupling between the electron spin and lattice arising from the Jahn-Teller effect of manganese ions plays an important role in the mechanism of colossal magnetoresistance and related properties of the rare earth manganites. The lattice effects in this class of oxides have been extensively studied through the application of hydrostatic as well as chemical pressures and magnetic fields. The recently observed giant ¹⁸O isotope effect provides direct evidence for the formation of lattice polarons in manganites. Here we report the preliminary results of our investigations on a variety of normal as well as ¹⁸O isotope-exchanged perovskite manganites exhibiting colossal magnetoresistance and charge ordering. The observed isotope shift of T_c as well as that of T_{co} is correlated with the key parameters controlling the lattice such as the Mn³⁺ content, the average ionic radius of the A-site cation $\langle r_A \rangle$, and the A-site ionic size disorder σ^2 .

1. Introduction

Rare earth manganites, $RMnO_3$ (R = rare earth) doped with divalent ions D such as Ca^{2+} , Sr^{2+} , Ba^{2+} as in $R_{1-x}D_xMnO_3$ have been known since the 1950s and exhibit interesting electrical and magnetic properties (Jonker and Van Santen 1950; Wollan and Koehler 1955). Doping of trivalent R ions with divalent D ions gives rise to mixed valence states of Mn^{3+} and Mn^{4+} , introducing holes in the Mn 3d band. A manganite with an optimal hole concentration or Mn⁴⁺ content undergoes a paramagnetic insulator (PI) to ferromagnetic metal (FM) like transition as the temperature is decreased, showing a peak in resistivity at a temperature T_{I-M} close to the ferromagnetic Curie temperature T_c . The simultaneous appearance of ferromagnetism and metal-like conductivity was explained by Zener (1951) through the introduction of a novel double exchange model. According to this model, the conductivity arises due to the hopping of the d-electron from the singly occupied Mn^{3+} eg orbital to the adjacent unoccupied Mn⁴⁺ e_g orbital via an intervening oxygen atom. The carriers preserve their spin orientation during hopping and are strongly coupled to the localised t_{2g} electrons (Hund's coupling J) thereby stabilising the ferromagnetic ground state. The transfer integral t_{ij} of the carriers is sensitive to the angle between the

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adjacent t_{2g} spins (θ_{ij}) and is given by $t_{ij} = t_0 \cos(\theta_{ij}/2)$. Thus t_{ij} is maximised when $\theta_{ij} = 0$ or the Mn–O–Mn bond angle ϕ ($\phi = 180 - \theta_{ij}$) is 180°. The *J* parameter enhances the magnetisation dependence of the resistivity below T_c .

The double exchange model based on t_{ij} and J, however, fails to account for many of the observed properties, including the insulating behaviour in the paramagnetic regime above $T_{\rm c}$ and the recently observed colossal magnetoresistance in manganites. It is also intriguing that unlike the resistivity behaviour below $T_{\rm c}$, which is markedly affected by the A-site doping, the behaviour above $T_{\rm c}$ is largely unaffected. Kusters et al. (1989) have proposed the existence of magnetic polarons, i.e. charge carriers surrounded by magnetic polarisation, above $T_{\rm c}$. De Teresa *et al.* (1997) have recently shown by means of volume thermal expansion, magnetic susceptibility and small-angle neutron scattering experiments that magnetic polarons do exist above T_c . Millis et al. (1995) have suggested that a polaron mechanism due to electron-phonon coupling originating from the dynamic Jahn-Teller (JT) effect (which lifts the degeneracy of the eg orbital of the Mn^{3+} ion) is essential to reduce the itinerant electron kinetic energy at $T_{\rm I-M}$. The electron-phonon coupling constant λ is directly proportional to the Jahn–Teller stabilisation energy and is inversely proportional to the eg electron transfer integral. Millis et al. (1995, 1996) have shown that the metal-insulator transition will occur when λ attains a critical value. A composite polaron consisting of magnetic and JT polarons has also been proposed (Zou et al. 1998).

The prevalence of polarons in manganites is supported by a range of structural as well as non-structural evidence. The structural evidence comes from the lattice distortion associated with the localised charge carriers. Billinge et al. (1996) have found from their pair distribution function (PDF) analysis of the neutron powder diffraction data of $La_{1-x}Ca_xMnO_3$, a local structure change at T_{I-M} due to the isotropic collapse of the oxygen octahedron around Mn^{4+} . These authors have visualised the polarons as a breathing mode distortion of oxygen around manganese. The JT distortion of the planar oxygen atoms leads to a separation of the neighbouring Mn–O bonds by 0.1 Å (above T_c), a value in agreement with the proposition of Millis et al. (1995, 1996) Louca et al. (1997) have showed from their PDF study of neutron diffraction data on $La_{1-x}Sr_xMnO_3$ that JT distortion is present locally in insulating as well as metallic states, and that there is a direct correspondence between the JT distortion and lattice polarons. Booth et al. (1996) have observed an unusual increase in the Debye–Waller parameters of Mn–O and Mn–Mn atom pairs near T_c in La_{1-x}A_xMnO₃ (A = Ca, Pb) for compositions exhibiting the I-M transition. The activated resistivity behaviour above $T_{\rm c}$ and the relatively lower value of the activation energy of the Hall coefficient compared with that of the electrical conductivity provide non-structural evidence for the formation of polarons (Snyder et al. 1996; Jaime et al. 1997).

The presence of polarons narrows down the effective band width $W_{\rm eff}$ according to the relation $W_{\rm eff} \propto W \exp(-\gamma E_{\rm p}/\hbar\omega)$, where $E_{\rm p}$ is the polaron stabilisation energy and ω is the optical phonon frequency. In the perovskite structure of manganites, each oxygen is shared by two manganese atoms and there exists a strong correlation between the Jahn–Teller polarons on neighboring sites. For simplicity, if we consider only nearest-neighbour interactions, $\omega^2 = 2F/M$ $(1-\cos ka)$, where F is the force constant of the classical oscillators with wavevector k, and M is the mass of atoms separated by a distance a. Hence ω depends on the lattice vibrations and is inversely proportional to the square root of the atomic mass, while $E_{\rm p}$ is related to F by $E_{\rm p} = g^2/F$, where g is the electron-phonon coupling strength (Millis et al. 1996). Thus it becomes evident that the polaron stabilisation energy depends on the phonon frequency and, in turn, the atomic mass. Here γ is a dimensionless factor and varies proportionally with $E_{\rm p}/W$. In the strong coupling limit, where J exceeds $W_{\rm eff}$, it can be shown that $T_{\rm c} \propto W_{\rm eff}$. Thus any perturbation in the lattice vibrations should affect $T_{\rm c}$. This has been demonstrated by Zhao *et al.* (1996) in the giant isotope shift of T_c $[T_{\rm c}(^{16}{\rm O}) - T_{\rm c}(^{18}{\rm O})]$. Here $T_{\rm c}$ was found to be lowered by more than 20 K when 16 O was replaced with 18 O in La_{0.8}Ca_{0.2}MnO₃, while the effect was negligible in a similar ferromagnetic perovskite oxide SrRu_{O3} with no JT effect, suggesting the presence of JT polarons in the former. The $W_{\rm eff}$ and hence $T_{\rm c}$ and related properties are also affected by the various factors (see Rao et al. 1996 for a review) responsible for lattice effects in manganites, such as hydrostatic pressure, magnetic field, Mn^{4+} content, average ionic radius of the A-site cation $\langle r_A \rangle$ and A-site ionic size disorder σ^2 . The incorporation of ¹⁸O in manganites therefore provides an effective means to systematically study the lattice effects. In this study, we have investigated a variety of normal and ¹⁸O-exchanged manganites exhibiting colossal magnetoresistance as well as charge ordering, and have tried to correlate the observed isotope shifts with the Mn³⁺ content, $\langle r_A \rangle$ and σ^2 .

2. Mn³⁺ Content and Giant Oxygen Isotope Effect

The seminal role of the Mn^{4+} content in determining the structure, magnetic and magnetoresistive properties of perovskite manganites has been clearly brought out by the investigations of undoped LaMnO₃ by Mahendiran *et al.* (1996). With increasing Mn^{4+} content, LaMnO₃ undergoes structural transitions from orthorhombic \rightarrow rhombohedral \rightarrow pseudocubic. (The formation of Mn^{4+} in the undoped LaMnO₃ could be imagined to be due to the creation of vacancies in the La as well as Mn sites keeping the oxygen content unaffected.) While both rhombohedral and pseudocubic LaMnO₃ show higher T_c and magnetoresistance, the orthorhombic phase, with relatively lower Mn⁴⁺ content, remains an antiferromagnetic insulator with very low magnetoresistance.

To explore the relationship between Mn^{3+} content (here we use Mn^{3+} instead of Mn^{4+} to highlight the JT effect in the former) and the oxygen isotope effect, we have investigated $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ compositions with x varying from $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ is an ideal system for such a study as La and Ca have nearly the same ionic radius. This rules out contributions from $\langle r_A \rangle$ and σ^2 . In addition, the orthorhombic symmetry is retained over the entire range of solid solution compositions (Cheong and Hwang 1999).

In a typical experiment we have four samples: the as-prepared, ¹⁶O heated, ¹⁸O exchanged and ¹⁸O \rightarrow ¹⁶O back-exchanged. The as-prepared samples are polycrystalline powders obtained by the conventional ceramic method, which are further subjected to ¹⁶O, ¹⁸O and back exchange. The details of the sample preparation are described elsewhere (Mahesh *et al.* 1995). The average isotope exchange rate is 85±5% and the back-exchange rate is 90±5% as determined from the weight change. Electrical resistivity measurements were carried out on various samples using the standard four-probe method, and magnetisation measurements were done using a Quantum Design MPMS magnetometer. The magnetisation



Fig. 1. Temperature dependence of (a) $\log \rho$ and $d \log \rho / d T^{-1}$ of $La_{0.9}Ca_{0.1}MnO_3$ (¹⁶O), and (b) magnetic susceptibility of ¹⁶O and ¹⁸O $La_{0.9}Ca_{0.1}MnO_3$ samples.

data were recorded on warming after the samples were cooled to 5 K in zero field. The results obtained with the back-exchanged samples have ensured the reversibility of the isotope exchange process.

In Fig. 1*a* we show the temperature variation of the resistivity of a ¹⁶O sample of La_{0.9}Ca_{0.1}MnO₃. The sample is insulating down to 50 K (the lowest temperature down to which measurements were carried out as the the sample became more resistive). It can be seen from the dlog ρ /d T^{-1} plot that this sample undergoes two successive transitions: (1) paramagnetic insulator \rightarrow ferromagnetic insulator around 145 K, and (2) ferromagnetic insulator \rightarrow charge-ordered insulator around 70 K, in agreement with the report of Cheong and Hwang (1999). The charge-ordered state of this sample is very weak, such that a magnetic field as low as 100 Oe is just sufficient to melt it. Hence the measurements were carried out at a very low applied field of 5 Oe. In Fig. 1*b* the magnetisation data of ¹⁶O and ¹⁸O samples are given. The T_c of the ¹⁸O sample is suppressed by 27 K. Zhou and Goodenough (1998) have shown that this remarkable suppression of T_c by ¹⁸O substitution is due to the mass-dependent trapping of mobile polarons above T_c . In Fig. 2 we plot the isotope shift of T_c obtained from the magnetisation data as a function of Mn³⁺ content. The isotope shift of T_c increases monotonically with Mn³⁺. It is to be noted that in La_{1-x}Ca_xMnO₃, T_c decreases with increasing

 $\rm Mn^{3+}$ content in the composition range studied here. As $T_{\rm c}$ increases, the isotope shift of $T_{\rm c}$ decreases. A higher $T_{\rm c}$ corresponds to a higher $W_{\rm eff}$, which in turn corresponds to weaker lattice–spin coupling. A larger isotope shift of $T_{\rm c}$ thus implies a stronger lattice–spin interaction. This could arise partly from the increase in magnitude of the JT effect with increasing $\rm Mn^{3+}$ content.



Fig. 2. Variation of the oxygen isotope shift of ferromagnetic Curie temperature T_c with Mn³⁺ content.

3. Critical Role of $\langle r_A \rangle$

The Mn–O–Mn angle ϕ , and hence the eg electron transfer integral t_{ij} , is markedly influenced by the size of the doping ion at the A-site (Mahesh *et al.* 1995; Hwang *et al.* 1995). The Mn–O–Mn angle decreases with decreasing average ionic radius of the A-site cation $\langle r_A \rangle$, resulting in the rotation of the MnO₆ octahedra to relieve the associated strain of the lattice. The effects of $\langle r_A \rangle$ on the properties of the manganites have been extensively reported in the literature. Generally speaking, with decreasing $\langle r_A \rangle$, T_c decreases while resistivity and magnetoresistance increase dramatically. Thus $\langle r_A \rangle$ provides an important chemically tunable parameter in manganites. Zhao *et al.* (1996) have shown that the oxygen isotope exponent α_0 (defined as $-d\ln T_c/d\ln M$, where M is the mass of the oxygen isotope) increases drastically with decreasing $\langle r_A \rangle$. In other words, the isotope shift of T_c decreases with increasing $\langle r_A \rangle$ or larger eg band width.

Decreasing $\langle r_A \rangle$ in manganites suppresses ferromagnetism and enhances the charge ordering instability. We have investigated the variation of the oxygen isotope shift of $T_{\rm co}$ (the charge ordering temperature) with $\langle r_A \rangle$. For this purpose, we have carried out isotope exchange in the well-known charge-ordered manganites Nd_{0.5}Sr_{0.5}MnO₃, La_{0.5}Ca_{0.5}MnO₃ and Pr_{0.5}Ca_{0.5}MnO₃, having $\langle r_A \rangle$ of 1·236, 1·198 and 1·179 Å respectively. In Fig. 3 we show the resistivity and magnetisation data of ¹⁶O, ¹⁸O and back-exchanged (¹⁸O \rightarrow ¹⁶O) samples of Nd_{0.5}Sr_{0.5}MnO₃. The charge ordering transition temperature is enhanced by 21 K. It is to be noted that T_c did not show any appreciable change, as is

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Fig. 3. Temperature dependence of (a) resistivity and (b) magnetic susceptibility of ¹⁶O, ¹⁸O and back-exchanged (¹⁸O \rightarrow ¹⁶O) samples of Nd_{0.5}Sr_{0.5}MnO₃.

expected of manganites with larger $\langle r_{\rm A} \rangle$. The increment in $T_{\rm co}$ may be due to the mass-enhanced localisation of charge carriers above $T_{\rm co}$. However, the actual mechanism of isotope enhancement of $T_{\rm co}$ is yet to be understood. In the case of $\Pr_{0.5}\operatorname{Ca}_{0.5}\operatorname{MnO}_3$, with its very small $\langle r_{\rm A} \rangle$ (see Fig. 4), the isotope shift of $T_{\rm co}$ is negligibly small. This may be due to the unusual stability of the charge-ordered state in the low- $\langle r_{\rm A} \rangle$ regime and the low mobility of carriers above $T_{\rm co}$. The isotope shift of $T_{\rm co}$ is appreciable only in manganites with relatively large $\langle r_{\rm A} \rangle$. At this point it is worth mentioning the report of Garcia-Landa *et al.* (1998), who have found that to melt charge ordering in $\Pr_{2/3}\operatorname{Ca}_{1/3}\operatorname{MnO}_3$, a magnetic field of 12 T is required for an ¹⁸O sample compared to 6 T in the case of a ¹⁶O sample, although there was no isotope shift of $T_{\rm co}$. The absence of an isotope shift of the transition temperature therefore does not necessarily mean the absence of an isotope effect.

4. A-site Size Disorder Effects

Undoped rare earth manganites are antiferromagnetic insulators. The rich variety of fascinating properties of manganites observed to date arises from doping. Doping by aliovalent ions at the A-site creates not only mixed Mn valency but also significant disorder at the A-site due to the differences in size of the rare



Fig. 4. Variation of oxygen isotope shift of charge ordering temperature $T_{\rm co}$ with average ionic radius of the A-site cation $\langle r_{\rm A} \rangle$.



Fig. 5. Variation of $T_{\rm c}$ ($T_{\rm I-M}$) with A-site disorder parameter σ^2 for manganites with fixed Mn³⁺ contents of 70% (adapted from Rodriguez-Martinez *et al.* 1996).

earth and dopant ions. The manifestation of the size disorder effects on the physical properties is primarily due to the displacement of oxygen atoms from their ideal crystallographic positions, the oxygen being an integral part of the Mn–O–Mn exchange interactions.

Rodriguez-Martinez and Attfield (1996) have quantified the A-site size disorder, making use of the variance of the A-site cation radius distribution σ^2 given by

 $\Sigma x_i r_i^2 - \langle r_A \rangle^2$, where $x_i (\Sigma x_i = 1)$ represents the fractional occupancy of ions of radius r_i , and $\langle r_A \rangle$ is the average ionic radius of the A-site cation as described earlier. The variation of T_c and T_{I-M} for a number of manganites with fixed Mn⁴⁺ contents of 30% and $\langle r_A \rangle$ of 1.23 Å, as obtained by these authors, is given in Fig. 5. Both T_c and T_{I-M} decrease rather steeply with increasing σ^2 .

in Fig. 5. Both T_c and T_{I-M} decrease rather steeply with increasing σ^2 . We have explored the effect of σ^2 on the isotope shift of T_c as well as T_{co} . La_{0.7}Ca_{0.3}MnO₃ ($\langle r_A \rangle = 1.205$ Å, $\sigma^2 = 2.7 \times 10^{-4}$ Å²) and Nd_{0.7}Sr_{0.3}MnO₃ ($\langle r_A \rangle = 1.207$ Å, $\sigma^2 = 4.5 \times 10^{-3}$ Å²) with nearly the same $\langle r_A \rangle$ and carrier concentration but with different σ^2 were subjected to isotope exchange. The resistivity data of the ¹⁶O and ¹⁸O samples are shown in Fig. 6. La_{0.7}Ca_{0.3}MnO₃, with its relatively smaller σ^2 , shows higher T_c , but the isotope shift of T_c (13 K) is smaller compared with that of Nd_{0.7}Sr_{0.3}MnO₃, which shows a lower T_c but a larger shift of 32 K. A higher σ^2 implies a larger distortion of the lattice and stronger coupling. To investigate the effect of σ^2 on the shift of T_{co} we have carried out isotope exchange on La_{0.5}(Ca,Sr)_{0.5}MnO₃ with $\langle r_A \rangle$ (1·236 Å) the same as that of the well-known charge-ordered manganite Nd_{0.5}Sr_{0.5}MnO₃. The σ^2 value for the former is $2 \cdot 4 \times 10^{-3}$ Å²; for the latter it is $5 \cdot 4 \times 10^{-3}$ Å. La_{0.5}(Ca,Sr)_{0.5}MnO₃, with smaller σ^2 , shows smaller isotope shift of T_{co} of 16 K (see Fig. 7) as against 21 K (see Fig. 3) for Nd_{0.5}Sr_{0.5}MnO₃.



Fig. 6. Temperature dependence of resisitivity of ^{16}O and ^{18}O samples of La_{0.7}Ca_{0.3}MnO₃ and Nd_{0.7}Sr_{0.3}MnO₃, showing the extent of the oxygen isotope shift.

It is worth while at this point to reinvestigate the additional effect of σ^2 on the isotope shift of $T_{\rm co}$ in the charge-ordered manganites discussed in Section 3. Apart from $\langle r_{\rm A} \rangle$, σ^2 also decreases in the order Nd_{0.5}Sr_{0.5}MnO₃ > La_{0.5}Ca_{0.5}MnO₃ > Pr_{0.5}Ca_{0.5}MnO₃ (see Table 1). Since the manganites with smaller σ^2 also exhibit smaller isotope shifts of $T_{\rm co}$, the isolation of the independent effect of decreasing $\langle r_{\rm A} \rangle$ is rather difficult in this case. We believe that the observed shift of $T_{\rm co}$ in these manganites is due to the combined effects of $\langle r_{\rm A} \rangle$ and σ^2 , both being in the same direction.



Fig. 7. Temperature dependence of magnetic susceptibility of ${\rm ^{16}O}$ and ${\rm ^{18}O}$ samples of La_{0.5}(Ca,Sr)_{0.5}MnO₃.

Table 1. Values of $\langle r_A \rangle$, σ^2 , Mn^{3+} content, T_{co} and ΔT_{co} of various charge-ordered manganates

A-site composition	$\langle r_{\rm A} \rangle$ (Å)	σ^2 (Å ²)	${\rm Mn}^{3+}$ (%)	$T_{\rm co}$ (K)	$\Delta T_{\rm co}$ (K)
Pr _{0.5} Ca _{0.5}	$1 \cdot 179$	2.5×10^{-7}	50	230	3
$La_{0.5}Ca_{0.5}$	$1 \cdot 198$	3.2×10^{-4}	50	180	16
$Nd_{0.5}Sr_{0.5}$	$1 \cdot 236$	5.4×10^{-3}	50	160	21
$\mathrm{La}_{0.5}(\mathrm{Ca,Sr})_{0.5}$	1.236	$2 \cdot 4 \times 10^{-3}$	50	180	16

5. Conclusions

The oxygen isotope shift of T_c and T_{co} in perovskite manganites shows systematic dependences on the Mn³⁺ content, $\langle r_A \rangle$ and σ^2 , and hence provide an *in situ* probe with which to study the lattice–spin coupling. The isotope shift of T_c increases with the content of the Jahn–Teller-active Mn³⁺ ion. For fixed Mn³⁺ content and $\langle r_A \rangle$, an enhanced shift of T_c is observed with increasing σ^2 . We find that the isotope shift of T_{co} increases with $\langle r_A \rangle$. For given Mn³⁺ content and $\langle r_A \rangle$, an increased isotope shift of T_{co} is found with increasing σ^2 . A dominant isotope shift of T_c as well as T_{co} is observed in the intermediate range of $\langle r_A \rangle$.

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