On O^{16}–O^{18} Isotope Effects in Manganese Perovskites

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Abstract. Large isotope effects which have been found by others [1,2] in some colossal magneto resistance manganite perovskites, $AMnO_3$, are evidence of unusually strong interactions between the lattice and magnetism. We offer a model which is based upon the approximate degeneracy of two Mn^{+3} states: one with high spin $S = 2$, and the other with low spin $S = 1$. These states have different radii and different electron form factors. They thus have different force constants governing the interaction with neighboring oxygen ions which provide the sought for link between magnetism and oxygen mass. The experiments can be understood with the reasonable assumption that the LS has greater force constants than HS. The dependence of changes in T_c with isotopic substitution as a function of the A-ion radius, the metal insulator transitions and the Mossbauer effect changes, are discussed in terms of this model.

Keywords: isotope, magnetic manganite structures, spin states

Introduction

Revealing the underlying mechanisms for abnormally large changes observed under isotopic O^{16}–O^{18} exchange in some compositions of manganite perovskite structures is a major challenge. The increase in the Curie temperature, T_c, described by the coefficient $\alpha_{T_c} = \ln T_c / d \ln M$ attains values of 4 or more [2] in contrast to changes in phonon frequencies which are an order of magnitude less. Exchange of O^{16} by O^{18} can convert a ferromagnetic metal into a non-magnetic insulator [2]. None of the existing models we are aware of offer satisfactory explanations.

We present a new model that has the potential for doing so. This model is based upon a near degeneracy of two crystal field states of the octahedrally-coordinated Mn^{+3} ion. The first is the usual high-spin (HS) spin $S = 2$ state which has been used as the basis state in all models to date. The second is the low spin, $S = 1$, (LS) configuration. Previous analyses all seem to have ruled the latter out on the basis of the configuration in the free ion and in the undoped $LaMnO_3$ (where the structure indicates an orbitally ordered, Jahn-Teller-split HS state) [3]. In the doped $Mn^{+3} - Mn^{+4}$ disordered systems we argue that things

are quite different and there can be a significant contribution from the $S = 1$ state. While in the present paper we are restricting the discussion to isotopic properties, our model provides explanations for much of the unusual behavior exhibited by these oxides.

We first show from simple physico-chemical considerations why the LS configuration should not be ruled out. We then argue that the relative proportions of HS/LS in the Mn^{+3} state can be altered by changing the mass of the surrounding octahedra of oxygen ions. It then follows that the substitution of O^{18} for O^{16} favors the LS configuration. The fact that the LS configuration is more localized than the HS leads to a qualitative understanding of the isotope effects. While we have not attempted to obtain quantitative agreement with the measured isotopic shifts, simple arguments indicate that the magnitudes expected from the model are reasonable.

Near Degeneracy of High Spin-Low Spin States

In vacuum, the ground state for Mn^{+3} is the high spin (HS) state (Hund's rule). However, in an octahedral

crystal field *in a lattice*, the energy difference between the configurations $t_3(\uparrow\uparrow\uparrow)e_1(\uparrow)$ and $t_4(\uparrow\uparrow\uparrow\downarrow)$ states, which we write as

$$E(HS) - E(LS) = -(\vartheta - \Delta) \qquad (1)$$

can be small. Here ϑ is the level splitting due to the Hund interaction; Δ is the difference in the crystal field shifts of the LS and HS configurations. Spectroscopic optical data give a value for ϑ for free Mn^{+3} in the range of 20,000 to 25,000 cm^{-1} [4]; Δ for Mn^{+3} oxides is about 19,000 cm^{-1} [5]. A reasonable estimate for the energy difference of the states Eq. (1) is thus in the range of 1000 to 6000 cm^{-1}, and not enough to exclude the presence of significant contribution of LS.[1] In the doped CMR materials more factors come into play. Consider for example $La_{0.67}Ca_{0.33}MnO_3$, the prototypical CMR material, where the Mn is mixed valent, $1/3 Mn^{+4}$ and $2/3 Mn^{+3}$. Due to the greater mean charge on the Mn, and the significantly smaller radius of Mn^{+4}, the Coulomb, or chemical, pressure on neighboring Mn^{+3} is greater than in undoped $LaMnO_3$. This increased pressure favors the LS state because Mn^{+3} (LS) has a smaller radius (0.72 A) than Mn^{+3} (HS)(0.79 A). Furthermore the heterovalent lattice is actually a distorted ($GdFeO_3$) lattice. The large dispersion of the equilibrium lattice positions can be expected to favor LS population even more than in the undistorted lattice. Therefore we find it quite reasonable to assume that the Mn^{+3} site has a finite component of LS.

The compelling motivation for making this assumption is to introduce a rationale for the isotope results. Due to the smaller Mn^{+3} (LS) radius and the change in form of the electron cloud,[2] the oxygen ligands are closer and penetrate more deeply (Fig. 1) than for the HS. Vibrational force constants which depend upon the second derivative of energy with displacement, can be large. For ionic crystals where the overlap energy depends upon distance d as $d^{-n}, n \sim 10$, the fractional change in force constant change can be roughly two orders of magnitude greater than the fractional change in distance $(\Delta f/f \sim n^2 \Delta d/d)$. For the HS-LS where $\Delta d = 0.07\,A, d_{Mn-O} = 2\,\mathring{A}$, and $\Delta d/d = 3.5\%, \Delta f/f$ is roughly 300%. Consequently the characteristic phonon frequencies can be expected to shift almost a factor of 2 when HS converts to LS. The shift should even be larger for transverse modes because the form

factor of the LS electron cloud (Fig. 1) results in even stiffer modes.

Isotope Effects

Let us now turn to the different isotope effects which have been found to have strikingly large values at selected compositions. Zhao, Keller, Greene, and Müller review the data [2]. It is reassuring that the isotopic changes are reversible with back and forth exchanges of O^{16} and O^{18}. Among the observations to be accounted for upon the replacement of O^{16} by O^{18} are: (1) the decrease of T_c empirically described by the exponent α which increases from 0.07 to about 4 with decreasing T_c; (2) the dependence of α on $R\langle A\rangle$, the average radius of the ions on the A site, and its further dependence on the dispersion of R; (3) the metal-insulator transition at low temperatures evidenced by a resistance increase of more than 6 orders of magnitude; (4) strikingly different dependencies of the magnetization upon field and temperature; and (5) the increase of the charge ordering temperature, T_{co}.

The model we propose explains the above effects with two assumptions. Further, we think that other puzzling results in the literature can also be better understood using the same model.

Our model assumes: (1) The absolute value of the energy decrease of the LS state upon O^{18} exchange is greater than the corresponding decrease in the HS state as sketched in Fig. 2; (2) the LS is a shorter range and more localized state than HS.

These are reasonable assumptions in view of the arguments given in the preceding paragraphs. (1) Follows simply from the observation that the LS modes involving oxygen vibrations are stiffer than the corresponding HS modes as illustrated in Fig. 2; (2) is self-evident from the fact that the HS state e orbitals are more extended than the t orbitals belonging to the LS state.

The five isotope effects enumerated above are now understandable. Briefly, O^{18} increases the population of LS relative to HS because of the shifts in phonon frequencies, Fig. 2. Thus substituting O^{18} for O^{16} always increases localization. Increased localization of course favors the insulating state and thus lowers T_c, raises T_{co}, lowers the temperature of the metal-insulator transition, and accounts for the observed magnetic behavior. The empirically observed behavior of α with T_c depends upon the amplitudes of HS
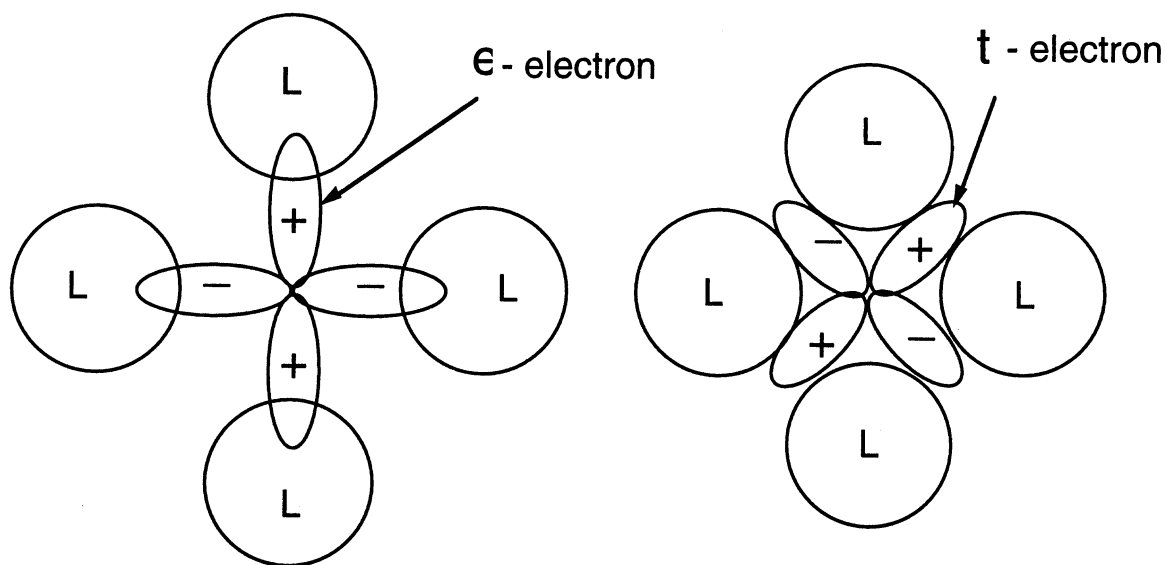
Fig. 1. e and t orbitals configurations in xy plane. The radii of $LS = 0.72\,\mathring{A}$ and $HS = 0.79\,\mathring{A}$ are from R. D. Shannon [*Acta Cryst.* **A32**, 751 (1976)].

and LS on the Mn^{+3} sites, which in turn depend upon the distortion. Thus the increase in α with decreasing T_c follows qualitatively simply from the fact that with decreasing T_c there is a greater lattice distortion. The exact same reasoning holds for the related dependence of T_c upon $R\langle A \rangle$.

While we have not attempted to develop this model quantitatively, a simple harmonic model suggests that the energetics are not out of line. Associated with each Mn ion there are nine oxygen degrees of freedom.

Thus, $\Delta E(O^{18} - O^{16}) \sim 9\,\hbar\omega/2 \times \Delta M/2M = 1/4\,\hbar\omega$ for $\Delta M/M = 1/9$. Oxygen vibrations are typically in the range of 300 to 600 K. Thus ΔE can be of the order of 100 K per unit cell which is sufficient to result in significant change in the LS/HS populations whenever the assumption about the near degeneracy of HS and LS is valid.

A recent investigation of the effect of isotopic exchange upon Mossbauer spectra [6] has found novel behavior which can also be explained by the HS/LS
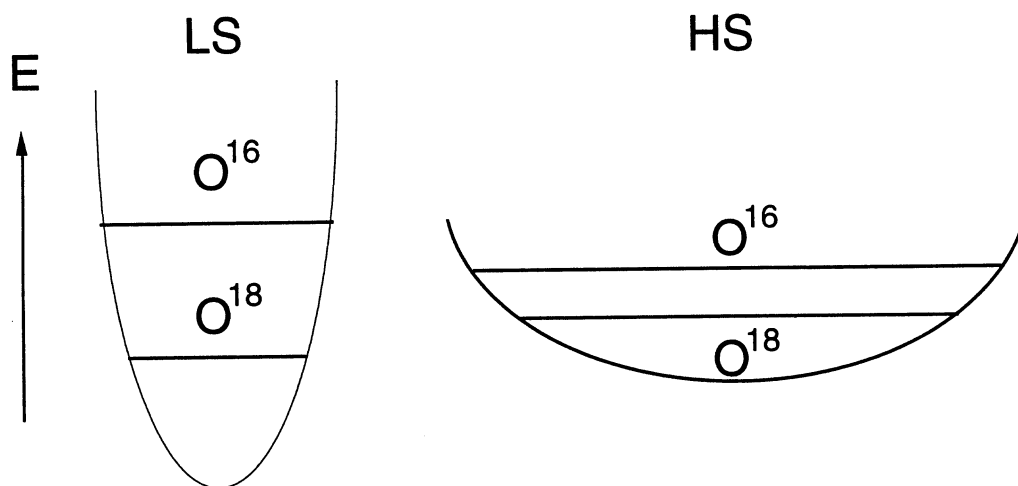

Fig. 2. Schematic representation of the vibrational levels of O^{16} and O^{18} in their relative positions at the specific composition where the metal-insulator transition is induced by isotopic substitution.

model. They find that exchange of O^{16} by O^{18} leads to a decreasing recoil free part of the spectra. The amplitude of the oscillation of the Co(Fe) probe atom in the O^{18} sample is thus greater than in the O^{16}. As we have discussed above, the LS contribution increases in the O^{18} leading to a decrease in the Mn-O bond length and consequently to the observed increase in the Co(Fe)-O distance in the Mn-O-Co chain. This should lead to a decrease in the force constant governing Co modes and thus to the observed increase in oscillation. The fact that the effective field on the Fe^{57} nucleus is changed a relatively small amount [6] is understandable because there is already a big hyperfine field at the nucleus from the core electron spins, and further, as we have argued above, the force constants are much more sensitive to LS/HS changes than other properties.

Conclusions

In this short paper we have concentrated upon discussing the isotope effects. The existing models in the literature are inadequate because they have no simple way of relating changes in mass and changes in spin. We were originally led to consider the HS/LS model as a way of accounting for the reduced saturation moments found in the $LaCaMnO_3$ series by Snyder [7] and then found that some of the other unusual effects could also be better understood. The model we have proposed puts forward an additional idea which actually does not preclude much of the physics of previous models. Without the isotope experiments it would require more quantitative investigations to distinguish between models. However with the advent of the isotope results we find compelling evidence for the LS/HS idea we have proposed. There remains much work to do to see how well our model can explain the isotope and the other effects in quantitative terms.

Acknowledgments

Notes

1. In fact, the octahedral field spitting can even be greater than the exchange, for example as in the $Mn^{+3}(CN)_6^{-1}$ complex LS, ref. 4, p. 706.
2. The importance of the shape of the electron cloud is clearly evident when comparing rates of exchange of ligands with transition metal ions in aqueous solution, Ref. 4, p. 1288–89. Ions which have only t electrons, especially t^3 and t^6 ions, exchange ligands (water molecules) much more slowly than other ions. For example, compare two pairs with the same charges and radii: $Cr^{+3}(t^3, R = 0.76\,\text{Å})$ vs. $V^{+3}(t^2, R = 0.78\,\text{Å})$ and $Cr^{+2}(t^3e, R = 0.94\,\text{Å})$ vs. $V^{+2}(t^3, R = 0.93\,\text{Å})$. For the first pair, exchange rates are $\tau^{-1} \sim 10^{-6}\text{sec}^{-1}$ for Cr^{+3} vs. $\tau^{-1} \sim 10^3\text{sec}^{-1}$ for V^{+3}. For the second pair $\tau^{-1} \sim 10^9$ for Cr^{+2} vs. $\tau^{-1} \sim 10^2$ for V^{+2}.

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