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Formation and relaxation energies of electronic holes in $LaMnO_3$ crystal

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Abstract

We use the Mott–Littleton approach to evaluate the electronic and ionic polarisation energies in $LaMnO_3$ lattice associated with holes localised on both Mn^{3+} cation and O^{2-} anion. The full lattice relaxation energy for a hole localised at the O-site is estimated as 2.4 eV which is appreciably greater than that of 0.8 eV for a hole localised at the Mn-site, indicating the strong electron–phonon interaction in the former case. The calculated thermal energies of the hole formation predict that the electronic hole is marginally more stable in the Mn^{4+} state in $LaMnO_3$ host lattice, but the energy of a hole in the O^- state is only higher by a small amount, rather suggesting that both possibilities should be treated seriously. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Colossal magnetoresistance (CMR); Localised holes; Polaron key energies

The striking behaviour of CMR oxides of $R_{1-x}A_xMnO_3$ arises from the inter-play of several distinct energy terms: magnetic interactions, electronic band structure energies, crystal field splittings, vibrational energies and electron lattice coupling, including small polaron ideas and the Jahn–Teller (JT) effect. Understanding this behaviour has helped greatly by the use of models to map the various regimes of behaviour [1]. The experimental evidence [2] suggests that manganites are doped charge-transfer insulators having O(2p) holes as the current carriers rather than Mn^{3+} (3d) electrons. However, whether holes reside at O- and/or Mn-sites is still a subject of controversy. Using the shell model Mott–Littleton calculations, we address some of the issues in physics of CMR systems for which the polarisation energies are crucial. First, we calculate the electronic and ionic polarisation energies due to holes localised on Mn^{3+} and O^{2-} ions in order to estimate the key polaron energies. Second, we examine the controversial question as to whether holes reside at Mn- or O-sites in non-stoichiometric or slightly doped "parent" $LaMnO_3$ compound.

Aiming at estimating the key polarisation energies associated with polaron-type charge carriers in high-temperature insulating quasicubic phase of the CMR lattices, we perform the shell model calculations for the cubic perovskite $LaMnO_3$ crystal. The short-range potentials used for the shell–shell (oxygen–oxygen) and core–shell (metal–oxygen) interactions are of the Buckingham form

$$V_{ij} = A_{ij} \exp(-r/\rho_{ij}) - C_{ij}/r^6. \quad (1)$$

The Buckingham parameters for the shell–shell O^{2-}: O^{2-}, core–shell Mn^{3+}: O^{2-} and La^{3+}: O^{2-} interactions were fitted in this work using the experimental data including the lattice parameter, the dielectric constants, and the frequencies of the transverse optical phonons in the $LaMnO_3$ crystal. The oxygen shell charge $Y(|e|)$ was taken as $-2.48\ |e|$ and the shell-core spring constant k was chosen to give the correct value of the static dielectric constant ε_0 (Table 1). The calculated and experimental properties of $LaMnO_3$ (Pm3m) are summarised in Table 2. We apply then the shell model

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Table 1
Parameters for short-range potentials in $LaMnO_3$ (Pm3m); $r_{cutoff} = 20$ Å

	A (eV)	ρ (Å)	C (eV Å $^{-6}$)	$Y(\|e\|)$	k (eV Å $^{-2}$)
La^{3+}: O^{2-}	1516.3	0.3639	0.00		
Mn^{3+}: O^{2-}	1235.9	0.31525	0.00		
O^{2-}: O^{2-}	22 764.3	0.1490	20.37	−2.48	16.8

Table 2
Crystal properties of $LaMnO_3$ (Pm3m) calculated using the shell model potentials (Table 1) and compared with the experimental data

	Lattice const., a_0 (Å)	Cohesive energy, E_{lat} (eV)	ε_0	ε_∞	ω_{TO_1}	ω_{TO_2}	ω_{TO_3}
					(cm^{-1})		
Exp.	3.889		18±2	4.9	172	360	560
Calc.	3.889	−140.52	15.6	4.9	172	308	513

Table 3
Formation and polarisation energies for localised holes in $LaMnO_3$

α-hole	E_h^α(opt)	E_h^α(th)	$I^\alpha(E_{IV}^\alpha)$	S_{opt}^α	S_{th}^α	U_M^α	R_{opt}^α	ΔR_{th}^α	E_{PES}^α
Mn^{4+}	2.56	1.73	47.41 (51.20)	−44.85	−45.68	−38.3	−6.55	−0.83	1.2
O^-	4.86	2.48	−13.91	18.77	16.39	22.1	−3.33	−2.38	3.5
La^{4+}	18.36	17.63	49.45 (49.45)	−31.09	−31.82	−27.4	−3.68	−0.73	17.0

parameters elaborated to estimate the key electronic defect energies using the well-known Mott–Littleton method. We study the possible hole localisation (self-trapping) [3] on Mn^{3+} and O^{2-} ions in the $LaMnO_3$ crystal. The process of the hole formation can be generally seen as the ionisation of the *in-crystal* ion with an electron being taken out of the crystal and put on the vacuum level. The energy required in this process (hole formation energy, E_h^α, $\alpha = $ Mn, O, La) is the work done against the *in-crystal* ionic core potential, I^α, and the crystalline electrostatic potential, U_M^α, less the energy gain due to the lattice polarisation effects, R^α

$$E_h^\alpha = I^\alpha + U_M^\alpha + R^\alpha. \quad (2)$$

It is useful to distinguish the 'electronic' and 'ionic' terms in the polarisation energy. The former term, which we will call R_{opt}^α, is due to the 'electronic' polarisation of ions by the momentarily localised hole, which in our method is represented by the displacements of shells with respect to the cores which are fixed at their perfect crystal positions. It takes into account the lattice response after e.g. Franck–Condon photoionisation. The lattice distortion term due to displacements of cores and related adjustment of shells after complete lattice relaxation, denoted as ΔR_{th}^α, is the difference between the full polarisation energy, R^α, and the R_{opt}^α

$$\Delta R_{th}^\alpha = R^\alpha - R_{opt}^\alpha. \quad (3)$$

It represents the hole relaxation energy. If this energy exceeds the localisation energy, i.e. the kinetic energy rise due to complete hole localisation on this site, then one can talk about the hole being self-trapped on this site. Given this assumption, Eq. (2) takes the form

$$E_h^\alpha = I^\alpha + U_M^\alpha + R_{opt}^\alpha + \Delta R_{th}^\alpha. \quad (4)$$

The shell-model Mott–Littleton calculations give the cumulative energy of the second and third term, S_{opt}^α, or of the last three terms, S_{th}^α, in Eq. (4) depending on whether both shells and cores or shells only were allowed to relax. The values of S_{opt}^α, S_{th}^α and the calculated terms of U_M^α, R_{opt}^α, and ΔR_{th}^α are summarised in Table 3. It follows from these calculations that there is a large difference in the lattice relaxation energies for O^- and Mn^{4+} holes. The lattice relaxation energy, $-\Delta R_{th}^\alpha$, caused by the hole localisation at the O-site (2.38 eV) appears to be significantly larger than that for the hole localised at the Mn-site (0.83 eV). This result is indicative of the strong electron–phonon interaction in the case of the hole localised at the O-site and could suggest that the hole trapping is more preferential in the oxygen sublattice. However, the width of the Mn(3d) subband in the density of states, which determines the hole localisation energy, is much narrower than that of the O(2p) related subband [4]. Therefore, without a much fuller electronic structure calculation of the localisation energy it is impossible to finally conclude in which sublattice the holes could be localised.

In order to evaluate the hole formation energy, we need to estimate the values of the unknown *in-crystal* ionisation energies, I^{α}. We estimated the ionisation potentials from the experimental photoemission spectroscopy (PES) data, assuming that calculated optical energies of the hole formation could be juxtaposed with experimental PES binding energies, $E^{\alpha}_{\mathrm{PES}}$. The optical and thermal energies of hole formation, $E^{\alpha}_{\mathrm{h}}(\mathrm{opt})$ and $E^{\alpha}_{\mathrm{h}}(\mathrm{th})$, are calculated using these effective values of the *in-crystal* ionisation energies and presented in Table 3 (the free-metal ionisation potentials are given for comparison in brackets). Taking into account the CF splitting effect we have found out that the electronic hole is marginally more stable at the Mn-site than at the O-site in the $LaMnO_3$ lattice, but the energy difference between the thermal energies of the hole formation, $E^{\alpha}_{\mathrm{h}}(\mathrm{th})$, is too small (0.75 eV). This result rather suggests that both possibilities should be treated seriously. Providing the balance between the localisation and relaxation energies favours the possibilities for the hole self-trapping at the Mn- and O-sites, the electronic hole in $LaMnO_3$ will be likely localised on the manganese, or on both oxygen anion and transition metal cation, rather than on the oxygen ion alone.

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References

[1] A.J. Millis, R. Mueller, B.I. Shraiman, Phys. Rev. B 54 (1996) 5405.
[2] H.L. Ju, H.-C. Sohn, Kannan M. Krishnan, Phys. Rev. Lett. 79 (1997) 3230.
[3] A.L. Shluger, A.M. Stoneham, J. Phys.: Condens. Matter 5 (1993) 3049.
[4] W.E. Pickett, D.J. Singh, Phys. Rev. B 53 (1996) 1146.