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Physica B 312–313 (2002) 737–739

PHYSICA B

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Optical transitions in non-stoichiometric $LaMnO_3$ identifying the charge-transfer transitions

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Abstract

Using the Mott–Littleton approach we examine the energies of a number of fundamental optical transitions, as well as those involving self-trapped holes of Mn^{4+} and O^- in $LaMnO_3$ lattice. The reasonable agreement with the experiment of our predicted energies, linewidths and oscillator strengths leads us to plausible assignments of the optical bands observed. We deduce that the optical band near 5 eV is associated with O(2p)–Mn(3d) transition of charge-transfer character, whereas the band near 2.3 eV is rather associated with the presence of Mn^{4+} and/or O^- self-trapped holes in the as-grown non-stoichiometric $LaMnO_3$ compound. We do not exclude other contributions to the latter band.

Keywords: Colossal magnetoresistance (CMR); Optical conductivity; Charge-transfer (CT) transitions

Polaronic-type charge carriers mostly determine specific transport properties of CMR materials in their high-temperature insulating paramagnetic phase, which are always associated with photo-induced CT transitions. In hole-doped systems of $R_{1-x}A_xMnO_3$ manganites, the main important CT transitions associated with localized charge carriers will be apparently those involving Mn^{4+} and O^- self-trapped holes. In this article, we perform the shell model Mott–Littleton calculations for the main optical CT transitions which involve self-trapped holes of Mn^{4+} and O^- in $LaMnO_3$ essentially relying on the results of our companion article [1]. We analyze the contribution of these CT transitions to the experimental optical conductivity in $LaMnO_3$ crystal to make the assignment of the bands in the optical conductivity spectrum more clear-cut.

Using a Born–Haber cycle and the shell model, we can consider both thermally assisted and optical CT processes. This can be illustrated for a hypothetical case of two ions $X^{(m+1)+}$, $Y^{(n-1)+}$ transformation into X^{m+}, Y^{n+} in which an electron is transferred from Y to X (or a hole from X to Y),

$$X^{(m+1)+} + Y^{(n-1)+} \Rightarrow X^{m+} + Y^{n+}. \quad (1)$$

There are two basic steps: (1) Remove an electron from the *in-crystal* $Y^{(n-1)+}$ ion to infinity, outside the crystal. (2) Add an electron from the infinity, outside the crystal, to the *in-crystal* $X^{(m+1)+}$ ion. Whether or not shells alone, or shells and cores, are relaxed depends on which transition is being calculated. In the case of thermally assisted hopping, the shell and core positions are considered to be fully relaxed in both charge states and the transition energy is denoted by E_{th}. Comparison of the two charge states gives an additional indication as to which species are more stable. For optical transitions, the Franck–Condon approximation is used and their energies E_{opt} are calculated on the assumption that only shells are able to relax, whereas the cores remain in the positions corresponding to the initial state. The major contributions to these energies come from ionisation energies, I_n^Y, $I_{(m+1)}^X$, and the Madelung and polarisation terms, whose cumulative energies for defect configura-

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0921-4526/02/$ - see front matter
PII: S0921-4526(01)01204-2

tion corresponds to the CT transition considered, $S[X^{m+}, Y^{n+}]_{(opt,th)}$, which results from the Mott–Littleton calculations. If the CT transition includes the localized hole in thermal equilibrium in the initial state (these energies S^{α}_{th} for $LaMnO_3$ lattice are presented in Table III of Ref. [1]), then the corresponding thermal energy for initial defect configuration, $S[X^{(m+1)+}, Y^{(n-1)+}]_{th}$, must be subtracted. Thus, the thermal and optical energies of the CT transitions can be calculated as follows:

$$E_{(opt,th)} = I^{Y}_{n} - I^{X}_{m+1} + S[X^{m+}, Y^{n+}]_{(opt,th)} - S[X^{(m+1)+}, Y^{(n-1)+}]_{th}. \quad (2)$$

The CT optical transitions for nearest neighbours are likely to dominate and the relevant key cases have been calculated.

The room temperature optical conductivity spectrum of $LaMnO_3$ crystal reveals the optical gap near 1.3 eV and includes several broad absorption bands with maxima at $\sim$2.3, 5 and 9 eV [2]. According to the analysis of the optical conductivity spectrum made by Arima and Tokura, the gap is assumed to be of the CT-type. The first transition at $\sim$2.3 eV has been suggested to be of the O(2p)–Mn(3d) character. The band at $\sim$5 eV is thought to be due to the excitations to a higher-lying Mn 3d e_g antiparallel spin configuration, separated by a Hund's rule-coupling energy. The wide band observed around 9 eV in the optical conductivity spectrum is assigned to the O(2p)–La(5d) interband optical transition [2]. To properly estimate the contribution to the experimental optical conductivity from the CT transitions we performed a dispersion analysis of the imaginary part of the dielectric function $\varepsilon_2(v)$ in $LaMnO_3$ crystal [2], and found it to be well described by the sum of three Lorentzian bands, with the maxima E_i at 1.93, 4.75 and 9.07 eV and widths γ_i of 1.46, 2.0 and 5.1 eV, respectively. Our results of the dispersion analysis are in a reasonable agreement with those obtained earlier for the optical conductivity spectrum by Jung et al. [3], but we suggest that the dispersion analysis of the $\varepsilon_2(v)$ function is the more correct procedure. The cumulative thermal and optical energies following from the Mott–Littleton calculations, S_{th} and S_{opt}, for the CT transitions involving Mn^{4+} and O^{-}species, and those characterizing fundamental electronic transitions in $LaMnO_3$ lattice, such as, Mn(3d) gap transition, O(2p)–Mn(3d) and O(2p)–La(5d), are presented in the table by the transitions 1–3 and 4–6, respectively. To calculate the optical and thermal energies we used the self-consistent set of the ionisation potentials (see Table III, in Ref. [1]). Having assigned the fundamental electronic transitions in $LaMnO_3$ crystal, transitions 4–6 in the table, in accordance with the results of our calculations, we should note that the assignment of the optical conductivity band at $\sim$2.3 eV (the related excitation in the $\varepsilon_2(v)$ at 1.93 eV) still remains controversial. The other assignment for this band due to electron transition between the two e_g Jahn–Teller splitted bands has been suggested in many works, for example in Ref. [3]. However, we could also expect significant contribution to the band at $\sim$2.3 eV due to the presence of Mn^{4+} and/or O^{-} localized holes in $LaMnO_3$ crystal, which is known to exhibit strongly non-stoichiometric behaviour with respect to oxygen content, up to 0.1 in the as-grown crystal. Indeed, if an optical band is associated with a CT transition in a crystal lattice, then its maximum position, hv_{max}, and the half-width, ΔW, are known to be linked by a simple formula in the high temperature limit

$$hv_{max} = (16(\ln 2)kT)^{-1}\,\Delta W^2. \quad (3)$$

Using this expression, estimates for $T = 300$ K show good consistency between the half-width and maximum energy of the first Lorentzian band: from $\Delta W \simeq 0.73$ eV, we obtain $hv_{max} \simeq 1.92$ eV, which matches well with the maximum position estimated to be near 1.93 eV from the dispersion analysis of the ε_2 function. This is consistent with the view that these transitions could be of CT-type, associated with the presence of localized charge carriers in $LaMnO_3$ lattice.

Relying on the correlation between the calculated (estimating the fundamental transitions 4–6) and experimental optical energies we can try to refine the values of the ionisation potentials of I^{Mn}_{III} and I^{Mn}_{IV}, whose

Table 1
Calculated optical, E_{opt}, and thermal, E_{th}, energies for the main optical CT transitions in $LaMnO_3$

CT transition		Optical energy, E_{opt} (eV)	Exp. (eV)	Thermal energy, E_{th} (eV)	S_{opt} (eV)	S_{th} (eV)
1. $Mn^{4+} + Mn^{3+} \Rightarrow Mn^{3+} + Mn^{4+}$		1.33		0.00	−44.35	−45.68
2. $O^{-} + Mn^{3+} \Rightarrow O^{2-} + Mn^{4+}$		1.43 (2.29)	1.93	−0.75 (0.12)	−43.50	−45.66
3. $Mn^{4+} + O^{2-} \Rightarrow Mn^{3+} + O^{-}$		2.98 (2.12)	1.93	0.75 (−0.12)	18.62	16.39
4. $2Mn^{3+} \Rightarrow Mn^{4+} + Mn^{2+}$	Mn(3d) gap	3.72	3.5	2.68	−13.06	−14.10
5. $Mn^{3+} + O^{2-} \Rightarrow Mn^{2+} + O^{-}$	O(2p)–Mn(3d)	5.61 (4.75)	4.75	3.50	50.15	48.04
6. $La^{3+} + O^{2-} \Rightarrow La^{2+} + O^{-}$	O(2p)–La(5d)	8.93	9.07	6.47	42.02	39.56

determination of *in-crystal* presents difficulties due to un-closed 3d shell of Mn^{3+} ion. Then using these corrected values we recalculated the energies of transitions 2 and 3 associated with the CT transitions of O^- and Mn^{4+} self-trapped holes and obtained similar values of optical energies $E_{opt} = 2.29$ and 2.12 eV, respectively (given in Table 1 in brackets), wherein both are in good agreement with the excitation in the $\varepsilon_2(v)$ at 1.93 eV. Thus, we can conclude that it would be reasonable to expect the appreciable contribution to this band due to transitions 2 and 3 associated with the presence of the localized holes of Mn^{4+} and O^- involved in the CT transitions along a chain Mn^{4+}–O^{2-}–Mn^{3+} in the as-grown non-stoichiometric $LaMnO_3$ crystal.

The authors thank J. Gale for making available General Utility Lattice Programme used in the present calculations. We are grateful to Royal Society/NATO in approving the visit of N. Kovaleva to University College London.

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