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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

A Model for the Charge Transport in La0.67Ca0.33MnO3 at Temperatures above Tp

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Version of record first published: 18 Oct 2010

To cite this article: O. Pana*, R. Turcu, A. Bot, I. Deac, A. Darabont, E. Burzo & I. Chicinas (2004): A Model for the Charge Transport in La0.67Ca0.33MnO3 at Temperatures above Tp, Molecular Crystals and Liquid Crystals, 417:1, 57-65

To link to this article: http://dx.doi.org/10.1080/15421400490478849

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Mol. Cryst. Liq. Cryst., Vol. 417, pp. 57/[541]–65/[549], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490478849

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A MODEL FOR THE CHARGE TRANSPORT IN $La_{0.67}Ca_{0.33}MnO_3$ AT TEMPERATURES ABOVE T_p

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We develop a new model describing the charge transport process in perovskite like manganites $La_{1-x}Ca_xMnO_6$ for temperatures above the metal-insulator transition temperature T_p. At the $x = 0.33$ doping level four bipolaronic energy bands are expected to be present into the Jann-Teller energy gap of electronic states e_{2g}. For comparison with experiment the conductivity and magneto-conductivity of $La_{0.67}Ca_{0.33}MnO_6$ samples, sintered at temperatures between $700°C$ and $1100°C$ were determined in the temperature range $4.2K-300K$. By analyzing the experimental data of conductivity vs temperature, in the framework of our model we from found the best fit, in the temperature range above T_P indications for the presence of small bipolarons even above this temperature.

1. INTRODUCTION

The physical properties of nano-structured materials and especially nano-structured perovskites with colossal magneto-resistance (CMR) have been studied, in recent years, for both basic and applicative purposes [1,2]. The present work deals with some aspects concerning the magneto-transport process in nano-structured CMR perovskites manganites of $La_{1-x}Ca_x MnO_3$ type.

Essentially two mechanisms were found to be the most important referring to the specific properties of perovkite-like CMR manganites: (i) the

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double exchange mechanism (DE) and (ii) the Jahn-Teller (JT) effect. The former allows charge and spin transfer between neighboring Mn^{3+} ions and the second one couples the phonon field to the electron existing into the e_g state. The result of the JT effect is a permanent distortion of the MnO_6 octahedrons. A so called co-operative JT effect generate an ordered arrangement of distorted octahedrons doubling the in plane lattice constants (Fig. 1). If, as a result of Ca doping, the central position in a octahedron is occupied by a Mn^{4+} ion, the JT effect is no longer present and the corresponding octahedron remains undistorted. The associated hole state is usually called an JT polaron.

In developing the present model the following presumption are considered: (i) the JT effect splits the e_g energy band into two energy bands, the lower one [valence band (VB)] being completely filled with electrons coupled with parallel spins while the upper one [conduction band (CB)] is empty; (ii) the hole states introduced into the lower energy band by Ca doping produces spatially extended polaron (P) and bipolaron (BP) states; as a consequence, two states are removed from the VB and CB respectively and placed into the energy gap; the lower localized state,

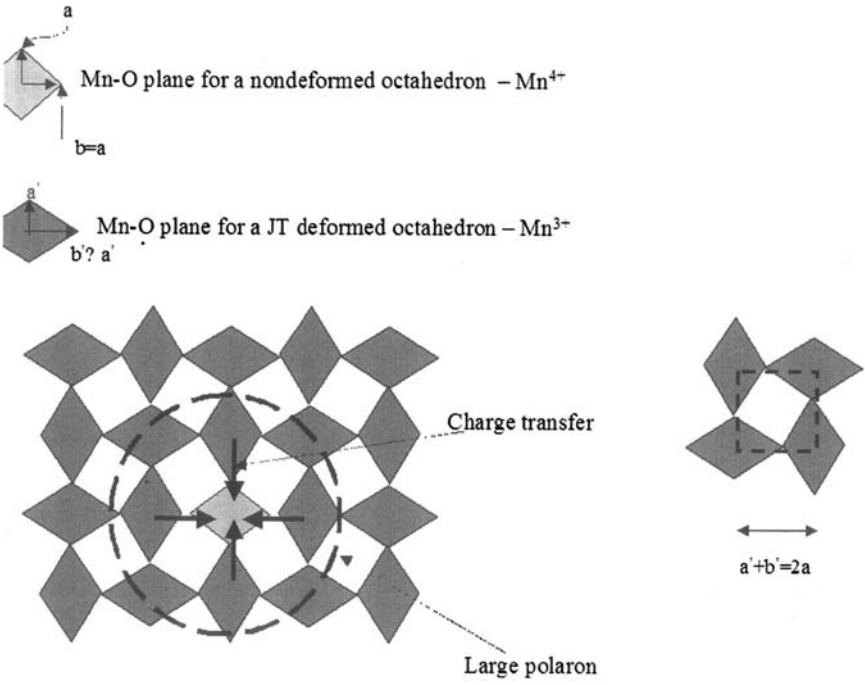

FIGURE 1 Illustration of the co-operative Jahn-Teller effect.

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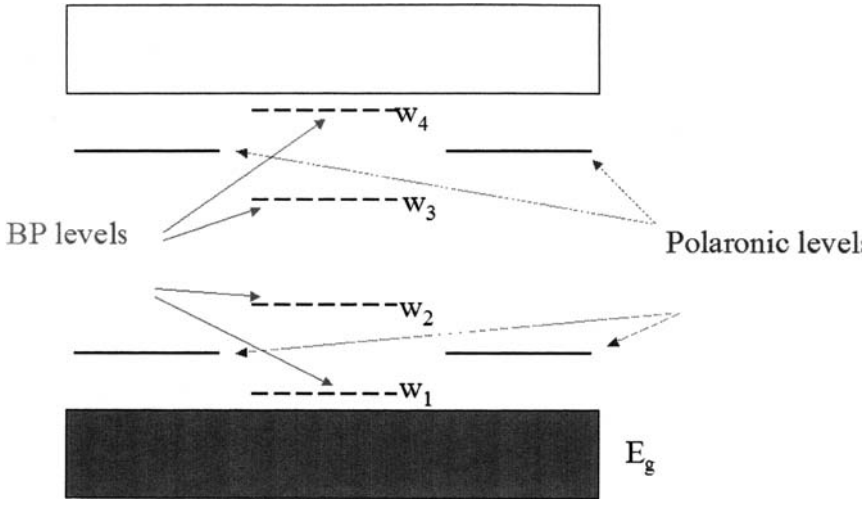

FIGURE 2 Polarons and bipolarons levels inside the band gap of the e_{2g} band.

coming from the VB, has one electron and the upper one is unoccupied; (iii) the occupied energy level contains states transferred from the neighbor Mn sites by the DE mechanism; due to this charge transfers, the e_g density of states is reduced for the neighboring manganese ions, and the JT distortion effect is also reduced; the polaron state extends also over neighboring Mn sites (Fig. 1); (iv) two polarons combine to form a bipolaron state, with four levels inside the energy gap (Fig. 2); at sufficiently high Ca doping the four levels form four energy bands B_1–B_4.

2. DESCRIPTION OF THE CONDUCTION PROCESS

The formation of a bipolaronic state can be seen as a result of the confinement of two neighboring polarons. Due to their mutual configurational attraction four energy levels will result as bonding and antibonding states for the two polaron localized levels (Fig. 2). The states corresponding to $w_1 - w_4$ BP levels or $B_1 - B_4$ BP bands are created as a result of the electron-phonon coupling and do not interact with the states belonging to the valence and conduction e_g bands. Therefore, we consider that any electronic state from the bipolaronic bands could not "see" the electrons from the valence and conduction bands and the phonons producing the JT distortions.

The interaction between the electrons of the bipolarons energy band and the *new phonon modes* introduced by the existence of the bipolaronic

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array represents the driving process for *dc* charge transport in in medeium $(0.2 < x < 0.4)$ doped $La_{1-x}Ca_xMnO_3$.

The following transition processes, represented in Figure 3, contribute to the charge transport: the process labelled as (I) involves the transition from the bipolaronic band B_1 up to the localized polaronic level. It is thermally activated by the phonons of the bipolaronic lattice. A polaronic state localized at the site n_0 into the bipolaronic lattice is considered. This isolated polaronic state extends, by tunnelling without reflection, over neighboring bipolarons. Due to the polaron extension, one hole generated into the B_1 band at n_0 position moves, under the applied electric field $\vec{E}$ to the site $n_0 - 1$ where it can recombine with one of the electrons from the localized polaronic level. The process labelled (II) consists of the thermally activated transition of the electron from the localize polaronic level to the empty energy band B_2. Under the electric field the excited electron moves from the site n_0 to the site $n_0 + 1$ where it undergoes a dawn transition (relaxation) to the polaronic level.

The third proces (III), represents the direct transition from the top of the B_1 bad to the bottom of the B_2 band. By carefully analyzing the mentioned process one can see that the transition of an electronic state from the completely filled B_1 bipolaronic band to the empty B_2 band represents the splitting of one bipolaron into two polarons at the same position. It is thermally activated by the phonons of the bipolaronic lattice and the activation energy is not, simply, the width of the band gap 2Δ, but the much

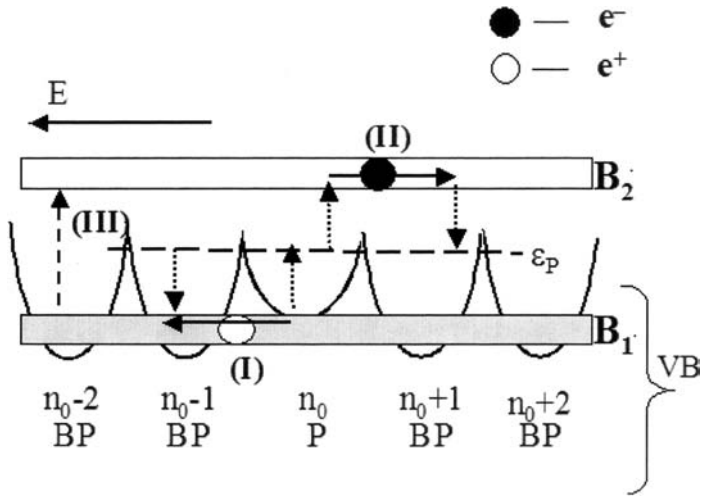

FIGURE 3 Illustration of the processes which contribute to the charge transport.

larger energy, representing the difference between a two polarons state and one bipolaron state $E_a = 2E_P - E_B + 2\Delta$.

3. CHARGE TRANSPORT MODEL

Let us consider a 2D lattice of bipolarons with one polaron "impurity" at position "n_0". The total Hamiltonian is considered as the sum of three contributions

$$H = H_0 + H_b + H_{ep} \tag{1}$$

Here the first term has the following form

$$H_0 = \sum_{n \neq n_0} \varepsilon_n a_n^+ a_n + \varepsilon_p d_{n_0}^+ d_{n_0} + \sum_q \omega_q b_q^+ b_q \tag{2}$$

and represents the sum of kinetic energies for, respectively, the electronic states B_1 band, the energy of the single occupied polaronic level ε_p and the phonon term. The operators b_q^+ and b_q acts on the phonon states with wave vector q. The operators a_n^+ and a_n are the usual creation and destruction operators of electronic states at position "n". In all equations they are considered as associated with Bloch–like states.

The next term, H_b, describes the band movement of the electrons in the bipolaronic band

$$H_b = \sum_{n,n' \neq n_0} I_{n,n'} a_n^+ a_{n'} \tag{3}$$

As usual $I_{n,n'}$ represents the transfer integral between positions n and n'.

The electron-phonon interaction could represented by the following general form

$$H_{ep} = \sum_n \sum_q M_q \left(b_q + b_{-q}^+ \right) \alpha_n^+ \alpha_n \tag{4}$$

M_q is the matrix element of the phonon-electron coupling. It depends upon phonon frequencies ω_q and wave vector q. [3,4] From Eq. (4), by different combinations of "a" and "d" operators, three terms results, as following

$$H_{ep}^{(a)} = \sum_n \sum_q B_q \left(b_q + b_{-q}^+ \right) a_n^+ a_n \tag{5}$$

for the interaction of phonons with the electron density of the B_1 band,

$$H_{ep}^{(d)} = \sum_j \sum_q P_q \left(b_q + b_{-q}^+ \right) d_{n_0 \pm j}^+ d_{n_0 \pm j} \tag{6}$$

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for the interaction of phonons with the electron existing on the polaronic isolated energy level, and finally

$$H_{ep}^{(t)} = \sum_j \sum_q \frac{V_q}{\sqrt{N\hbar\omega_q}} \left(\frac{\hbar^2 q^2}{2M}\right)^{1/2} \left(b_q + b_{-q}^+\right) d_{n_0\pm j}^+ a_{n_0\pm j} + c.c. \quad (7)$$

the term describing the phonon induced transitions between the B_1 band and the polaronic level. The B_q factors in Eq. (5) and P_q factors in Eq. (6) refer to bipolarons and polarons respectively. Here, n_0 represents the position of the polaron center. The summations over "j" extents around n_0 and express the polaron spatial extension. The existence of spatial distribution probability for the polaron statte enable the existence of the Fourier transforms of operators "d" and their localization in "k-space". In order to simplify the calculations we considered that the matrix elements of the coupling have significant values only at the polaron centre n_0 and, in Eqs. (6)–(7) we can drop the summation over "j". Finally one get for $H_{ep}^{(t)}$

$$H_{ep}^{(t)} = \Delta\left(\lambda_{n_0} d_{n_0}^+ a_{n_0} - \lambda_{n_0'} a_{n_0'}^+ d_{n_0'}\right) \quad (8)$$

Here λ_{n_0} and $\lambda_{n_0'}$ behave like coupling constants and represent the probabilities to find the localized polaronic state of energy ε_p at, respectively, positions n_0 and n_0' and $\Delta > 0$ is the energy difference between the bottom of the bipolaronic band and the energy of the localized polaronic state.

Next, two successively Holstein's canonical transformations are necessary [3] to eliminate the electron-phonon parts in the Hamiltonian. The double transformed Hamiltonian reads as

$$\overline{H} = e^{S'}\left(e^S H e^{-S}\right)e^{-S'} \quad (9)$$

where, the operator S refers to the first transformation

$$S = -\sum_n \sum_q a_n^+ a_n e^{iqR_n} \frac{B_q}{\omega_q}\left(b_q - b_q^+\right) \quad (10)$$

and the operator S'

$$S' = -\sum_n d_n^+ d_n e^{iq\delta} \frac{P_q}{\omega_q}\left(b_q - b_q^+\right) \quad (11)$$

to the second one. Finally the resulted transformed Hamiltonian reads as

$$\begin{aligned}\overline{H} = &\sum_n \eta_n a_n^+ a_n + \eta_p d_{n_0}^+ d_{n_0} + \sum_q \omega_q b_q' b_q \\ &+ 2t_0 f_1\left(\sum_n a_n^+ a_{n+1} + hc\right) \\ &+ \Delta f_2\, \lambda_{n_0}\left(d_{n_0}^+ a_{n_0} - \gamma\, a_{n_0-1}^+ d_{n_0-1}\right)\end{aligned} \quad (12)$$

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Here γ represents the ratio $\lambda_{n_0}/\lambda_{n_0-1}$ and, for the neighboring hops, could be approximated as $\gamma \approx 1$.

For polarons hopping, the real part of the conductivity was evaluated by Lang and Frisov [3] in the the small polarons case by using $\mathcal{J}-\mathcal{J}$ correlation functions

$$\mathrm{Re}(\sigma) = \frac{1-\mathrm{e}^{-\beta\omega'}}{2\omega'}\int dt\,\mathrm{e}^{\omega' t}\langle j^{+}(t)j(0)\rangle \tag{13}$$

$$j = i\frac{Je}{\hbar}\delta\sum_{n} a_n^{+}a_{n+1}X_n^{+}X_{n+1} \tag{14}$$

Here j is the current density operator modified by the canonical transformations and ω' is the frequency of the applied external photon field. In zero order approximation the electronic correlation function from Eq. (13) was evaluated as

$$\left\langle a_n^{+}(t)a_{n+1}(t)a_{n'+1}^{+}(0)a_{n'}(0)\right\rangle = \delta_{n,n'}\langle v_n(1-v_{n+1})\rangle \tag{15}$$

The correlation function contains the product $c(1-c)$, where c is the occupancy probability of the initial position and $(1-c)$ the probability that the final position is unoccupied.

The evaluation of these probabilities allows the calculation of the temperature dependence of conductivity. Generally one have $c \sim \mathcal{N}_1\,\tau$ and $(1-c) \sim \mathcal{N}_2\,\tau$, where $\mathcal{N}_1, \mathcal{N}_2$ represents the density of occupied states at the initial position and unoccupied states at the final position respectively. Here τ is the life time of an excited state. For processes (I) and (II) $\mathcal{N}_1$ and $\mathcal{N}_2$ are equal with unity (one electron is removed at the polaron position). The life time for these processes, considered as being of diagonal type [3], was calculated by using the imaginary part of the self-energy of the Green's functions in the Matsubara formalism [8]

$$\langle\tau^{(I)}\rangle = \langle\tau^{(II)}\rangle = \frac{1}{\langle \mathrm{Im}\Sigma^{(II)}\rangle} = \frac{2K_B\,T}{(f\Delta)^2} \tag{16}$$

Here f is the so called thermal factor $f = \exp(2\xi\Delta)$. For processes of type (III) the life time is temperature independent and the product $c(1-c)$ is $c(1-c) \sim T^{5/2}$ (it a similar situation with the "masses law" in semiconductors for a 2D case). Finally one obtains for the dc conductivity, generated by processes (I–III), the following expression

$$\sigma = C_1\,T\exp(2\xi_2 T)\exp\left(\frac{-\Delta}{K_B T}\right) + C_2\,T\exp\left(\frac{-E_a}{2K_B T}\right) \tag{17}$$

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4. COMPARISON WITH EXPERIMENT AND DISCUSSIONS

$La_{0.67}Ca_{0.33}MnO_3$ samples with different particle sizes were prepared via the sol-gel route followed by the heat treatment at two different temperatures, namely 900°C (labelled as sample #1) and 1100°C (labelled as sample #2). X-ray diffraction confirmed the expected perovkite structure. By the X-ray line-profile analysis were determined the dimensions of nanocrystallites The resistance and the magnetoresistance were measured with the usual four probe method by using an Oxford Instruments set-up, from liquid He to the room temperature. The size of the grains and the sample compositions were determined by using SEM-EDX analysis was performed on a JEOL LV microscope. The main characteristics of samples are summarized in Table 1.

In order to perform the, generally ambiguous, five parameters theoretical function of the conductivity, the parameters were spitted into two groups and then an iterative method was used. The significant fitting parameters are summarized in Table 2.

The model allows an interpretation of the conductivity behaviour of $La_{0.67}Ca_{0.33}MnO_3$ compounds. Higher doping levels produce the so called charge ordering and the model is no longer adequate.

The negative values of the $E_{PB} = 2E_P - E_B$ resulted in the case of magneto-conductivity could be regarded as arising from from the fact that a bipolaron state is unstable against a two polarons state. On the other hand, recent X-ray diffraction and neutron inelastic scattering studies [9] on moderate doped perovskites $(0.25 < x < 0.4)$ show that, even above the metal- insulator transition temperature, T_p, small polarons (bipolarons) continue to coexist with medium or large bipolarons; the negative values of the EBP energy could be attributed to fact that, above TP, a state of two large polarons is more stable against a small bipolaron state; as the temperature increases, the number of small bipolarons diminish and the present model is fully applicable; a more realistic picture should include the rate of small polarons evolution with the temperature and with

TABLE 1 The Main Characteristics of Samples

Sample	t_s [°C]	T_P [K]	$\frac{\sigma(T_P)}{\sigma(300)}$	Grains sise [nm]	Crystallites size [nm]
#1	900	200	0.084	140	22.5
#2	1100	225	0.65	220	50.5

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TABLE 2 The Values of the Fit Parameters as Resulted by the Fitting with Eq. (17)

Sample	$2\xi_2$ [K^{-1}]	Δ [K]	C_2 [$K^{-1/2}$]	E_{PB} [K]
#1 0 T	3^{-3}	1171	7^{-2}	2070
#1 5 T	1.6^{-6}	1171	0.52^{-3}	−3849
#2 0 T	6.1^{-3}	1268	12^{-2}	2461
#2 5 T	1.3^{-6}	1268	0.3^{-3}	−3574

necessity the physical mechanisms leading to large (medium) bipolarons to small bipolarons (polarons) transition.

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