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Abstract – We performed high-pressure experiments in $La_{0.8}Ca_{0.2-x}Sr_xMnO_3$ (LCSMO)($0 \leqslant x \leqslant 0.2$) ceramic samples in order to analyze the validity of the well-known relation between the A-cation mean ionic radius ($\langle r_A \rangle$) and the Curie temperature T_c of hole-doped manganites at a fixed doping level and for doping values below the 0.3 (Mn^{+4}/Mn^{+3}) ratio. By considering our results and collecting others from the literature, we were able to propose a phenomenological relation that considers the systematic dependence of T_c with structural and electronic parameters. The proposed expression predicts fairly well the pressure sensitivity of T_c, its dependence with the A-cation radius disorder and its evolution in the high-pressure range. Considering a Double-Exchange model, modified by polaronic effects, the phenomenological law obtained for T_c can be associated with the product of two terms: the polaronic modified bandwidth and an effective hole doping.

Introduction.

Introduction. – Many efforts have been devoted to determine the relevant electronic and structural parameters that fix the Curie temperature (T_c) of manganites [1–3]. The Double-Exchange model [4,5] (DE) was initially applied in order to correlate electrical transport properties and magnetic ordering in these compounds. But early experiments such as the temperature dependence of the Hall coefficient [6], the differences in the activation energy between thermopower and conductivity [7], and the isotope effect [8] demonstrated the polaronic nature of the carriers. This evidence showed the necessity for introducing polaronic corrections to the electronic bandwidth that determines T_c.

On the other hand, it was experimentally established that, for hole-doped manganites and particularly for the family $A'_{0.7}A''_{0.3}MnO_3$ (where A' is a trivalent rare-earth ion and A'' a divalent alkaline-earth ion), the resulting A mean ionic radius ($\langle r_A \rangle$) has a clear influence on T_c [9]. Experiments also showed that $\langle r_A \rangle$ can be varied both by chemical replacement or by an external pressure [9], where in the former case, both the Mn-O bond distance and the

Mn-O-Mn bond angle vary while in the latter case, most of the variation comes from the Mn-O bond distance [2]. Although the $T_c(\langle r_A \rangle)$ dependence can be well reproduced by varying the pressure just by considering a linear dependence $\delta \langle r_A \rangle = \gamma \delta P$ (with $\gamma \simeq 3.75 \cdot 10^{-4} \text{Å/kbar}$) for $P \leqslant 20$ kbar. In this low pressure range, T_c varies linearly with P, while for higher pressures, T_c reaches a maximum value and decreases for a further increase of P [10,11]. This behavior seems to be related to pressure-dependent competing interactions, like the ferromagnetic (F) and the antiferromagnetic (AF) coupling between the core spins, as suggested by Sacchetti *et al.* [12], although other factors that govern the polaronic modified DE model can play a major role. On the other hand, Rivadulla *et al.* [13] made a good quantitative description of the $\langle r_A \rangle$-dependence of T_c at constant doping based on a mean-field model where the reduction of the volume fraction of the itinerant electrons produced by the phase separation is responsible for the observed behavior. In the same way, the microscopic model introduced by Dey *et al.* [14] reproduces the changes in T_c observed in manganite films due to bulk and Jahn-Teller strains produced by the substrate mismatch, while Millis *et al.* [15] points out the extreme sensitivity of T_c to the biaxial strain in respect to the bulk compression contribution.

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Empirically, the temperature dependence of the pressure (P) sensitivity of T_c ($d\ln T_c/dP$) was established, which seems to represent a universal behavior for many moderated hole-doped manganites [16]. This curve could be described qualitatively within the small polaron modified DE model, but even so we were far from a convenient quantitative explanation [17]. Even considering polarons in the more suitable intermediate electron-phonon coupling regime did not produce a better understanding [18].

In this paper we present a phenomenological model based on the $\langle r_A \rangle$-dependence of T_c for intermediate-to-large bandwidth AMnO$_3$ hole-doped perovskites which usefully describes the quantitative dependence of $T_c(P)$. A DE interaction, modified by polaronic effects and also an effective doping of the MnO planes, both controlled by $\langle r_A \rangle$ are suggested as the two microscopic ingredients that govern the proposed relation.

Experimental. – Previous experiments [9] showed that T_c follows a parabolic dependence with $\langle r_A \rangle$ for La$_{1-y}$T$_y$MnO$_3$ (T = Sr; Ca; Pr) for a fixed doping level $y \sim 0.3$. Here, in order to test the validity of this dependence for other doping levels ($y = 0.2$), we performed resistivity measurements as a function of temperature and pressure on La$_{0.8}$Ca$_{0.2-x}$Sr$_x$MnO$_3$ (LCSMO)($0 \leqslant x \leqslant 0.2$) ceramic samples. These samples were synthesised following a similar process to the one published elsewhere [19]. The temperature dependence of resistivity was measured using a conventional 4-terminal DC technique in a CuBe pinston-cylinder hydrostatic cell described previously [20]. Pressures up to 10 kbar were applied using a 50% mixture of kerosene and transformer oil as the pressure transmitting medium. Pressure was measured at room temperature by using a calibrated InSb sensor and it remains constant over all the temperature range (within a 10% of variation for a temperature span of 77 K to 350 K) in spite of thermal contractions. Temperature was measured using a calibrated carbon-glass thermometer in good thermal contact with the cell's body.

Results and Discussion. – The normalized resistivity as a function of temperature of the LCSMO series with $0 \leqslant x \leqslant 0.2$ and $y = 0.2$ can be observed in fig. 1. All the curves show a change in the conduction regime that can be associated with a metal to insulator transition (T_{MI}), which increases with increasing Sr content.

The pressure sensitivity of the resistivity is shown in fig. 2 for samples LCSMO with $x = 0$; 0.06 and 0.20. Pressure increases both T_{MI} and the conductivity of these materials.

T_{MI} does not necessarily coincide with the Curie temperature, so we determine T_c from the resistivity curves as the temperature at which a sudden increase in the logarithmic temperature derivative of the resistivity is observed. It has been shown previously that this coincides with the T_c determined by magnetization measurements [21]. By following this criteria and by
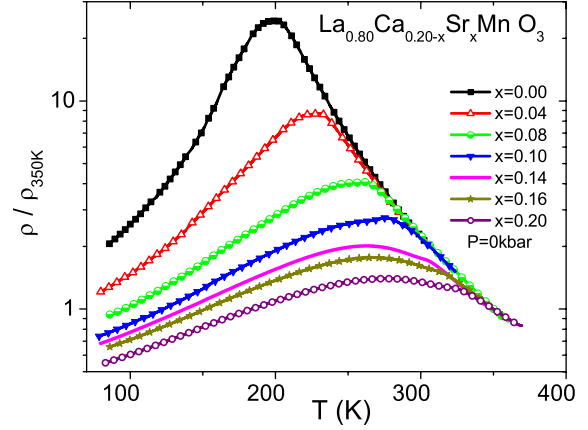

Fig. 1: (Color online) Temperature dependence of the normalized resistivity of La$_{0.8}$Ca$_{0.2-x}$Sr$_x$MnO$_3$ ($0 \leqslant x \leqslant 0.2$).
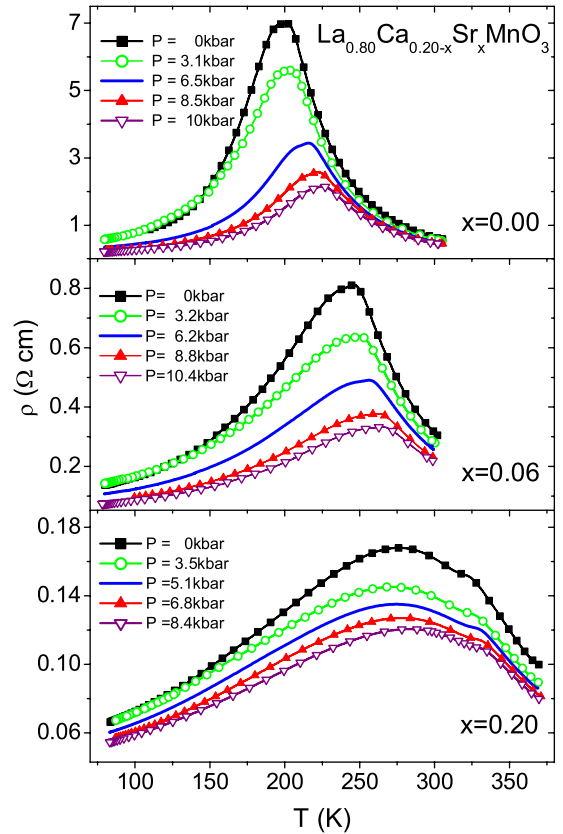

Fig. 2: (Color online) Pressure sensitivity of the resistivity as a function of temperature of La$_{0.8}$Ca$_{0.2-x}$Sr$_x$MnO$_3$ ($x = 0$; 0.06; 0.2).

calculating the variation on $\langle r_A \rangle$ generated by chemical replacements (from Shannon's tables of ionic radii [22]) or by external pressure (assuming that γ is independent of the doping level and that $\langle r_A \rangle$ is the only pressure-dependent parameter), we obtain the dependence of T_c as a function of $\langle r_A \rangle$ for the LCSMO ($y = 0.2$) samples, shown in fig. 3.
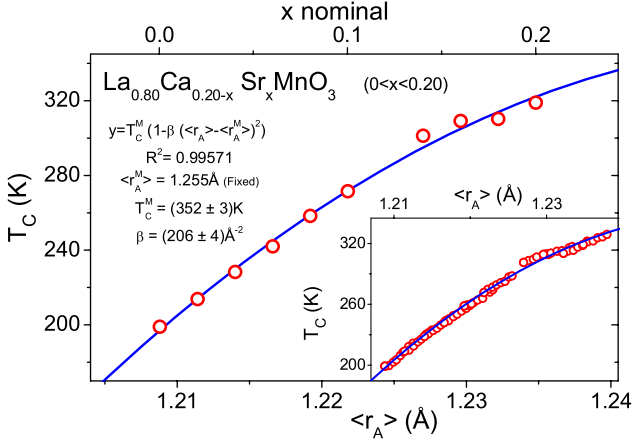
Fig. 3: (Color online) T_c vs. the Sr concentration (x) or the average ionic radius of the cation in the A site ($\langle r_A \rangle$) at constant doping $y = 0.2$. The line is a fit using eq. (1); the fitting parameters are displayed. The inset also shows T_c vs. $\langle r_A \rangle$, but where the variation of $\langle r_A \rangle$ is due to both chemical replacements and external pressure (assuming that $\delta T_c^M/\mathrm{d}P = \delta \beta/\mathrm{d}P = 0$ and $\delta \langle r_A \rangle = \gamma \delta P$, with $\gamma = 3.75 \cdot 10^{-4}$ Å/kbar).
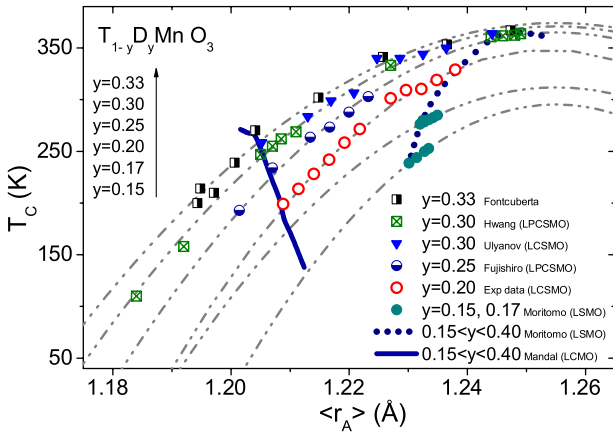

Fig. 4: (Color online) The phase diagram of $T_{1-y}D_y MnO_3$ (where T is a trivalent lanthanide as La, Sm, Nd, and D a divalent alkaline earth as Ca, Sr) for $0.15 \leqslant y \leqslant 0.33$ as a function of $\langle r_A \rangle$. Data was extracted from references [9,23–27]. The dashed lines are parabolic fits corresponding to eq. (1) at constant doping y. The evolution of T_c and $\langle r_A \rangle$ is also shown for the Sr and Ca-doped LMO samples (i.e. samples with a varying y).

The data is very well represented by a quadratic law for the whole pressure and doping intervals considered, which indicates that the assumptions we made were quite reasonable. A small departure from the ideal dependence can be observed for $\langle r_A \rangle \simeq 1.227$ Å, which coincides with a structural transition reported for this series [23].

From our data and the data already published we can extend the study of the $T_c(\langle r_A \rangle)$ dependence for other manganites and for doping levels y in the $0.15 \leqslant y \leqslant 0.33$ range. The obtained $T_c(y, \langle r_A \rangle)$ curves, shown in fig. 4, follow the same general behavior: a parabolic law
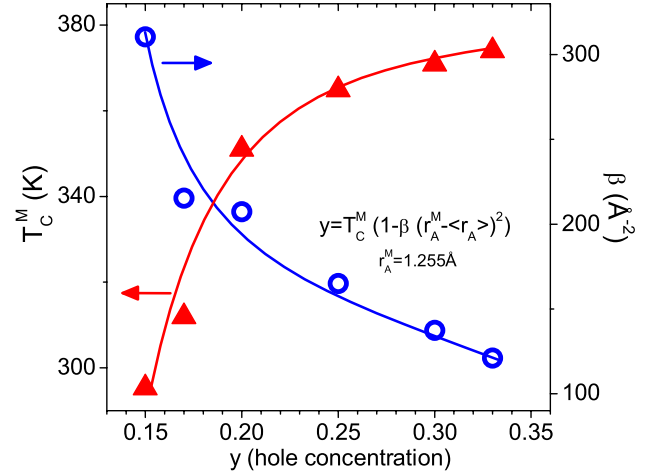

Fig. 5: (Color online) The fitted parameters T_c^M and β as a function of the hole concentration y. Lines are guides to the eye.

for each doping concentration and a doping-dependent maximum $[T_c^M(y)]$ located at $\langle r_A^M \rangle \simeq 1.255$ Å. We propose to represent this dependence by an expression of the form

$$T_c(y, \langle r_A \rangle) = T_c^M(y)\, y_{eff}, \tag{1}$$

with $y_{eff} = [1 - \beta(y)(\langle r_A \rangle(x, y) - \langle r_A^M \rangle)^2]$, that, as will be discussed later, may represent an effective doping fraction, expressed as a function of $\langle r_A \rangle$, $\langle r_A^M \rangle$ and β, an empiric parameter.

By fitting the data presented in fig. 4 we can determine the doping sensitivity of parameters T_c^M and β, as can be observed in fig. 5. As was shown in a previous study [28], the local structural disorder, generated by the occupation of the A site by cations with different sizes, produces a reduction of the ideal T_c that would be measured in case that this disorder does not exist. The disorder can be quantified by the variance σ^2 of the A-cation radius distribution. In order to perform the fits, minimizing in this way the contribution of disorder in the obtained parameters, we choose from the $T_c(y, \langle r_A \rangle, \sigma)$ data the points with small σ^2 ($<10^{-3}$ Å^2).

On the other hand, if we assume that eq. (1) gives the T_c of a manganite with negligible A-cation radius disorder $[T_c^\star(x, \langle r_A \rangle) = T_c(x, \langle r_A \rangle, \sigma = 0)]$, we can estimate the T_c of a manganite with a structural disorder σ in r_A as the mean T_c resulting from a uniform distribution of cells with A-cation radii within the interval $r_A \pm \sigma$. The result gives an expression of the form

$$\langle T_c[y, \langle r_A \rangle, \sigma^2] \rangle = T_c^\star(y, \langle r_A \rangle) - (T_c^M(y)\beta(y)/3)\sigma^2, \tag{2}$$

which gives a simple explanation of the linear dependence of T_c on σ^2 already published for the perovskite family $A'_{0.7}A''_{0.3}MnO_3$ [28]. The σ^2's pre-factor can be calculated from the fitted parameters shown in fig. 5. For $y = 0.3$ we obtain a value of (17.000 ± 1000) KÅ^{-2}, quite similar to the experimental data published.
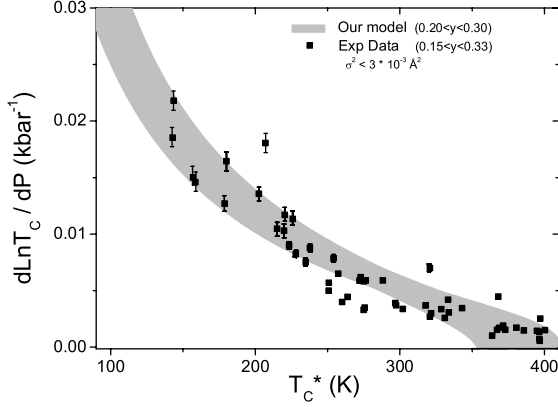
Fig. 6: Pressure sensitivity as a function of $T_c^\star$ for compounds of the $La_{1-y}T_yMnO_3$ family (T = Sr; Ca; Y, Dy) in the $0.15 \leqslant y \leqslant 0.33$ range. To guarantee the range of validity of eq. (2) in order to estimate $T_c^\star$, data points with $\sigma < 3 \cdot 10^{-3}$ Å^2 were extracted from refs. [9–11,17,18,23,24,26,29,30] and from our measurements. The shaded area represents the predictions of the model (eq. (3)) taking into account the different values of the fitted parameters (β and T_c^M) and their uncertainties.

Also, we can qualitatively estimate the influence of disorder on the pressure sensitivity of T_c by taking the pressure derivative of eq. (2). If we compare the data of previous papers [11,31] it is clear that $d\sigma^2/dP$ is an increasing function of σ, the second term of the right part of the derived equation would indicate a reduction of the expected pressure sensitivity of manganite with increasing σ^2, as was experimentally obtained previously [32].

Besides, considering the similarity of eq. (1) with the one developed by Bean and Rodbell [33] to describe the coupling of magnetic order to structural distortions, a first order magnetic phase transition at T_c can be predicted for large values of β, as was demonstrated experimentally by Otero-Leal et al. [32].

The expression of the pressure sensitivity of T_c, shown in eq. (3), can be easily obtained from eq. (1) as

$$\frac{d\ln Tc}{dP} = \frac{d\ln T_c^M}{dP} + 2\gamma\sqrt{\beta}\sqrt{\frac{T_c^M}{T_c}\left(\frac{T_c^M}{T_c} - 1\right)}. \quad (3)$$

By using eq. (3) and the fitted parameters $T_c^M(y)$ and $\beta(y)$, the pressure sensitivity of T_c at low pressures can be predicted for many compounds. A good accordance between experimental points and the predicted behavior, represented by a shaded area as we considered the doping dependence of the fitted parameters, can be observed in fig. 6. Here, we included data points where T_c was determined by different criteria and techniques (ac susceptibility or resistivity) which accounts for the dispersion of data. We only applied the restriction that the selected data points should be derived from compounds with a small structural disorder in r_A ($\sigma < 3 \cdot 10^{-2}$ Å). Although some of the pressure sensitivities seem to be overestimated, the general behavior is very well predicted

as a direct consequence of the validity of eq. (1) and the linear dependence of $\langle r_A \rangle$ to describe the general behavior of intermediate-to-large bandwidth manganites in the low pressure range considered here ($P < 1$ GPa). Indeed, our description based on eq. (1) predicts the observed parabolic evolution of T_c with pressure in the intermediate-pressure range ($P < 2$ GPa) [10]. Also, if we consider the fact that $\langle r_A \rangle$ deviates from a linear behavior [11] and reaches a limit value for $P > 6$ GPa, we may obtain a simple qualitative explanation of the experimental results where the parabolic $T_c(P)$ law is followed by an asymptotic behavior for increasing pressures [30]. On the other hand, in this high-pressure range, pressure induces additional Jahn-Teller distortions of the MnO_6 octahedra [11], not taken into account by our description, that may be at the origin of the abrupt reduction of T_c reported for some compounds [21,31].

Finally, we would like to gain insight on the physical origin of each term in eq. (1).

As for the DE model $T_c \sim Wn$, where W is the bandwidth and n is related to the electronic density of itinerant carriers [34], we may associate T_c^M with W, and y_{eff} with n.

As part of the carriers are localized in the polaronic phase, n does not depend solely on the nominal doping value y. Within this framework, the given expression between brackets for y_{eff} may represent the dependence with $\langle r_A \rangle$ of the effective density fraction of itinerant carriers. As shown in the model derived by Rivadulla et al. [13], the value of n needed to determine the $T_c(x)$ dependence at constant doping ($y = 1/3$) for the system $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ should take into account this polaronic reduction of the itinerant carriers (in their notation $n = 1 - n_{JT}$, where n_{JT} is the volume fraction of electrons in the polaronic phase). Indeed, in the microscopic model developed by Dey et al. [14], T_c is calculated considering an electronic occupancy of the relevant orbitals that is 60–70% of the one expected from the nominal hole-doping level.

This implies that, not only the steric factors that govern the hopping energy and the polaronic coupling constant that modifies the bandwidth will affect T_c of the manganite by changing T_c^M, but also, and quantitatively more important, variations on $\langle r_A \rangle$ will determine its value by modifying the effective value of n.

In this way, we may associate T_c^M with structural parameters and with the polaronic narrowing of the bandwidth as [35]

$$T_c^M \sim W_0 \ F(E_b) = \frac{\cos(w)}{d^{3.5}} \ F(E_b), \quad (4)$$

where W_0 is the bare bandwidth, w is the tilt angle in the plane of the Mn-O bond, d the Mn-O bond length, E_b the binding energy of polarons and F the appropriate function that accounts for the polaronic bandwidth reduction.

In fig. 7 we have plotted the relative variation of the experimental T_c with $\langle r_A \rangle$ for samples of the LSMO family.
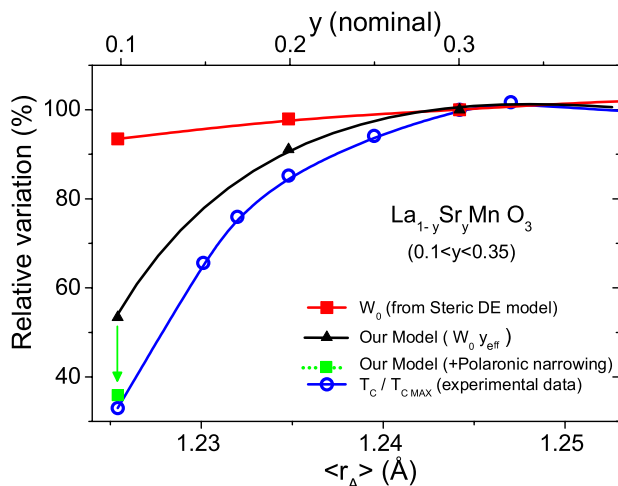
Fig. 7: (Color online) The relative variation of the bare bandwidth W_0, of the bare bandwidth times the relative effective doping ($W_0\, y_{eff}$) and of the experimental T_c (from ref. [26]), as a function of the nominal doping y or of $\langle r_A \rangle$. The arrow shows the correction added by polaronic effects (only valid for low doping levels).

In the same figure we considered the relative variation of W_0, based on the modification of the steric factors. Again, it is clear that the DE model is far to explain the experimental variation of T_c. If we include the correction of the effective doping proposed in our phenomenological model a much better agreement is obtained ($W_0\, y_{eff}$). Finally, if we use the expression $F(E_b) = \exp(\frac{\gamma E_b}{\hbar\omega})$, only valid for low doping levels as, in this range, we are near the frontier from strong to intermediate electron-phonon coupling [36,37], we can additionally estimate the polaronic bandwidth reduction of W_0 by using the appropriate constants [38]. The excellent agreement with the measured data obtained (marked with an arrow in fig. 7) indicates that the association of T_c^M with W is a reliable assumption.

Conclusions. – The empirical law that determines the T_c of $T_{1-y}D_y\text{MnO}_3$ compounds as a function of $\langle r_A \rangle$ and the doping level y was experimentally extended, using our data and data already published in the literature for dopings in the $0.15 \leqslant y \leqslant 0.33$ range. For these compounds and in the pressure range where a linear dependence of $\langle r_A \rangle$ with pressure is still valid, the influence of cationic disorder and the pressure sensitivity of T_c was quantitatively described by an empirical relation. This expression can be derived from the DE model, where the T_c^M parameter would be related to the polaronic-modified bandwidth, while a second multiplying term should be included, controlled by $\langle r_A \rangle$ and associated with an effective doping level fraction.

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REFERENCES

[1] Hwang H. Y., Cheong S.-W., Radaelli P. G., Marezio M. and Batlogg B., *Phys. Rev. Lett.*, **75** (1995) 914.
[2] Radaelli P. G., Iannone G., Marezio M., Hwang H. Y., Cheong S.-W., Jorgensen J. D. and Argyriou D. N., *Phys. Rev. B*, **56** (1997) 8265.
[3] Dagotto E., Hotta T. and Moreo A., *Phys. Rep.*, **344** (2001) 1.
[4] Zener C., *Phys. Rev.*, **82** (1951) 403.
[5] Anderson P. W. and Hasagawa H., *Phys. Rev.*, **100** (1955) 675.
[6] Jaime M., Hardner H. T., Salamon M. B., Rubinstein M., Dorsey P. and Emin D., *Phys. Rev. Lett.*, **78** (1997) 951.
[7] Jaime M., Salamon M. B., Rubinstein M., Treece R. E., Horwitz J. S. and Chrisey D. B., *Phys. Rev. B*, **54** (1996) 11914.
[8] Babushkina N. A., Belova L. M., Gorbenko O. Y., Kaul A. R., Bosak A. A., Ozhogin V. I. and Kugel K. I., *Nature*, **385** (1998) 236.
[9] Hwang H. Y., Palstra T. T., Cheong S.-W. and Batlogg B., *Phys. Rev. B*, **52** (1995) 15046.
[10] Neumeier J. J., Hundley M. F., Thompson J. D. and Heffner R. H., *Phys. Rev. B*, **52** (1995) R7006.
[11] Meneghini C., Levy D., Mobilio S., Ortolani M., Nunez-Reguero M., Kumar A. and Sarma D. D., *Phys. Rev. B*, **65** (2001) 012111.
[12] Sacchetti A., Postorino P. and Capone M., *New J. Phys.*, **8** (2006) 3.
[13] Rivadulla F., Otero-Leal M., Espinosa A., de Andrés A., Ramos C., Rivas J. and Goodenough J. B., *Phys. Rev. Lett.*, **96** (2006) 016402.
[14] Dey P., Nath T. K. and Taraphder A., *Appl. Phys. Lett.*, **91** (2007) 012511.
[15] Millis A. J., Darling T. and Migliori A., *J. Appl. Phys.*, **83** (1997) 1588.
[16] Moritomo Y., Kuwahara H. and Tokura Y., *J. Phys. Soc. Jpn.*, **66** (1997) 556.
[17] Laukhin V., Fontcuberta J., Garcia-Muñoz J. L. and Obradors X., *Phys. Rev. B*, **56** (1997) R10009.
[18] Lorenz B., Heilman A. K., Wang Y. S., Xue Y. Y., Chu C. W., Zhang G. and Franck J. P., *Phys. Rev. B*, **63** (2001) 144405.
[19] Ulyanov A. N., Gusakov G. V., Borodin V. A., Starostyuk N. Y. and Mukhin A. B., *Solid State Commun.*, **118** (2001) 103.
[20] Garbarino G., Acha C., Levy P., Koo T. Y. and Cheong S.-W., *Phys. Rev. B*, **74** (2006) 100401.
[21] Cui C. and Tyson T. A., *Phys. Rev. B*, **70** (2004) 094409.
[22] Shannon R. D., *Acta Crystallogr. A*, **32** (2003) 751.

[23] Ulyanov A. N., Maksimov I. S., Nyeanchi E. B., Medvedev Y. V., Yu S. C., Starostyuk N. Y. and Sundqvist B., *J. Appl. Phys.*, **91** (2002) 7739.

[24] Fontcuberta J., Laukhin V. and Obradors X., *Appl. Phys. Lett.*, **72** (1998) 2607.

[25] Fujishiro H., Ikebe M., Kikuchi T. and Ozawa H., *Physica B*, **281-282** (2000) 491.

[26] Moritomo Y., Asamitsu A. and Tokura Y., *Phys. Rev. B*, **51** (1995) 16491.

[27] Mandal P. and Ghosh B., *Phys. Rev. B*, **68** (2003) 014422.

[28] Rodriguez-Martinez L. M. and Attfield J. P., *Phys. Rev. B*, **54** (1996) R15622.

[29] De Teresa J. M., Ibarra M. R., Blasco J., García J., Marquina C., Algarabel P. A., Arnold Z., Kamenev K., Ritter C. and von Helmolt R., *Phys. Rev. B*, **54** (1996) 1187.

[30] Postorino P., Congeduti A., Dore P., Sacchetti A., Gorelli F., Ulivi L., Kumar A. and Sarma D. D., *Phys. Rev. Lett.*, **91** (2003) 175501.

[31] Cui C., Tyson T. A., Zhong Z., Carlo J. P. and Qin Y., *Phys. Rev. B*, **67** (2003) 104107.

[32] Otero-Leal M., Rivadulla F. and Rivas J., *Phys. Rev. B*, **76** (2007) 174413.

[33] Bean C. P. and Rodbell D. S., *Phys. Rev.*, **126** (1962) 104.

[34] Millis A. J., Littlewood P. B. and Shraiman B. I., *Phys. Rev. Lett.*, **74** (1995) 5144.

[35] Medarde M., Mesot J., Lacorre P., Rosenkranz S., Fischer P. and Gobrecht K., *Phys. Rev. B*, **52** (1995) 9248.

[36] Alexandrov A. S., Kabanov V. V. and Ray D. K., *Phys. Rev. B*, **49** (1994) 9915.

[37] Garbarino G., Acha C., Vega D., Leyva G., Polla G., Martin C., Maignan A. and Raveau B., *Phys. Rev. B*, **70** (2004) 014414.

[38] De Teresa J. M., Dörr K., Müller K. H., Schultz L. and Chakalova R. I., *Phys. Rev. B*, **58** (1998) R5928.