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Jahn-Teller vibrational anisotropy determines the magnetic structure in orthomanganites

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It is demonstrated that a critical Mn-O-Mn angle determines a crossover between Q_2 and Q_3 Jahn-Teller vibrational modes in O' orthomanganites, which is coincident with a sudden variation of the ferromagnetic moment. The role played by the vibrational anisotropy Q_3/Q_2 in charge/orbital ordering is discussed. Our results suggest that vibrational anisotropy can be at the origin of the phase separation mechanism that determines colossal magnetoresistance in low-T_C manganites.

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The nature of the magnetic structure in ferromagnetic Mn-based perovskites has been studied for a long time. The first key words on the subject established the double-exchange (DE) mechanism[1] as the basis of the magnetic coupling between Mn moments. Nevertheless, with the increase of research activity on these materials it has become evident that the DE picture needs to be amended, as it does not predict some of the complex magnetic structures (like charge/orbital ordering CO/OO, insulating-ferromagnetic behavior, etc.) found in the phase diagram of these materials. A scenario including not only DE but also the electron-lattice coupling,[2,3] electronic phase separation,[4–6] and on-site Coulomb and superexchange interactions, seems to be more adequate for a deep knowledge of these systems. The link between cooperative Jahn-Teller (JT) deformations and electron-phonon coupling has been studied from the theoretical point of view.[2] But in these works, the rotation of the MnO_6 octahedra, which bends the Mn-O-Mn angle (θ) and produces the observed $Pbnm$ symmetry, is neglected. The noninclusion of this lattice distortion might constitute an oversimplification of the problem. The e_g degeneracy of Mn^{3+} ions can be removed by a local JT distortion that, at high concentrations of this ion, can be static and cooperative, changing the orthorhombic axial ratio from $c/a > \sqrt{2}$ to $c/a < \sqrt{2}$ ($O' - Pbmn$). Orthomanganites have a vibrational degeneracy arising from the fact that there are two stable configurations (called Q_2 and Q_3 modes) geometrically equivalent, and therefore with the same energies able to split the twofold degenerate e_g state.[7] In this paper we argue that the cooperative rotation of the MnO_6 octahedra determines vibrational anisotropy between JT modes (Q_3/Q_2) and, subsequently, the competition between DE and the instability associated with electron-lattice coupling in the system $(La,Pr)_{2/3}(Ca,Sr)_{1/3}MnO_3$. The result might be a notable variation of the macroscopic magnetic behavior of the material.

$Pr_{2/3}Ca_{1/3}MnO_3$, $La_{2/3}Ca_{1/3}MnO_3$, and $Pr_{2/3}Sr_{1/3}MnO_3$ were obtained by conventional solid-state reaction. The election of these particular compounds allows us to explore a wide range of the T_C vs $\langle r_A \rangle$ phase diagram of manganites. While $Pr_{2/3}Ca_{1/3}MnO_3$ ($\theta = 157°$) is CO below 225 K and develops a small ferromagnetic (FM) moment at low temperatures ($T_C = 110$ K), $La_{2/3}Ca_{1/3}MnO_3$ ($\theta = 161°$) and $Pr_{2/3}Sr_{1/3}MnO_3$ ($\theta = 162°$) present the typical metal-insulator transition at T_C and nearly the full saturation moment at low temperature. Room-temperature ($T > T_C$ in every case) structural parameters were extracted from a careful Rietveld analysis of x-ray diffraction patterns. The lattice parameters obtained by x rays have been checked with those extracted from neutron diffraction experiments available in the literature. The structure is $O' - Pbnm$ for all of them.

Kanamori[8] showed that the ratio Q_3/Q_2 present in a given static distortion is

$$\tan \Phi = \frac{(2/\sqrt{6})(2m - l - s)}{\pm (2/\sqrt{2})(l - s)},$$

where s and l are the short and long Mn-O bond lengths pointing along the [100] and [010] axes alternatively, m is the bond length along [001], $s \leq m \leq l$, and Φ is the angle between the state vectors and the Q_2 axis. In the high-anisotropy limit, $m = s$, only the Q_3 mode is present ($\Phi = 30$), while for the low-anisotropy case $\Phi = 0$ there is only Q_2. In a real situation, the orbital degeneracy is removed by resonance between these two modes and a contribution from each mode is present.

From the l, m and s obtained from x-ray analysis of our samples, the values of Φ were derived for each case. While $Pr_{2/3}Ca_{1/3}MnO_3$ is near the high-anisotropy limit ($\Phi \approx 22°$), the values of $\Phi \approx 3°$ for $La_{2/3}Ca_{1/3}MnO_3$ and $\Phi \approx 5°$ for $Pr_{2/3}Sr_{1/3}MnO_3$ indicate only a modest anisotropy. As we kept constant the electronic number of carriers, the only difference between these compounds is the variation of θ as a consequence of the mean radius at the rare-earth position $\langle r_A \rangle$.

Our results suggest a dependence of vibrational anisotropy with cooperative buckling of MnO_6 octahedra. In order to confirm our hypothesis we calculate the values of Φ for other manganites (keeping $x = \frac{1}{3}$) from crystallographic data available in the literature. For the low-angle compound $Tb_{2/3}Ca_{1/3}MnO_3$ ($\theta \approx 150°$) (Ref. 9) $\Phi \approx 23°$, while for $(La_{0.78}Pr_{0.22})_{2/3}Ca_{1/3}MnO_3$ ($\theta \approx 159.5°$) (Ref. 10) $\Phi \approx 2.5°$.

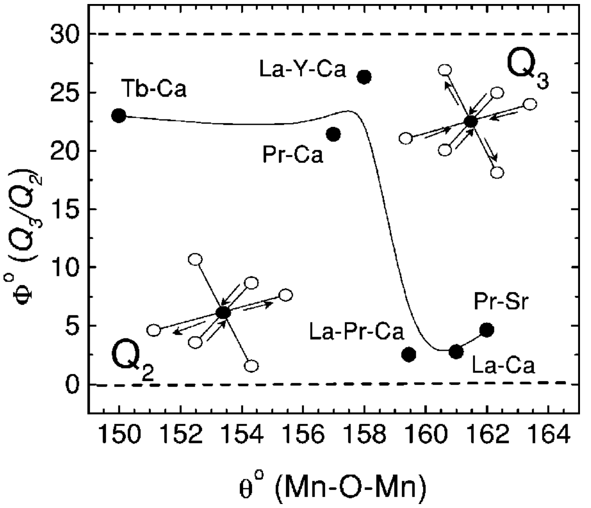

FIG. 1. Variation of the Jahn-Teller vibrational anisotropy as a function of the Mn-O-Mn angle (the line is a guide to the eye). Around $\theta_c \sim 158°$ a critical crossover between compounds with high and low JT anisotropy takes place.

The results, along with those for $(La_{0.775}Y_{0.225})_{2/3}Ca_{1/3}MnO_3$ (Ref. 11), are plotted in Fig. 1.

Our results show the existence of a critical Mn-O-Mn angle (θ_c) that separates high- and low-anisotropy compounds. From Fig. 1 it follows that this θ_c is in the interval 158°–159°, which corresponds to $\langle r_A \rangle \sim 1.19$ Å (calculated for nine fold coordination from values tabulated in Ref. 12). In low-angle compounds ($\theta < \theta_c$) the predominant mode is Q_3, while only a small contribution of this mode is present when $\theta > \theta_c$ (Q_2 is the predominant mode in this case).

In fact, neutron-diffraction experiments carried out by Jirák *et al.*[13] suggested that the only normal coordinate of the MnO_6 distortion which is non-negligible in the system $Pr_{1-x}Ca_xMnO_3$ ($x < 0.3$, $O' - Pbnm$, $\theta < \theta_c$) is that which characterizes tetragonal elongation, i.e., the Q_3 mode. On the other hand, Sapathy *et al.*[14] established that the Q_2 JT mode is responsible for the gap opening in Mn e_g bands of $La_{1-x}Ca_xMnO_3$. This supports the hypothesis of a crossover between Q_2 and Q_3 modes.

But, how does vibrational anisotropy affect magnetic ordering in manganites? Capone, Feinberg, and Grilli[15] found that the ratio between Q_2 and Q_3 modes plays a fundamental role in the magnetic structure of O'-$LaMnO_3$. They calculated, by exact diagonalization, the superexchange couplings of both e_g and t_{2g} orbitals and found that the system is close to the point where the FFA (ferromagnetic *ab* planes coupled antiferromagnetically along the *c* axis) layered magnetic structure becomes unstable towards FFF coupling. But they vary the ratio Q_3/Q_2 arbitrarily in their simulations and explicitly neglect the tilting of the MnO_6 octahedra.

The Q_3 mode completely splits the $d_{x^2-y^2}$ and d_{z^2} orbitals, and the high-anisotropy limit (only Q_3) is characterized by a cooperative d_{z^2}-OO in the *ab* plane with zero electron density along the *c* axis.[7] This OO is responsible for the *A*-type antiferromagnetic (AF) ground state found in $LaMnO_3$ and $PrMnO_3$.[7,13] In mixed-valence manganites, OO is normally associated with CO structures, then played against the stabilization of a long-range FM-DE interaction. This prediction has been confirmed by low-temperature magnetic structures of $Tb_{2/3}Ca_{1/3}MnO_3$ and $Pr_{2/3}Ca_{1/3}MnO_3$. In particular, the behavior of $Pr_{2/3}Ca_{1/3}MnO_3$ in the paramagnetic (PM) phase is similar to other manganites with $x \approx 1/3$ but in contrast to what happens, for example, in $La_{2/3}Ca_{1/3}MnO_3$, it undergoes a CO and an AF transition before T_C.[16,17] In the range $T_N < T < T_{CO}$, the JT polarons freeze into a long-range coherent CO/OO superstructure, and below T_N Mn spins in CO regions are AF ordered into pseudo-CE structures.[13,16,18] The overall FM moment results from the competition between FM and AF coupling along the [001] direction, but to discriminate between a canting or an inhomogeneous model (Zener-FM polarones in an AF matrix) is extremely difficult. On the other hand, the Q_2 mode stabilizes a mixture of both $d_{x^2-y^2}$ and d_{z^2} orbitals, and hence the tendency towards OO/CO is less pronounced. As a result, an almost homogeneous FM-DE picture is expected in compounds with $\theta > \theta_c$. If this idea is true, one should expect crossover from small to high values of the average ferromagnetic moment at the Mn site around θ_c. Saturation moments extracted from neutron diffraction at 5 K (from literature) are plotted vs the Mn-O-Mn angle in Fig. 2. The variation of μ_{Mn} fully confirms our hypothesis. It should be noted that a variation of θ of more than 6° far from θ_c does not appreciably change the magnetic moment, but less than 1.5° around θ_c changes $\mu_{Mn} \sim 31\%$, showing the critical character of this crossover.

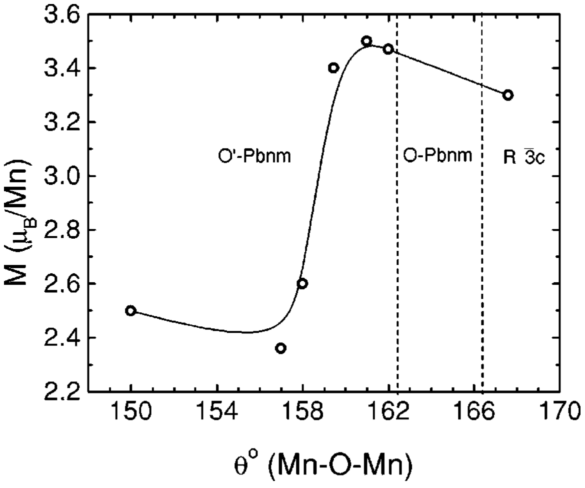

FIG. 2. Ferromagnetic saturation moment at 5 K obtained from neutron-diffraction experiments available in the literature (the line is a guide to the eye). As in the case of vibrational anisotropy, a clear crossover takes place at $\theta_c \sim 158°$. A low magnetic moment is associated with the predominance of the Q_3 mode and a high magnetic moment with the Q_2 mode.

It seems that the contribution of the Q_3 mode to vibrational anisotropy could be playing a role in the phase separation mechanism, now believed to underlay CMR in low-T_C manganites. The existence of two competing phases needed to stabilize the phase-separated scenario is provided in our case by the contribution of Q_3 and Q_2 in each point of Fig. 1. Although low- (high-) angle manganites represent a high- (low-) vibrational anisotropy situation, not one of the samples showed in this figure reaches the $\Phi=30°$ or $\Phi=0°$ corresponding to a pure high- and low-anisotropy limit, respectively, i.e., a certain contribution of each mode is present in every sample (although the ratio between the modes is severely modified by θ).

Uehara *et al.*[5] observed a sharp decrease of the saturation moment at 5 K in $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ (3/8=0.375, very close to 1/3=0.333) for $x \geqslant 0.3$, i.e., $\langle r_A \rangle \sim 1.337$ Å for coordination XII. This value corresponds to 1.191 Å in a ninefold coordination, exactly the value determined for us at θ_c. The μ_{Mn} vs $\langle r_A \rangle$ curve shows a universal character as it does not depend on the nature of the ions at the rare-earth position. This coincidence reinforces our idea about the implication of JT vibrational anisotropy in the phase-separation mechanism. It should be noticed that the values of μ_{Mn} obtained by Uehara *et al.* for low $\langle r_A \rangle$ compounds are smaller than those obtained for us from available literature. However, the drop of μ_{Mn} with $\langle r_A \rangle$, which is the key point of the subject, is the same in both cases.

The anomalies observed around T_C in the M vs H curves of $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ ($x \geqslant 0.3$) were also taken as a direct indication of the two-phase coexistence.[5] We recently reported the existence of these anomalies in the case of $La_{2/3}Ca_{1/3}MnO_3$ and the suppression of such effects when increasing $\langle r_A \rangle$ in the system $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$.[19] This observation suggests the existence of phase separation on a reduced scale even for larger $\langle r_A \rangle$ compounds. Very recently, μSR data by Heffner *et al.*[20] showed the existence of a spatially inhomogeneous spin-lattice relaxation near the FM state of $La_{2/3}Ca_{1/3}MnO_3$, the length scale of the inhomogeneity being $\leqslant 30$ Å.

In Ref. 5 it is also pointed out that the phase separation relevant to CMR is the one between $x=\frac{1}{2}$-type CO and FM states with submicrometric scale length. From neutron-diffraction experiments and following Goodenough's approach,[21] Cox *et al.*[18] reasoned that the pseudo-CE structure found in $Pr_{2/3}Ca_{1/3}MnO_3$ can be obtained from a CO structure with orbital ordering in the (001) plane, but with a net FM interlayer coupling. This gives rise to a magnetic structure very similar to the three Mn sublattices found in $La_{0.5}Ca_{0.5}MnO_3$.[22] On the other hand, Khomskii and Van den Brink[23] recently demonstrated that the CO/OO found in half-doped manganites can be stabilized by anharmonic effects that favor the local elongation of $Mn^{3+}O_6$ octahedra. This anharmonicity adds an extra term in the potential energy of the form $\zeta \cos 3\Theta$, the more probable stable state favoring $\cos 3\Theta=1$, i.e., $\Theta=0$, $\pm 2\pi/3$, which correspond to the high-anisotropy term Q_3 with the tetragonal distortion along the z, x, and y axes, respectively (for a complete discussion see Refs. 8 and 23). These authors remark on the role played by this factor in other situations like the stripe phases in the overdoped regime. Then, the CO/OO induced by the Q_3 mode can be similar to that present in $x=1/2$, and hence could be at the origin of CO phases in the inhomogeneous phase separation model of low-T_C manganites.

On the other hand, Moreo *et al.*[24] showed how the introduction of disorder on hopping and exchange amplitudes near a first-order transition of nondisordered strongly coupled systems leads to the existence of large coexisting metallic and insulating clusters with equal electronic density. For the scenario represented in Fig. 1, the proximity of the discontinuous transition at θ_c could lead to a phase separation, where larger clusters in low-angle manganites are induced by the lower values of W with respect to high θ compounds. However, samples like that of Tb-Ca are very far from the first-order transition, and there are no available calculations about how near to the first-order transition one must be to observe this effect.

Yunoki *et al.*[25] recently demonstrated that half-doped manganites easily stabilize a CO/OO state in the presence of a large electron-phonon coupling. The strength of the electron-phonon interaction is characterized in their simulation by a dimensionless parameter λ, previously defined by Millis and co-workers as the ratio of the interaction energy to the electron kinetic energy.[26] Within our hypothesis, a situation of large λ is equivalent to the high anisotropy limit, whereas low-anisotropy compounds show low values of λ. This gives a physical origin to λ and relates it with physical parameters of the system. In fact, Millis[27] has already suggested that different materials should have different values of λ, but he did not give any clue about the origin of this effect in a real system. From neutron-diffraction data at different temperatures for $(La_{0.775}Y_{0.225})_{2/3}Ca_{1/3}MnO_3$ (Ref. 11) we calculated the values of Φ on approaching T_C from above. These results show a reduction in the vibrational anisotropy from $\Phi \sim 26.3°$ at 300 K to $\Phi \sim 17.3°$ at 140 K, where a μ_{Mn} starts to growth. The reduction of the contribution of the Q_3 mode through T_C is equivalent to the reduction in λ produced by the spin alignment in the FM state (or by the effect of a magnetic field). We think that the different coupling energies between e_g electrons and the Q_2/Q_3 modes should be considered separately in theoretical simulations. In this case λ should emerge naturally as a function $Q_3/Q_2 = f(\text{Mn-O-Mn})$. We would like to mention that after the submission of this paper, we were aware of the existence of a review[28] in which the possibility of different coupling constants of the e_g electrons with Q_2 and Q_3 vibrational modes is suggested, in perfect accordance with our experimental findings.

In summary, we have demonstrated the existence of a critical Mn-O-Mn angle at which a crossover for the Q_3/Q_2 ratio takes place in low-T_C orthomanganites. Such crossover is coincident with a critical variation of the average ferromagnetic moment of the Mn sublattice, which demonstrates the crucial role played by the JT vibrational anisotropy in the final magnetotransport behavior of low-T_C orthomanganites. This demonstration constitutes, to the best of our knowledge, the first experimental correlation between the Q_3/Q_2 ratio and the Mn-O-Mn angle for a fixed carrier concentration and provides a possible explanation for the phase-separation mechanism proposed for the CMR. Our results also give a reasonable explanation for the origin for the electron-phonon coupling parameter λ.

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