Jahn-Teller Phonon Anomaly and Dynamic Phase Fluctuations in $La_{0.7}Ca_{0.3}MnO_3$

Jiandi Zhang,[1] Pengcheng Dai,[2] J. A. Fernandez-Baca,[2] E. W. Plummer,[2,3] Y. Tomioka,[4] and Y. Tokura[4,5]

[1]*Department of Physics, Florida International University, Miami, Florida 33199*

[2]*Solid State Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee 37831*

[3]*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996*

[4]*Joint Research Center for Atomic Technology (JRCAT), Tsukuba 305-0046, Japan*

[5]*Department of Applied Physics, University of Tokyo, Tokyo 113-0033, Japan*

(Received 18 October 2000)

Inelastic neutron scattering was used to study the temperature (T) dependence of the lattice excitations in $La_{0.7}Ca_{0.3}MnO_3$. An optical Jahn-Teller phonon exhibits continuous but anomalous damping with increasing temperature in the ferromagnetic-metallic phase and collapses above the Curie temperature T_C (240 K). We attribute this anomaly to the growing *dynamic* phase segregation as $T \rightarrow T_C$, thus providing evidence of local fluctuations associated with the short-range polaron or charge/orbital ordering in the ferromagnetic-metallic state.

DOI: 10.1103/PhysRevLett.86.3823 PACS numbers: 71.30.+h, 61.12.–q, 63.20.Dj, 75.30.Vn

It is known that the richness of the novel properties of colossal magnetoresistance (CMR) manganites originates from the strong interplay between the charge, lattice, orbital, and spin degrees of freedom found in these systems [1]. Although several mechanisms, involving double-exchange (DE) [2], electron-phonon interactions [3], and electron-electron correlations [4], have been proposed to explain the observed CMR effect in this class of materials, a clear understanding of its microscopic origin is still lacking. In particular, if dynamic Jahn-Teller (JT) distortions of the MnO_6 octahedra are crucial to the metal-to-insulator transition (MIT) and the CMR effect [5], the lattice vibrations associated with such distortions (i.e., the so-called *JT phonons*) would be expected to exhibit unusual behavior across the MIT/magnetic transition temperature (T_C). The T dependence of the optical phonons in $La_{1-x}Ca_xMnO_3$ [6] and in $La_{1-x}Sr_xMnO_3$ [7] has been studied with infrared reflectivity and optical conductivity, and the observed energy shifts across T_C [6] were attributed to a strong electron-phonon interaction. Recently, Reichardt and Braden [8] have measured the full phonon dispersion curves of $La_{1-x}Sr_xMnO_3$ ($x = 0.2$ and 0.3) using inelastic neutron scattering. They observed an anomalous zone boundary softening of the high-energy optical phonon branches, which would indicate a tendency to JT instability and charge ordering. However, how these phonons evolve with temperature across the phase transition at T_C is still unclear.

In this work, we use inelastic neutron scattering to demonstrate that the JT phonons in $La_{0.7}Ca_{0.3}MnO_3$ do indeed exhibit an abnormal behavior across the MIT/magnetic transition temperature. As in the other CMR manganites, the optimally doped $La_{0.7}Ca_{0.3}MnO_3$ exhibits a ferromagnetic (FM) to paramagnetic (PM) transition and a simultaneous MIT at $T_C \cong 240$ K. While its structure maintains the slightly distorted cubic perovskite (orthorhombic-*pnma*) symmetry, there are small incoherent dynamic distortions [9] across T_C. In general, the electron-phonon coupling across T_C should renormalize the phonon energies without drastically changing their intensities. This should be especially true for the high-energy optical phonons because the change in their population factors is negligible across T_C. Surprisingly, we have discovered that one of the Mn-O stretching JT phonon modes shows anomalous damping with increasing temperature in the FM phase and vanishes around T_C, in concurrence with FM ordering and metallicity of the system. Such drastic T-dependent damping cannot be explained with simple arguments based on the dynamic JT distortions at individual JT sites. We argue that this behavior may be directly related to decoherence effects due to the growing *dynamic phase fluctuations* of the short-range polaron or charge/orbital ordering associated with JT distortion in the FM metallic phase matrix as $T \rightarrow T_C$.

The single crystal of $La_{0.7}Ca_{0.3}MnO_3$ (~ 0.4 cm^3 in volume) used for this study was grown by the floating zone technique [10]. The experiments were performed using the HB-1, HB-2, and HB-3 triple-axis spectrometers at the High-Flux Isotope Reactor at the Oak Ridge National Laboratory. The final neutron energy was fixed at $E_F = 13.6$ or 30.5 meV. The analyzers and filters were all pyrolytic graphite (PG) crystals while the monochromator was either PG (002) or Be (101). The components (Q_x, Q_y, Q_z) of the momentum transfer vector $\mathbf{Q}$ are expressed in reciprocal lattice units (rlu) [1 rlu $= 2\pi/a$, where a ($= 3.86$ Å) is the lattice parameter of the pseudocubic unit cell]. Our measurements were made in the constant-momentum-transfer $\mathbf{Q}$ mode, where $\mathbf{Q} = \mathbf{q} + \boldsymbol{\tau}$, and $\boldsymbol{\tau}$ is a reciprocal lattice point. We chose $\boldsymbol{\tau} = \{4, 1, 1\}$ and $\{3,1,0\}$, which are large enough to make the Mn magnetic form factor negligible. This ensures that the measured scattering originates mostly from the lattice vibrations (phonons) rather than from magnetic scattering

(magnons). Although the sample is slightly orthorhombic in both FM and PM phases, the measured phonon branches bear a close resemblance to their analogs in the cubic parent structure. This enables us to simplify our discussion in terms of the cubic notation, providing a greater transparency.

Figure 1 shows the measured phonon dispersion of $La_{0.7}Ca_{0.3}MnO_3$ at $T = 10$ K along the $q = [\xi, 0, 0]$ and $[\xi, \xi, 0]$ directions. For comparison purposes, we also show the measured (open symbols) and calculated phonon energies (solid lines) of $La_{0.7}Sr_{0.3}MnO_3$ by Reichardt and Braden [8]. These phonon branches can be classified into three categories: external, bending, and stretching/breathing modes of MnO_6 octahedra, the building blocks of the perovskite structure. The lowest energy branch $\omega_1 \sim 23$ meV at the Brillouin zone center (Γ point) is the external longitudinal optical (LO) mode, corresponding to the vibration of the La/Ca ions against the MnO_6 octahedra. The branches with zone-center energies of $\sim$37 meV (ω_2^a) and $\sim$45 meV (ω_2^b) are due to the excitation of two JT phonon modes with bending and linear-breathing characters. The highest energy branch ω_3 of 71 meV at Γ corresponds to another JT phonon mode with Mn-O bond stretching character [8]. The corresponding transverse optical modes at the Γ point (with energies of 21, 42, and 72 meV, respectively) have been observed with infrared reflectivity in several CMR materials [6,7]. Another feature with an energy of $\sim$54 meV (ω_2^c) at Γ softens slightly along the [100] direction and merges with the higher energy branch (ω_3) toward the zone boundary. This feature was observed only along the [100] direction in $La_{0.7}Ca_{0.3}MnO_3$ (not in $La_{0.7}Sr_{0.3}MnO_3$ [8]) and its origin is not known. Several weak phonons are also present in our measured spectra (as shown in Fig. 2), reflecting the intrinsic orthorhombic distortion.

The stretching mode ω_3 exhibits an anomalous softening as it approaches the zone boundary along the [100] direction, from $\sim$71 meV at Γ to $\sim$50 meV, similar to that measured in $La_{0.7}Sr_{0.3}MnO_3$ [8]. Similar unusual dispersion of LO phonons have been observed in the doped high-T_C superconducting cuprates [11]. Reichardt and Braden [8] argued that such a softening reflects a tendency to a JT instability, the instability causing JT lattice distortion. However, this mode in $La_{0.7}Ca_{0.3}MnO_3$ does not appear (or has no measurable intensity) in the [110] direction, which is different from that in $La_{0.7}Sr_{0.3}MnO_3$. Furthermore, this mode was not reproduced by the shell model calculations under cubic symmetry (see Fig. 1) [8].

The linear-breathing mode ω_2^b shows a dispersion from 45 meV at Γ to $\sim$71 meV at the zone boundary along the [110] direction, which is greater than that in $La_{0.7}Sr_{0.3}MnO_3$. Also in contrast with the case of

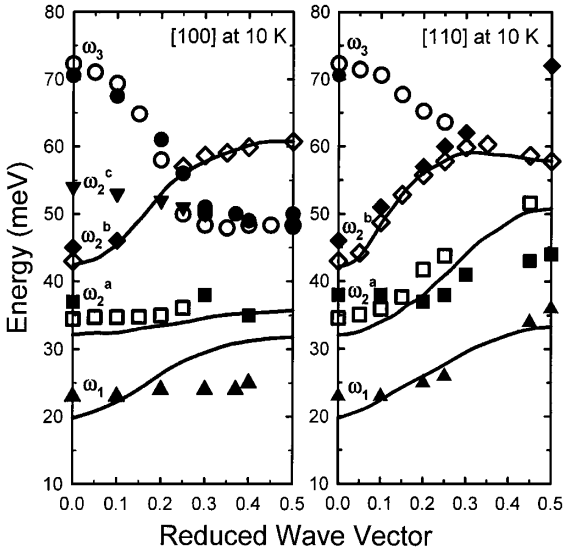

FIG. 1. The measured optical phonon dispersion curves in $La_{0.7}Ca_{0.3}MnO_3$ (solid symbols) at 10 K treated in the notation of the cubic parent structure with inelastic neutron scattering, as compared with these in $La_{0.7}Sr_{0.3}MnO_3$ (open symbols) at 15 K (Ref. [8]). Solid lines were the results calculated by a screen shell model from Ref. [8] under the cubic symmetry.

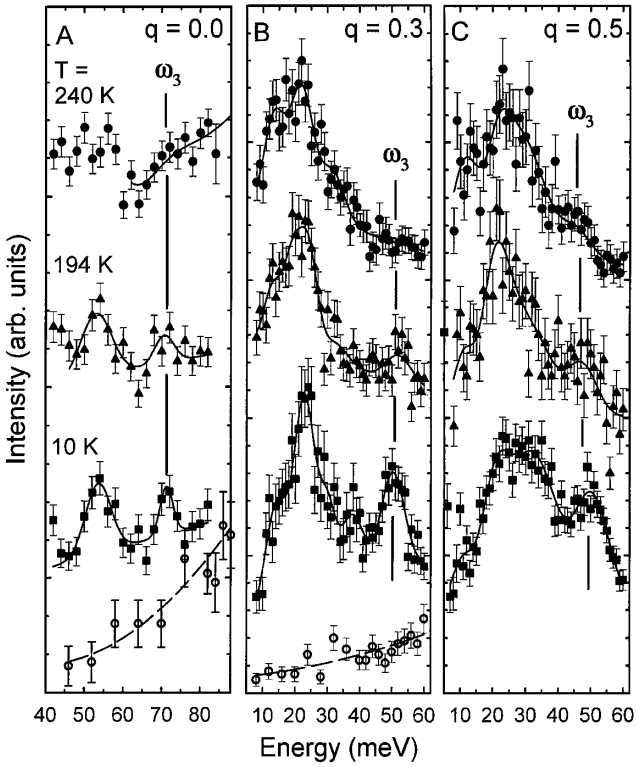

FIG. 2. The temperature-dependent inelastic neutron scattering spectra of $La_{0.7}Ca_{0.3}MnO_3$ (solid symbols) and background (open symbols) at the zone center Γ (A: $\mathbf{Q} = \{4, 1, 1\}$), the middle of the zone (B: $\mathbf{Q} = \{3.7, 1, 1\}$), and the zone boundary (C: $\mathbf{Q} = \{3.5, 1, 1\}$) along [1,0,0] direction. The JT phonon mode (ω_3), which exhibits an anomalous temperature dependence, is marked. The solid curves are the results of several Gaussian functions drawn as a guide to the eye.

$La_{0.7}Sr_{0.3}MnO_3$, this mode becomes increasingly difficult to observe along the [100] direction and eventually disappears when approaching the zone boundary.

We performed constant-momentum-transfer $\mathbf{q}$ scans with several particular $\mathbf{q}$ values along the [100] and [110] directions at various temperatures. Here, we focus on special $\mathbf{q}$ points including the zone center (Γ), the middle of the zone, and the zone boundary. Figure 2 presents the T dependence of scans at $\mathbf{q} = (0, 0, 0)$ [Fig. 2(A)], $\mathbf{q} = (0.3, 0, 0)$ [Fig. 2(B)], and $\mathbf{q} = (0, 0, 0.5)$ [Fig. 2(C)] along the [100] direction, especially focusing on the evolution of the stretching mode (ω_3). On the other hand, Fig. 3 shows the T dependence of scans at $\mathbf{q} = (0, 0, 0)$ [Fig. 3(A)] and $\mathbf{q} = (0.5, 0.5, 0)$ [Fig. 3(B)] along the [110] direction, focusing on the evolution of the linear-breathing mode (ω_2^b). In general these phonons exhibit small energy shifts with increasing temperature from 10 K to T_C. The ω_2^b mode (see Fig. 3), as the external mode (ω_1), exhibits no drastic change when $T \rightarrow T_C$, though it shows a quite large dispersion in the [110] direction. We did not observe new phonon features with increasing temperature, indicating no static lattice distortion with changing symmetry across T_C, consistent with early crystal structure characterizations on this system [9]. *However, the most striking discovery is that the stretching mode ω_3 exhibits anomalous damping with increasing temperature.* As shown in Fig. 2(A), the phonon peaks at Γ, at $\mathbf{q} = (0, 0, 0.3)$, and at the zone boundary, are severely damped and eventually disappear when $T \rightarrow T_C$. To further address this anomalous behavior, we plot in Fig. 4(A) the T dependence of the intensity of this mode in the middle of the zone [$\mathbf{q} = (0.3, 0, 0)$] and at the zone boundary [$\mathbf{q} = (0.5, 0, 0)$]. The vanishing of this JT phonon feature coincides with the disappearance of FM ordering and metallicity of the system.

There are several possible scenarios to account for the T-dependent phonon anomaly. It is conceivable that the observed anomaly is related to the incoherent dynamic JT distortion across T_C [9]. An anomalous increase in the crystallographic Debye-Waller factor was observed in $La_{1-x}Ca_xMnO_3$ as $T \rightarrow T_C$, indicating a drastic enhancement in the incoherent distortion at individual J-T sites near T_C [9]. This will diminish the phonon peak intensity due to the *Debye-Waller factor* $exp(-2W)$ in the scattering cross section. However, only a $\leq$25% decrease of the phonon intensity could be expected by our simple estimation as T increases from 10 K to T_C. Thus incoherent lattice distortion is not enough to explain the unusual disappearance of this mode. Another possibility would be the magnon-phonon interaction associated with a strong magnetoelastic coupling [12]. In principle, this coupling should affect both the phonon energy and lifetime due to the phonon renormalization. Yet, it is difficult to explain this unusual damping without obvious energy shifting.

Another possible explanation is based upon decoherence effects due to the growing *dynamic phase fluctuation* [13] of the short-range polaron (or charge/orbital) ordering or domain associated with JT distortion in the FM metallic phase matrix as $T \rightarrow T_C$. Transport property studies reveal that highly incoherent charge dynamics exists in these materials [14]. Meanwhile, neutron scattering

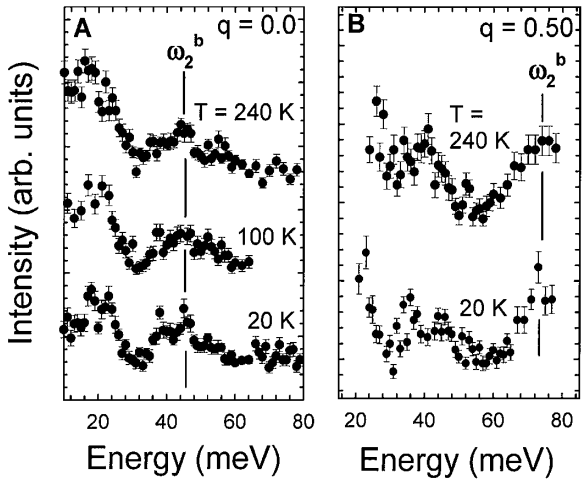

FIG. 3. The temperature-dependent inelastic neutron scattering spectra of $La_{0.7}Ca_{0.3}MnO_3$ at zone center Γ (A: $\mathbf{Q} = \{3, 1, 0\}$) and the zone boundary (B: $\mathbf{Q} = \{3.5, 1.5, 0\}$) along [1,1,0] direction. Note that there is no obvious change of phonon features with increasing temperature.

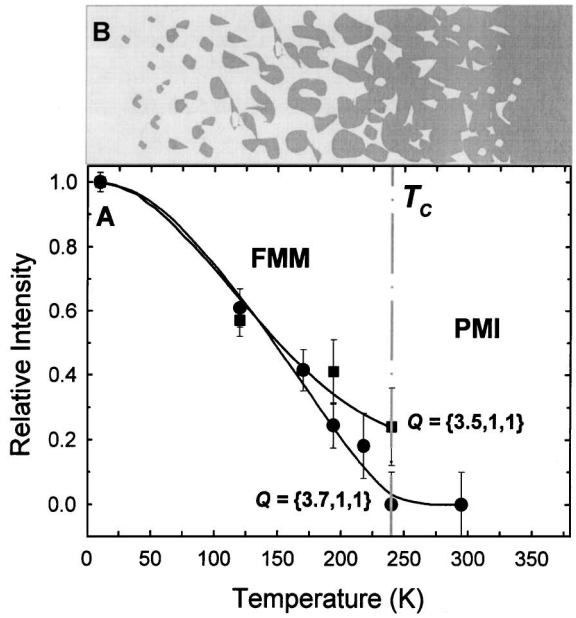

FIG. 4. (A) The relative integrated intensities of the JT breathing phonon mode as a function of temperature at the middle of the zone ($\mathbf{Q} = \{3.7, 1, 1\}$) and the zone boundary ($\mathbf{Q} = \{3.5, 1, 1\}$) along [1,0,0] direction. (B) A schematic illustration of the evolution of dynamic phase segregation with increasing temperature.

demonstrates that quasistatic short-range polaron correlation and charge/orbital ordering exist near and above T_C, and their populations are intimately related to the transport properties [15]. These suggest that the fluctuation of charge/orbital ordering or phase domain may directly account for the incoherent charge and lattice dynamics.

Figure 4(B) shows a schematic illustration for such a dynamic phase fluctuation evolving with increasing temperature. As a *snapshot,* the dark clusters represent these JT domains with short-range polaron (or charge/orbital) ordering, while the gray area the FM metallic phase matrix. In the pure FM metallic phase at low temperature, the system has well-defined phonon bands. Within the FM state but at intermediate temperature, these JT domains start to coexist dynamically with the FM metallic matrix. As the temperature increases, more and more JT domains fluctuate in the system. Consequently, the original JT phonons associated with the pure FM metallic phase become increasingly decoherent and damped. When $T \rightarrow T_C$, the system is largely dominated by the fluctuating JT domains, and the size of these original FM-metallic domains may be even smaller than the thermal coherent length of these original phonons. As a result, these relevant phonons will collapse at T_C as we observed for the particular JT stretching mode. The reason why this stretching mode would be especially sensitive to this dynamic phase fluctuation in the system can be understood based upon the two important facts. First, the anomalous zone boundary softening indicates its special relevance to JT instability or local JT distortions that cause the local JT insulating phase. Furthermore, the observed drastic damping of this mode is in the [100] direction. This direction is also the most relevant Mn-O-Mn bonding direction for e_g-electron hopping under the DE interaction, thus sensitive to any local lattice/electronic fluctuation.

In summary, we have studied the phonon band structure and the T-dependent behavior of some optical phonons in $La_{0.7}Ca_{0.3}MnO_3$. We discover that one of the JT stretching phonons along the Mn-O-Mn bonding direction shows anomalous damping as the temperature approaches T_C and collapses above T_C. We argue that this anomaly is the decoherent effects of the local dynamic phase fluctuation associated with short-range polaron or charge/orbital orderings when the system approaches T_C.

We thank S. J. L. Billinge, M. Braden, A. R. Bishop, R. M. Nicklow, and W. Reichardt for helpful discussions. This research was supported by JRCAT of Japan, by U.S. DOE under Contract No. DE-AC05-96OR22464 with UT-Battele, LLC, and by NSF DMR-0072998.

[1] *Colossal Magnetoresistive Oxides,* edited by Y. Tokura, (Gordon and Breach Science, New York, 2000), and references therein.
[2] C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, *ibid.* **100**, 675 (1955); P.-G. de Gennes, *ibid.* **118**, 141 (1960).
[3] A. J. Millis *et al.,* Phys. Rev. Lett. **74**, 5144 (1995); H. Röder *et al., ibid.* **76**, 1356 (1996).
[4] C. M. Varma, Phys. Rev. B **54**, 7328 (1996).
[5] A. J. Millis, Nature (London) **392**, 147 (1998).
[6] K. H. Kim *et al.,* Phys. Rev. Lett. **77**, 1877 (1996); A. V. Boris *et al.,* Phys. Rev. B **59**, R697 (1999).
[7] Y. Okimoto *et al.,* Phys. Rev. B **55**, 4206 (1997).
[8] W. Reichardt and M. Braden, Physica (Amsterdam) **263B**, 416 (1999).
[9] P. Dai *et al.,* Phys. Rev. B **54**, 3694 (1996); P. G. Radaelli *et al.,* Phys. Rev. B **56**, 8265 (1997); C. H. Booth *et al., ibid.* **57**, 10 440 (1998).
[10] T. Okuda *et al.,* Phys. Rev. B **61**, 8009 (2000).
[11] R. J. McQueeney *et al.,* Phys. Rev. Lett. **82**, 628 (1999); L. Pintschovius and M. Braden, Phys. Rev. B **60**, R15 039 (1999).
[12] H. Y. Hwang *et al.,* Phys. Rev. Lett. **80**, 1316 (1998); J. A. Fernandez-Baca *et al., ibid.* **80**, 4012 (1998); P. Dai *et al.,* Phys. Rev. B **61**, 9553 (2000); N. Furukawa, J. Phys. Soc. Jpn. **68**, 2522 (1999).
[13] It is worth pointing out that this cannot be a static phase separation though a growing static phase inhomogeneity with increasing temperature could also cause the damping of phonons. We would expect a new phonon mode induced in a static inhomogeneous phase near T_C as compared with the pure FM metallic phase at low temperature.
[14] T. Okuda *et al.,* Phys. Rev. Lett. **81**, 3203 (1998); R. D. Merithew *et al., ibid.* **84**, 3442 (2000); B. Raquet *et al., ibid.* **84**, 4485 (2000); M. Jaime *et al.,* Phys. Rev. B **60**, 1028 (1999).
[15] P. Dai *et al.,* Phys. Rev. Lett. **85**, 2553 (2000); R. H. Heffner *et al., ibid.* **85**, 3285 (2000); C. P. Adams *et al., ibid.* **85**, 3954 (2000).