I. INTRODUCTION

Interplay between the charge, spin, and lattice degrees of freedom in perovskite manganites results in a multitude of unconventional properties of fundamental as well as practical interest. Ferromagnetic alignment of Mn core spins appears at some stoichiometry entries due to the double exchange interaction and the ferromagnetic-paramagnetic (FM) transition in these systems is accompanied by large magnetoresistance (MR). As predicted by theory, polarons forming and condensing above the FM transition temperature, $T_c$, have been observed by neutron scattering in La$_{0.7}$Ca$_{0.3}$MnO$_3$ and other manganites exhibiting colossal magnetoresistance (CMR) [1][2]. Trapping of conduction electrons by these polarons is held responsible for the CMR effect. While the presence of polarons above $T_c$ demonstrates that electron-phonon coupling due to the Jahn-Teller effect is crucial to understanding the essential physics, relatively little is known about phonons in these materials.

"113" manganites such as La$_{1-x}$Ca$_x$MnO$_3$ and La$_{1-x}$Sr$_x$MnO$_3$ have a cubic perovskite structure except for a rotation of the MnO$_6$ octahedra, which doubles the unit cell. In this paper we will use the notation based on the cubic unit cell of the undistorted structure, which makes the analysis easier to understand. Use of this notation requires folding in extra phonon branches that arise from the doubled unit cell. For example, some phonons observed only at the zone boundary in the undistorted structure have nonzero structure factor at the zone center in the distorted structure, etc.) A previous study of oxygen phonons in La$_{0.7}$Sr$_{0.3}$MnO$_3$ found anomalous downward dispersion of the bond-stretching vibration in the (1 0 0) direction, but it did not examine effects of interactions of these vibrations with the folded-in branches allowed by the tilt of the octahedra.

According to the presently accepted view of the physics of the ferromagnetic manganites, the strongest temperature dependence is observed for the Jahn-Teller modes, whose wavevectors are (0 0 0.5) and (0.5 0.5 0). But investigations of La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Sr$_{0.3}$MnO$_3$ found that these phonons did not have strong temperature dependence. Instead, a significant intensity loss on raising the temperature towards the FM transition was reported for phonons with wavevectors dispersing in the (1 0 0) direction. These results motivated us to go beyond the study of Reznik and Braden. We measured phonon dispersions with higher resolution where possible and identified eigenvectors of $q = (0 0 0)$ phonons in La$_{0.7}$Sr$_{0.3}$MnO$_3$ including interactions with the folded-in branches into the analysis. Although the crystals are twinned, the (1 0 0) direction is the same for the two domains.
II. EXPERIMENTAL AND CALCULATION DETAILS

The experiments were carried out on the triple-axis spectrometer IT located at the ORPHEE reactor using doubly focusing Cu111 and Cu220 monochromator crystals and PG002 analyzer xed at 13.7, 14.8, or 30.5 m eV. Our samples were two high-quality single crystals of La$_{0.7}$Sr$_{0.3}$MnO$_3$ with the FM transition temperature measured at 355 K. The volume of each crystal was 0.5 cm$^3$. The results were the same for the two crystals. All measurements were performed in the ferromagnetic phase at 100 K (we did not go to lower temperatures for technical reasons). Since the FM transition temperature is much higher, we expect to get the same results at lower temperatures. This was confirmed by repeating some scans at 12 K.

We performed measurements in several Bril loul zones and, guided by shellmodel predictions and symmetry constraints, found by trial and error approximate phonon eigenvectors that correctly give the observed intensities. In this procedure we ignored all transverse atom-atom displacements, since these would not affect longitudinal phonon intensities in the Bril loul zones that were measured. They should exist due to the rhombohedral distortion.

III. CALCULATION RESULTS

Ignoring the rhombohedral distortion of the lattice, we expect to observe two optical oxygen branches intrinsic to the cubic perovskite structure above 35 m eV. These are the bond-stretching and bond-bending modes. The rhombohedral distortion doubles the unit cell along one of the (111) directions and thus the number of phonon branches is expected to double as well. Shellmodel calculations show that the bond-bending and the bond-stretching branches should survive in the distorted structure, plus two additional branches of bond-bending character should be folded into the cubic Brillouin zone due to the unit cell doubling. At the zone center one of the folded-in modes has a vanishing structure factor, whereas the other one has a vanishing structure factor at the zone boundary. Thus there should be three modes with nonzero intensity at the zone center and the zone boundary and four modes in the middle of the zone. According to the model, the original bond-bending branch should disperse upwards, whereas the bond-stretching and the folded-in branches should be approximately at. (See Fig. 1)

Structure factors of the bond-bending and folded-in modes are very sensitive to the value of M n-O-M n bond angle whereas the structure factor of the bond-stretching vibration is not. The bond angle depends on the magnitude of the rhombohedral distortion of the lattice and is reported to be 164$^\circ$ for La$_{0.7}$Sr$_{0.3}$MnO$_3$. In the absence of the rhombohedral distortion, i.e., when the M n-O-M n bond angle is 180$^\circ$, all longitudinal phonon intensities should be proportional to $Q^2$.

IV. EXPERIMENTAL RESULTS

A. Zone Center

We observe the zone center phonons at 42 m eV, 53 m eV, and 72 m eV. (Fig. 2a) According to the shell model these should be the energies of the bond-bending, folded-in, and the bond-stretching modes respectively (Fig. 2b). This assignment can be verified by structure factor calculations for the corresponding polarization patterns. The 42 m eV bond-bending vibration decreases in intensity by a factor of 1.82 (Fig. 2a) while the structure factor of the corresponding (leftmost) polarization pattern in figure 2b gives 2.17. The increase of the 53 m eV phonon intensity from $Q = (400)$ to $Q = (5$
 FIG. 2: (Color online) a) Zone center phonons measured in two Brillouin zones. Resolution was lower at $Q = (5 0 0)$. b) Approximate eigenvectors of the zone boundary modes at 100K deduced from the measured intensities. Mode frequencies left to right are: 42 m eV, 53 m eV, 73 m eV. Only pairs of MnO$_6$ octahedra are shown.

$Q = (0 0 0)$ is 1.42 vs the calculated value of 1.96. The 72 m eV mode intensity increases by a factor of 1.28 vs. the calculated 1.53. Considering that we ignore small deviations from the cubic high-symmetry directions as discussed above as well as small admixtures of other modes, structure factor calculations confirm our assignment.

B. Zone Boundary

$q = (0.5 0 0)$ (zone boundary) is another high-symmetry point of the reciprocal lattice. We performed measurements in different Brillouin zones in order to gain insight into the zone boundary phonon eigenvectors. Three longitudinal oxygen modes appear at 38, 47, and 61 m eV.

We begin the analysis with the 61 m eV phonon. Its intensity decreases with increasing $Q$ and almost vanishes at $Q = (5.5 0 0)$. That is precisely what is expected from the bond-bending zone boundary mode (rightmost polarization pattern in figure 3b) as discussed for the zone center modes. In fact structure factor calculations for this
O-Mn bond angle. Most of the bond-stretching occurs in the octahedra and should decrease with increasing Mn-O-Mn bond angle. Most of the bond-stretching character at the zone boundary is at 47 m eV with a smaller contribution at 38 m eV. These energies are much lower than the prediction of the shell model and indicate strong electron-phonon coupling.

C. Between the Zone Center and the Zone Boundary

Deducing the eigenvectors between the zone center and the zone boundary as was done at the zone center and the zone boundary is much more difficult due to lower symmetry. However, on a qualitative level, this analysis is still useful. Figure 5 shows the phonon spectra at three reduced reciprocal lattice vectors each measured in two Brillouin zones. There are four phonon peaks in agreement with the predictions of the shell model.

We start with the bond-bending branch, which is the easiest one to identify by its intensity decrease towards large Q (see above). The intensity of the highest energy mode at X = 0.4 and 0.3 decreases from Q = (4-X 0 0) to Q = (4+X 0 0) (Fig. 5). It is also very strong at Q = (2.3 0 0) (data not shown). Such behavior is similar to the 61 m eV mode at the zone boundary, thus we conclude that the highest energy phonons at X = 0.4 and 0.3 are of bond-bending character. The bond-bending branch originates at 42 m eV at the zone center (Fig. 2) and disperses upwards crossing the 53 m eV branch at Q (0.15 0 0) (data not shown). Mixing with the bond-bending branch may be the reason that the 53 m eV peak is stronger at Q = (3.8 0 0) than at Q = (4.2 0 0). Between q=0.1 and q=0.3 it hybridizes with the other branches emerging again as a pure mode at q= (0.3 0 0) - (0.5 0 0) around 60 m eV.

Identification of the dispersion of the bond-bending branch allows us to assign the other modes to either the bond-stretching or the folded-in branches. The mode at q= (0.2 0 0) and 65 m eV has mostly bond-stretching character, since its intensity is stronger at Q = (4.2 0 0) than at Q = (3.8 0 0). We also know that the mode at q= (0.3 0 0) and 57 m eV is bond-bending. This indicates that the bond-stretching branch has a very steep downward dispersion between q= (0.2 0 0) and (0.3 0 0). This steep dispersion is responsible for the very large energy width of this mode at q= (0.2 0 0) due to the finite q-resolution of the spectrometer. At q= (0.3-0.5 0 0) the bond-stretching mode continues to disperse to lower energies, but not as steeply. In this range of wavevectors it hy-
FIGURE 5: (Color online) Phonons between the zone center and the zone boundary measured in two Brillouin zones bridges with the two folded-in branches. As a result we observe three peaks below 55 meV. All are of mixed folded-in/bond-stretching character as is clear from strong intensity changes between \( Q = (4-X \ 0 \ 0) \) and \( Q = (4+X \ 0 \ 0) \) (see discussion above for the zone boundary). Figure 6 illustrates the dispersion of the bond-stretching vibration (marked with arrows) in the data covering \( Q = (4-0.500) \). It disperses downward away from the zone center and at \( q = (0.2 \ 0 \ 0) \) it contributes to more than one mode due to its interaction with other branches.

V. SUMMARY

Figure 7 shows the dispersion of the longitudinal oxygen phonons in the 1 0 0 direction summarizing the above results. The shell model gives a good prediction for the frequencies of the bond-bending and folded-in branches, however, it does not predict a strong downward dispersion of the bond-stretching branch away from the zone center as previously reported. This anomaly has been observed in almost all metallic perovskite oxides and is generally interpreted as a signature of strong electron-phonon coupling. As a result of the downward dispersion, the bond-stretching branch crosses the bond-bending branch at \( q = 0.2 \) and hybridizes with the folded-in branches at \( q = (0.2-0.5 \ 0 \ 0) \). The bond-bending branch has an upward dispersion in

FIGURE 6: Evolution of the phonon spectra between \( Q = 4 \ 0 \ 0 \) and \( Q = 4.5 \ 0 \ 0 \). Arrows mark modes with bond-stretching character.

FIGURE 7: (Color online) Circles represent measured longitudinal phonon peak positions at 100K. Vertical bars represent peak widths. Solid lines are guides to the eye showing dispersions of the bond-stretching (downward-dispersing) and bond-bending (upward-dispersing) vibrations in the absence of interactions with other branches and each other. Their crossing of each other and of the folded-in branches (see text) results in complex phonon polarization patterns. Dashed lines show results of the shell model calculations.
good agreement with the shell model. The folded-in branches are nearly at, but they are affected by the interaction with the bond-stretching branch at $q = (0.2,0.5,0,0)$.

VI. CONCLUSIONS

In conclusion, we have demonstrated that the rhombohedral distortion of the lattice has a profound effect on the longitudinal oxygen phonons dispersing in the 1 0 0 cubic direction. It results in two nearly at folded-in branches which couple strongly to the upward-dispersing bond-bending and the downward-dispersing bond-stretching branches. The latter appears as a pure mode only near the zone center hybridizing with the folded-in branches throughout most of the zone including the zone boundary.

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