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Role of electronic correlations on the phonon modes of MnO and NiO

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The possibility of magnetic-order induced phonon anisotropy in single crystals of MnO and NiO is investigated using inelastic neutron scattering. Below T_N both compounds exhibit a splitting in their transverse-optical phonon spectra of approximately 10%. This behavior illustrates that, contrary to general assumption, the dynamic properties of MnO and NiO are substantially noncubic.

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The failure of *ab initio* approximations to correctly incorporate many-body effects such as electron exchange and correlation is an issue at the core of contemporary solid-state research. Although these effects are important in almost all solids, they are essential for a proper description of cooperative phenomena such as antiferromagnetism, charge-ordering, superconductivity, and colossal magnetoresistance.

Despite the status of MnO and NiO as benchmark materials for the study of correlated electron systems and frequent use in first-principles electronic structure investigations, many aspects of the physics of the 3*d* transition-metal monoxides require better theoretical explanation. For example, the basic physical properties predicted for MnO and NiO (e.g., band gaps, distortion angles, and phonon spectra) differ radically depending upon which techniques have been employed.[1,2]

In a recent publication comparing different *ab initio* and model band-structure models on MnO [including local spin-density approximation (LSDA) and ''LSDA+model'' calculations], Massidda *et al.*[2] suggest that although the electronic density in MnO is approximately cubic, the lowering of symmetry associated with antiferromagnetic ordering can induce an electronic response that is significantly noncubic. This results in the dynamical properties of the system, such as transverse optical (TO) phonons, exhibiting substantial ''*magnetic-order induced anisotropy*.''

One of the predicted features from such calculations is that the zone center (ZC) optical-phonon modes should split depending on their polarization. A higher energy occurs for a mode polarized along the [111] direction and a lower energy for degenerate modes polarized in the orthogonal ferromagnetic plane, see Table I. Massidda *et al.*[2] find that this effect arises *solely due to the magnetic ordering*, and would even occur in the absence of any rhombohedral distortion. By comparing results from four different approximation schemes, lower and upper bounds of 3–10% for the magnitude of the splitting are estimated. Variations in the splitting due to the distortion are calculated to be less than 1%.

Although similar theoretical calculations have not yet been performed for NiO, the results of measurements of NiO TO phonons are predicted to be qualitatively similar to those in MnO. Indeed, it has been suggested that the splitting in NiO may be even greater in absolute magnitude than in MnO due to the larger magnetic superexchange.[6]

MnO and NiO are classic examples of type-II antiferromagnets possessing the cubic rock-salt structure. Below T_N, exchange-striction causes contraction of the unit cell along the [111] direction perpendicular to the ferromagnetic planes.[7,8] This results in a small deviation from the perfect cube of 0.62° for MnO and 0.1° for NiO. In MnO the magnitude and temperature dependences of the rhombohedral distortion have been well characterized.[9] Since the distortion is considered weak, investigations of the dynamic properties of MnO and NiO are frequently carried out under the assumption of perfect cubic symmetry.

To examine the possibility of anisotropy in the optical phonon spectra of MnO (and NiO) (and to distinguish these effects from any changes due to the small rhombohedral distortion), TO phonons in single crystals of MnO and NiO were measured using inelastic neutron scattering. MnO and NiO crystals used in these experiments were grown using the floating-zone method at a rate of 10 mm/h in 1 atm of argon. Both crystals consisted of small cylindrical pillars approximately 0.5 cm in diameter and 2-cm long.

The optical phonons, magnon modes, and sublattice magnetization of our MnO crystal were studied using the IN8 triple axis spectrometer located at the high-flux reactor at the

TABLE I. Comparison of theoretical predictions and experimentally observed values for the energies of transverse optical phonons in MnO. Our results are in good agreement with previous experimental work, with the exception of the splitting, which is qualitatively consistent with ''LSDA+model'' calculations by Massidda *et al.*[2]

Method	TO mode(s) (meV)	
LCAO UHF	38.95	Towler *et al.* (Ref. 1)
(LAPW) LSDA	12.46	Massidda *et al.* (Ref. 2)
LSDA+model	28.6	
	33.9	Massidda *et al.* (Ref. 2)
Inelastic neutron	32.5	Haywood *et al.* (Ref. 3)
scattering (300 K)	32.2	Wagner *et al.* (Ref. 4)
	33.2±0.2	This work
Inelastic neutron	33.3±0.2, 36.4±0.3	
scattering (4.3 K)		This work
Optical absorption		
(below T_N)	32.54	Yokogawa *et al.* (Ref. 5)

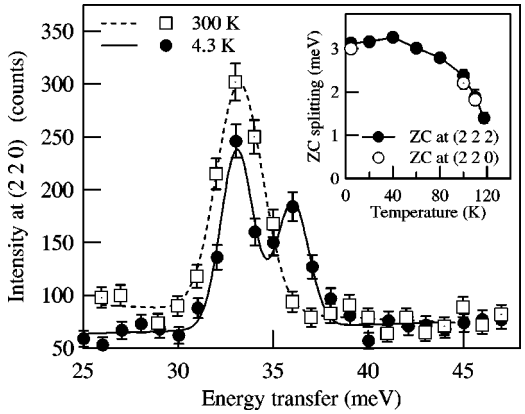

FIG. 1. Zone-center optical phonon modes measured at 4.3 K (full line, filled markers) and 300 K (dashed line, open markers). (Both scans were obtained with a monitor count of 1500.) The measurements shown are representative of scans obtained at $\mathbf{Q}=(220)$, $\mathbf{Q}=(004)$, $\mathbf{Q}=(222)$, and $\mathbf{Q}=(113)$. A higher-energy mode (possessing a third of the intensity of the original peak) is created at low temperature due to the magnetic ordering. The inset graph shows the temperature dependence of the magnitude of the MnO zone-center TO phonon splitting. The splitting is clearly associated with the onset of antiferromagnetic order at $T_N=118$ K.

Institut Laue Langevin (ILL), Grenoble. The Cu(111) reflection was used as monochromator in combination with a pyrolytic graphite (PG) filter, PG(002) analyzer, and Soller collimation. Measurements were made using constant-Q scans, with a fixed final energy of $E_f=14.69$ meV ($k_f=2.66$ Å). The crystal was oriented with the [110] direction vertical.

Operating the spectrometer in diffraction mode, measurements of the temperature evolution of the magnetic $(\frac{3}{2}\ \frac{3}{2}\ \frac{3}{2})$ reflection were obtained. The observed value of $T_N=118$ K, measured during slow cooling at a rate of 1° every 3 min, was in excellent agreement with previous reports.[10–12] Compression along equivalent [111] directions in the bulk crystal creates four possible orientations of twinning, or "T-domain," each with a distinct three-dimensional orientation of magnetic Brillouin zone. The scattering plane of the sample then comprises a superposition of slices through each of the magnetic Brillouin zones.[13,14]

Measurements of TO phonon modes were obtained along several directions in the crystal ([001], [111], and [110]) and around various Brillouin zone (BZ) centers [$\mathbf{Q}=(004)$, $\mathbf{Q}=(113)$, $\mathbf{Q}=(222)$, and $\mathbf{Q}=(220)$]. At 4.3 K, splitting of the modes was consistently observed in all of the measured BZ's. Representative zone center scans obtained at 4.3 K and 300 K are shown in Fig. 1.

The energy of the 300-K ZC excitation occurs at 33.2 ± 0.2 meV with a full-width at half-maximum of 2.87 ± 0.5 meV. In the antiferromagnetically ordered phase at 4.3 K two modes were consistently observed at energies of $E=33.3\pm 0.2$ meV and $E = 36.4 \pm 0.3$ meV. The zone center splitting at 4.3 K is approximately 3.1 meV, which corresponds to 9.3% of the energy of the original (degenerate) mode above T_N.

The uncertainty in reduced wave vector, $\mathbf{q}$, arising from the rhombohedral distortion was estimated for the measured

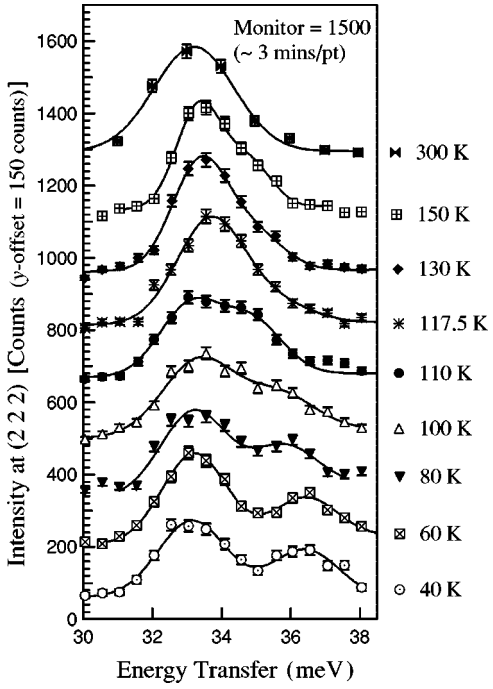

FIG. 2. Waterfall plot showing the temperature dependence of the MnO TO phonon spectra at $\mathbf{Q}=(222)$. (Scans have been offset by an arbitrary y value of 150 counts.)

Brillouin zones to range between $d\mathbf{q}=0.02$ and $d\mathbf{q}=0.04$ r.l.u. (reciprocal lattice units). At the ZC position where the dispersion of the TO modes is virtually flat, the effects of an uncertainty of this magnitude on the energy spectra would be negligible. We therefore conclude that the splitting is a real effect which cannot be attributed to the small static structural distortion.

The low-temperature data were fitted to a pair of Gaussian peaks of identical width. Peaks at each of the zone centers possessed widths of 2.43 ± 0.6 meV. The ratio of the integrated intensities of the two peaks was approximately 2:1 in favor of the lower mode at each of the measured zone-centers. The total integrated intensity of the two (split) peaks and the initial single peak were approximately conserved on passing through T_N. This behavior is consistent with the creation of a new higher-energy mode arising from excitations polarized along the [111] direction.[2] Although both modes are observed at a slightly higher energy than the "LSDA+model" value (Table I), the observed 9% anisotropy is within the suggested bounds of 3–10 %.[2]

Plots of the temperature evolution of the ZC phonon anisotropy are shown in Figs. 1 (inset) and 2. The splitting in the phonon spectra is clearly associated with the transition to magnetic order. Asymmetry in peaks measured at 130 K and 150 K (Fig. 2) hints that a small amount of anisotropy may be present at temperatures substantially above T_N, (i.e., when the unit cell is thought to be perfectly cubic.[9])

Dispersion curves obtained for TO modes along the [100] and [111] directions in MnO at 4.3 K and 150 K are presented in Figs. 3 and 4(a). Although the splitting extends throughout the Brillouin zone, the distortion is most clearly resolved at values of reduced wave vector ($\mathbf{q}$) close to the

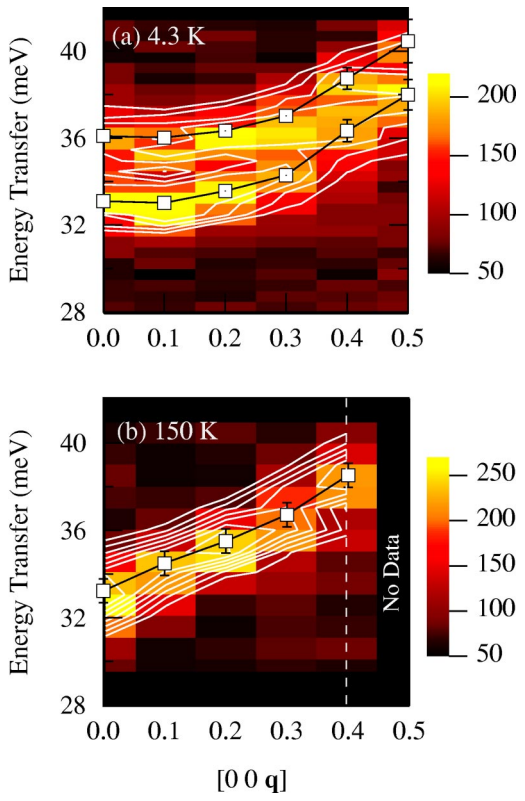

FIG. 3. (Color online) Dispersion curves for TO phonon modes in MnO measured at (a) 4.3 K and (b) 150 K along the [001] direction. The $\mathbf{q}=0$ position in both graphs corresponds to the (2 2 0) ZC. Markers indicate the peak positions of Gaussian fits to the data.

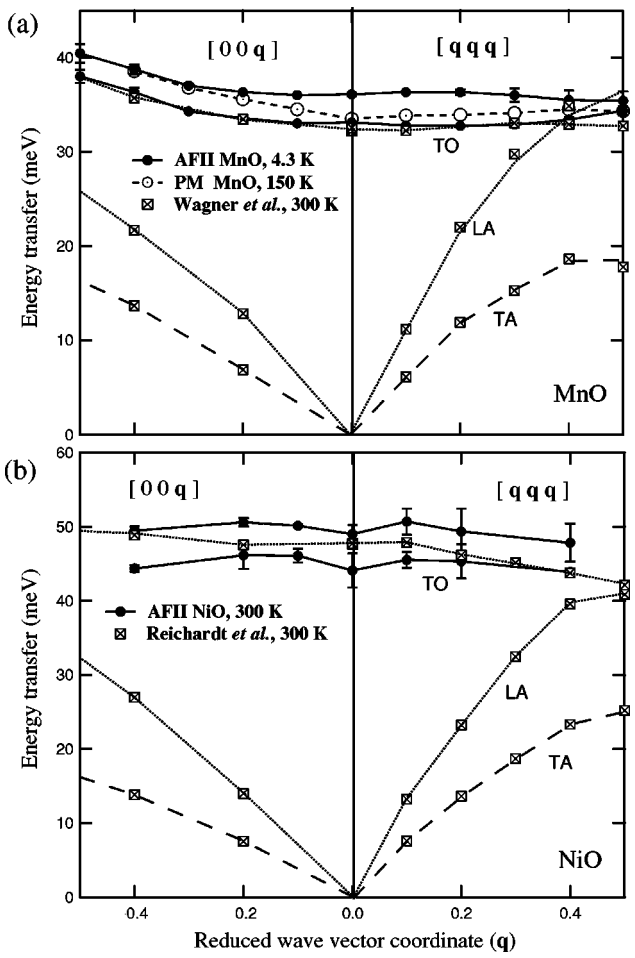

FIG. 4. (a) MnO phonon dispersion curves measured at 4.3 K (filled circles) and 150 K (open circles). Square markers show the room-temperature data of Wagner *et al.* (Ref. 4). (b) Room-temperature TO phonon dispersion curves measured for NiO. Filled round markers show measurements along the [001] and [111] directions [obtained around $\mathbf{Q}=(220)$ and $\mathbf{Q}=(222)$]. Square markers show the data of Reichardt *et al.* (Ref. 15).

zone center, see Fig. 3(a). Further from the ZC (where the scattering is less intense and the spectrometer may be less focussed), the presence of two modes is revealed by the deviation of the shape of the overall peak from Gaussian, and its increased width in comparison to the same measurement at 150 K, Fig. 3(b). As the crystal consisted of two domains, intensity from differently polarized magnons could be seen reasonably well in all of the measured directions.

The notion that a small splitting may be present in MnO above T_N is supported by the dispersion measured at 150 K, shown in Fig. 4(a). The 150-K data (open circles) were fitted to a single Gaussian peak but found to be slightly raised in energy in comparison to the lower energy mode (filled circles), and to the room-temperature data of Wagner *et al.*[4] (square markers).

To investigate whether a similar phonon splitting could be observed in the room-temperature dispersion of NiO, a preliminary survey was performed using the HB1 spectrometer located at the High Flux Isotope Reactor, Oak Ridge National Laboratory, USA. As before, the crystal was oriented with the [110] direction vertical, and the spectrometer operated in constant-Q mode with fixed final energy $E_f = 14.73$ meV.

Our NiO crystal was of less reliable quality than the MnO crystal, and spurious ''Bragg-Bragg-inelastic'' scattering was observed. This limited our measurements to regions surrounding ZC's located at $\mathbf{Q}=(220)$ and $\mathbf{Q}=(222)$. Room-temperature TO dispersion curves for the [111] and [001] directions of antiferromagnetically ordered NiO are presented in Fig. 4(b) (filled round markers). Squares represent the data of Reichardt *et al.*,[15] also collected at room temperature.

In our NiO data two peaks were observed occurring at energies of around 45 and 50 meV. This is in reasonable agreement with previous reports indicating a single TO excitation with an energy varying between 46 and 50 meV.[16,15] This would correspond to a ZC splitting of approximately 5 meV, which is larger in absolute magnitude than observed in MnO (despite the smaller distortion angle), and corresponds to roughly 10% of the average energy of the two modes.

Since both these data and data of previous researchers were collected at room temperature (where NiO is already magnetically ordered) it is necessary to ask why this effect had not been observed before. We suggest that the cause of the discrepancy lies in the poor energy resolution and flux of the early spectrometers, particularly at high-energy transfers. These experimental factors coupled with the expectation of a

single (degenerate) phonon mode may have led to fitting of the data to a single peak.

In principle, any anisotropy in the phonon modes of MnO and NiO should also have been observed in optical absorption (Table I),[5] or Raman spectroscopy data. These methods have better resolution than inelastic neutron scattering and should provide a good test of our observations. To the best of our understanding, previous Raman studies[17] have focussed mainly on magnon processes, and no such splitting in the TO phonon Raman spectra has so far been reported.

In summary, we have shown that below T_N the dynamic properties of MnO and NiO are substantially noncubic. The magnitude of the zone center anisotropy observed in transverse-optical modes in MnO and NiO corresponds to 9–10% of the energy of the original (degenerate) phonon. The intensities of the two optic modes in MnO and the form of the dispersion are consistent with the picture of the splitting described by recent band-structure calculations where a higher-energy mode is predicted for phonons polarized along [111].[2]

In MnO, we have shown that the splitting of the phonon modes is associated with the transition to magnetic order. Although exchange striction induces a small rhombohedral distortion, this static distortion in itself is too weak to explain the magnitude of the anisotropy. Furthermore, NiO possesses a significantly smaller distortion angle than MnO but a larger (5 meV) splitting. The strain associated with exchange striction (even in the undistorted structure considered by Massidda *et al.*[2]) defines a new potential well for the atoms, which may significantly influence the dynamics. However, further research will be required to investigate the mechanism underlying the splitting and to determine how the magnetic-order induced phonon anisotropy in MnO and NiO is mediated. Theoretical studies investigating the role of electronic correlations on the phonon modes of NiO are particularly encouraged. Although theorists have not provided any calculations for NiO as yet, we are confident that our preliminary findings of an even larger splitting will provide an impetus for them to do so.

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