Effects of Anisotropic Charge on Transverse Optical Phonons in NiO

H. Uchiyama1,2, S. Tsutsui2, A. Q. R Baron1,2
1 Material Dynamics Laboratory, RIKEN, Sayo, Hyogo, 679-5148, Japan.
2 Japan Synchrotron Radiation Research Institute, Koto, Sayo, Hyogo, 679-5198, Japan.
(Dated: June 29, 2010)

Phonon dispersion of detwinned NiO is measured using inelastic x-ray scattering. It is found that, near the zone center, the energy of the transverse optical phonon mode polarized parallel to the antiferromagnetic order is $\sim$1 meV lower than that of the mode polarized perpendicular to the order, at room temperature. This is explained via anisotropic polarization of the Ni and O atoms, as confirmed using a Berry’s phase approach with first-principles calculations. Our explanation avoids an apparent contradiction in previous discussions focusing on Heisenberg interaction.

PACS numbers: 75.50.Ee, 75.30.Gw, 77.84.Bw, 63.20.dd

Transition-metal mono-oxides are fundamental materials for studying properties of magnetic and strongly correlated systems. Among them, NiO and MnO are antiferromagnetic (AFM) insulators with similar crystal structure and physical properties. The AFM order and lattice contraction occur along the [111] direction below the Néel temperature ($T_N =$523 K for NiO). The order consists of ferromagnetic (111) planes. Above $T_N$, both have a rock-salt structure. NiO and MnO are relatively simple, because they have non-degenerate electronic ground states, and are free from Jahn-Teller effects, unlike FeO and CoO.

The magnetism of these materials is often discussed in terms of a superexchange mechanism. MnO has antiferromagnetic interactions both in the nearest neighbor ($J_1$) and next nearest neighbor ($J_2$) exchanges, and these interactions reproduce the experimental results. On the other hand, $J_1$ for NiO still remains uncertain, perhaps because it is much smaller than the antiferromagnetic superexchange $J_2$ interaction, which is responsible for the AFM order. For example, local spin density approximation (LSDA)+$U$ calculations give ferromagnetic $J_1$, while some calculations such as GW show antiferromagnetic $J_1$. Experimentally, a measurement of spin-wave dispersion indicates ferromagnetic $J_1$, while one of magnetic susceptibility suggests antiferromagnetic $J_1$.

Another issue is that LSDA+$U$ calculation results are not easily reconciled with the exchange interaction picture of NiO. According to Refs., the lattice distortion is dominated by $J_1$ with no contribution from $J_2$, and antiferromagnetic $J_1$ causes the contraction in [111], if $|J_1|$ decreases with increasing the distance between the nearest-neighbor Ni atoms. Based on this discussion, the calculated ferromagnetic $J_1$ is not consistent with the calculated (and observed) contraction in NiO, suggesting an additional ingredient is needed to understand the calculation results.

The energy of transverse optical (TO) phonons can be used as a direct probe of microscopic couplings. TO modes that would be degenerate in a cubic rock-salt structure, are split at the zone center under the AFM order, with the energy of the mode polarized along the order ($E^{\text{TO}}_{\|}$) different than that of the mode polarized in the plane perpendicular to the order ($E^{\text{TO}}_{\perp}$). As discussed in Ref., the sign of this difference ($E^{\text{TO}}_{\|} - E^{\text{TO}}_{\perp}$) can be linked to the sign of $J_1$. The picture is generally consistent for MnO, where the observed shift is in agreement with theory, however question remains about NiO, where preliminary measurements disagree with the LSDA+$U$ calculations.

We have made careful measurements of the TO phonon dispersion in detwinned NiO at room temperature (RT), and find $E^{\text{TO}}_{\|} - E^{\text{TO}}_{\perp} \sim -1.0$ meV in the vicinity of the zone center, in reasonable agreement with the LSDA+$U$ calculations. In order to understand this, we introduce the anisotropic polarization derived from a Berry’s phase. This anisotropy yields an anisotropic effective Born charge, which was introduced into AFM materials by Ref., after tremendous success in ferroelectric materials. This spin-dependent term dominates the splitting and provides the missing ingredient to explain the observed lattice distortion and phonon splitting simultaneously.

NiO samples with (111) surface were detwinned in accordance with Ref., giving the AFM order and lattice contraction along the [111] direction (in this report, indices of cubic symmetry are used). The single structural domain ($T$-domain) was confirmed by the (333) Bragg peak (Fig. 1(a)); a peak from another domain with a different direction for the contraction, if any, would appear at lower angle (the bar in Fig. 1(a)). NiO may also have a different type of domains, originating from the different spin-axis orientation ($S$-domain). However, Ref. shows that a field of $>2$ kOe along [110] may be used to align the spin axes along [112]. When the field reaches 5 kOe, a single $S$-domain is obtained, but the $T$-domain wall starts to move. Considering these facts, magnetic field of 4.5 kOe was applied parallel to [110] during the measurements.

Phonon measurements using inelastic x-ray scattering (IXS) were performed at BL35XU of SPring-8 with a total energy resolution of $\sim$1.6 meV and a momentum resolution of $\sim$0.08 Å$^{-1}$. The incident energy is 21.75 keV. The measurements were achieved at RT ($\sim$300 K ($<T_N$)) to prevent introducing a new domain caused by tiny stresses or thermal gradients. We also performed
FIG. 1. (Color Online) (a) The θ scan around the (333) Bragg peak. The bar indicates the expected peak position of (333). (b) IXS spectra at |q|=0.1, 0.1, 0.1. LA denotes longitudinal acoustic phonon. TA (LA), while TA (LA) does the anti-Stokes line. (c) The enlarged view of (b) at around the TO phonons. Dotted lines are results of curve fitting, and the bars show the peak positions.

FIG. 2. (Color Online) (a) Phonon dispersion of NiO in the |q|=|qqq| direction, which is determined theoretically (lines), and experimentally (the dots). (b) Simulated TO phonon distribution in the vicinity of |Q|=333 (solid line). Dotted line shows the spectrum broadened by a 0.4 meV resolution function. (c) The band structure along |qqq| and |qqq| obtained by LSDA+U. Solid lines are the valence bands which are used in calculating the Berry’s phase of polarization.

similar measurements under 1.7 kOe at some phonon vectors to study field induced effects, such as magnetoelectric effects. The results show the same phonon peak positions as at 4.5 kOe, within an experimental accuracy of ±0.3 meV. We confirmed the zero energy using the midpoint of the Stokes and anti-Stokes lines of the transverse acoustic (TA) phonons.

The experimental phonon dispersion very well. This agreement in dispersion lends credence to the idea that our approach, below, of modifying successively, the various components of the shell model, can be used to understand the material’s behavior.

First, just the effect of the non-cubic lattice was considered, holding all the other parameters fixed. The experimental lattice distortion of ~90.06° at RT gives TO phonon splitting of ~0.06 meV at |q|=0.1, 0.1, 0.1. This value is much smaller than the observed in Fig. 1(c), suggesting that only the lattice distortion can not describe the observed TO peak shift.

Next we introduce additional Born-von Kármán force constants to simulate the anisotropy of the Heisenberg exchange interaction. Effectively, the shell model includes J1 in the longitudinal force constant between nearest neighbor Ni-O atoms. As for J1, additional force constants along (001) (between parallel spin, T) and (011) (between antiparallel spin, −T) were included (as the cubic structure assumed, J1 deviation due to the lattice distortion is not considered). The parameter T was varied to fit the experimental results.

Using these additional force constants, the polarization vectors for the peaks in Fig. 1(c) can be determined as eigenvectors of the dynamical matrix. The spectra at q=(0.1, 0.1, −0.1) and (0.1, −0.1, 0.1) with τ=(333) are assigned to the modes polarized close to [112] (TO(112) and [121] (TO(121)) respectively. For q=(0.1, 0.1, 0.1) with τ=(151), the spectrum is dominated by the TO(121) mode, while the spectra at q=(0.1, 0.1, 0.1) with τ=(151) is assigned to TO⊥. In short, it is estimated from the experiment that the energy of TO(112) (E TO(112) ) is ~0.9 meV lower than E TO⊥.

The intensity around the zone center is simulated us-
the total charges.

The formulation of the shell model introduces matrices for shell model in different ways. In particular, the detailed dependent, extending, somewhat, the limits of Anderson, [111], \( Z_{ii} \) (\( i \neq j \)), for both O and Ni have a common value of \( Y_{ij}/Z_{ii} = 2.8 \times 10^{-2} \), we can reproduce the experimental results in Fig 1(c) and all assignments mentioned above. Based on Ref.15, which discusses the shell model in detail for a rock-salt structure, we then estimate the effective charge anisotropy as \( \Delta z^*/z^* = 5.6 \times 10^{-2} \) (\( z^* = \pm 2.21 \)).

Alternatively, we consider introductions of anisotropy directly in the static charge, \( Z \), of the shell model. Taking \( Z_{ij}/Z_{ii} = 3 \times 10^{-3} \) is sufficient to reproduce the results. This value corresponds to \( \Delta z^*/z^* = 8 \times 10^{-3} \) (\( z^* = \pm 2.19 \)). This agrees better with the LSDA+U calculations than the value from the anisotropic \( Y \) case above. However, it is also possible the larger \( \Delta z^*/z^* \) value is caused by lack of consideration of higher order moments than dipole in the shell model.16

It is interesting to consider if this anisotropy might be related to the static contraction along the [111] direction. According to Ref.12, Born effective charges have a correlation to the covalent bonding. This suggests the lattice distortion can be explained using the anisotropic Born charge, as a distance between two atoms at equilibrium may depend on the magnitude of the charges. Noting that the principle directions of \( Z_{ij} \) are orthogonal, the lattice distortion from cubic to rhombohedral can be estimated using Ref.12. In the anisotropic \( Z \) case, \( \Delta z^*/z^* = 8 \times 10^{-3} \) gives the lattice distortion of 90.15°, in fair agreement with the measured 90.06° at room temperature.13. If we take \( \Delta z^*/z^* = 5.6 \times 10^{-2} \), the distortion in the case of anisotropic \( Y \) is estimated, giving a large value, 91.11°.

The measured momentum dependence of the splitting is in agreement with both of these (anisotropic \( Y \) or anisotropic \( Z \)) models as can be seen in Fig. 3 (a,b). One notes that in all models, the phonon splitting is reduced towards the zone boundary, and the magnitude at the zone boundary depends on the detailed model. However, our resolution does not allow us to choose between the models. Meanwhile, Figure 3(c) depicts the TO distribution near \( |Q| = (333) \) for anisotropic \( Y \) and \( Z \), showing the similar distribution to Fig. 2(b) for the anisotropic force constant. It should be noted that, based on Ref.15, it is confirmed that these anisotropic charge models satisfy the generalized Lyddane-Sachs-Teller relation17,18 both along and perpendicular to the [111] direction.

In conclusion, we have two different methods of including the anisotropy of the material that fit our experimental results for the phonon splitting: (1) ad hoc addition of force constants to mimic a possible Heisenberg interaction and (2) inclusion of an anisotropy in the electrostatic terms of the shell model. The latter, which, qualitatively seems to match the anisotropy of the Born effective charge tensor calculated using the LSDA+U method, seems a more reasonable choice. Furthermore,
the latter description provides an additional ingredient that allows one to reconcile the observed lattice contraction with the ferromagnetic $J_1$ interactions calculated using LSDA+$U_{\text{eff}}$. These discussions suggest the anisotropic polarization should be considered in studying AFM compounds. Both the Berry’s phase calculations of polarization and Heisenberg exchange interaction have spin-dependent anisotropy. However, the exchange interaction applies to only magnetic atoms, while the anisotropic effective charge applies to both magnetic and non-magnetic atoms, as required by charge neutrality. In addition, in order to estimate the exchange interaction precisely, a deviation of the Wannier functions from the cubic symmetry should be considered, even if the lattice is assumed as cubic. This may be relevant to other AFM materials; for example, high-$T_c$ cuprates, or iron pnictides.

In summary, we observed TO phonon shifts for detwinned NiO at room temperature, and found that the energy of the TO phonon with atomic motions in the direction of the [111] magnetic ordering is $\sim 1.0$ meV lower than the TO mode with motions perpendicular to the ordering direction, near the zone center. We suggest this observation is most simply explained by considering the anisotropic polarization of the medium. While ultimately related to a spin dependent interaction, at a conceptual level this is an additional ingredient that should be considered, to understand the material behavior, distinct from the exchange interaction.

The synchrotron radiation experiments were performed at the BL35XU in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (Proposal No. 2008A1584).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{(Color Online) (a) TO phonon dispersion in the [111] and [111] directions. Dotted lines are results of curve fitting. (b) Comparison of TO$_{\perp}$ and TO$_{[11\bar{2}]}$ phonon modes between experimental (marks) and theoretical (lines) results. The calculations are based on the shell model with (solid and dotted lines)/without (dashed lines) effective charge anisotropy. (c) Simulated TO phonon distribution for the effective charge anisotropy in the vicinity of $|Q|=\langle333\rangle$.)
\end{figure}

1. J. Kanamori, Prog. Theor. Phys. 17, 197 (1957).
2. M. E. Lines, E. D Jones, Phys. Rev. 139, A1313 (1965), 141, 525 (1966).
3. W. Luo, P. Zhang, M. L. Cohen, Solid State Comm. 142, 504 (2007).
4. T. Kotani, M. van Schilfgaarde, J. Phys.: Cond. Mat. 20, 295214 (2008).
5. M. T. Hutchings, E. J. Samuelsen, Phys. Rev. B 6, 3447 (1972).
6. R. Shanker, R. A. Singh, Phys. Rev. B 7, 5000 (1973).
7. T. Yamada, J. Phys. Soc. Jpn. 18, 520 (1963).
8. S. Y. Park, H. J. Choi, Phys. Rev. B 80, 155122 (2009).
9. S. Massidda, M. Posternak, A. Baldereschi, R. Resta, Phys. Rev. Lett. 82, 430 (1999).
10. E. M. L. Chung, et al., Phys. Rev. B 68, 140406(R) (2003).
11. T. Rudolf, Ch. Kant, F. Mayr, A. Loidl, Phys. Rev. B 77, 024421 (2008).
12. R. Resta, D. Vanderbilt, in Physics of Ferroelectrics, edited by C. H. Ahn, K. M. Rabe, J. M. Triscone (Springer-Verlag, 2007), 31.
13. G. A. Slack, J. Appl. Phys. 31, 1571 (1960).
14. H. Kondoh, T. Takeda, J. Phys. Soc. Jpn. 19, 2041 (1964), E. Uchida, et al., ibid 23, 1197 (1967).
15. A. Q. R. Baron, et al., J. Phys. Chem. Solids 61, 461 (2000).
16. A. D. B. Woods, W. Cochran, B. N. Brockhouse, Phy. Rev. 119, 980 (1960), R. A. Cowley, W. Cochran, B. N. Brockhouse, A. D. B. Woods, ibid 131, 1030 (1963).
17. W. Reichardt, V. Wagner, W. Kress, J. Phys. C 8, 3955 (1975).
18. V. Wagner, W. Reichardt, W. Kress, Proc. Conf. Neutron Scattering 1, 175 (1976).
19. A. Mirone, M. d’Astuto, available at http://sourceforge.net/projects/openphonon.
20. Slight modification of some parameters is achieved to suit the experimental results better; $B_{12} = -5.07$ and $B_{22} = 0.13 (e^2/v)$ are different from Ref. 12.
21. X. Gonze, et al., Comput. Mater. Sci. 25, 478 (2002), M. Torrent, et al., ibid 42, 337 (2008). Available at http://www.abinit.org.
22. Q. Yin, A. Gordienko, X. Wan, S. Y. Savrasov, Phys. Rev. Lett. 100, 066406 (2008).
23. Z.-X. Shen, et al., Phys. Rev. B 44, 3604 (1991).
24. P. W. Anderson, Phys. Rev. 115, 2 (1959).
25. M. Posternak, R. Resta, A. Baldereschi, Phys. Rev. B 50, 8911 (1994).
26. I. D. Brown, D. Alterman, Acta Cryst. B41, 244 (1985).
27. W. Cochran, R. A. Cowley, J. Phys. Chem. Solids 23, 447 (1962).
28. R. M. Pick, M. H. Cohen, R.M. Martin, Phys. Rev. B 1, 910 (1970).