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Local lattice structure change in $PrNiO_3$ across the metal-insulator transition: X-ray absorption near-edge structure spectroscopy and *ab initio* calculations

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X-ray absorption near edge structure (XANES) measurements at the Ni *K* edge of $PrNiO_3$ across the metal insulator transition show that a change in the local lattice structure accompanies such transition. Theoretical calculations of the XANES show that the observed features of the spectra are consistent with the orthorhombic structure, reported by neutron diffraction, in the metallic phase. However, for the insulating phase, a change in the local symmetry, consistent with a monoclinic structure, is required to reproduce the spectra. This local symmetry change yields to two nickel sites with different local environment and implies a strong electron-lattice interaction at the local level. This claim is also supported by the observation of a ^{16}O-^{18}O isotopic shift in the temperature at which the XANES exhibits the change attributed to the switching of the local symmetry from orthorhombic to monoclinic.

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I. INTRODUCTION

Rare-earth nickel oxide perovskites have been intensively studied in order to understand the unusual behavior in the electronic, magnetic, and structural properties as a function of temperature and rare-earth ion size. These systems present a first-order metal to insulator transition (T_{MI}) as temperature decreases, except for $LaNiO_3$, which remains metallic at all temperatures.[1] T_{MI} is strongly influenced by hydrostatic and chemical pressure (induced by a change of the ionic radius of the rare-earth ion). Several studies have been performed to investigate the existence of structural modifications across the metal-insulator transition in these compounds. Long-range structural changes have been reported, going from a subtle change in the unit cell dimensions in the orthorhombic lattice up to a crystallographic symmetry group change.[2–4] The symmetry decrease is accompanied by changes in the Ni-O-Ni superexchange angles and in the Ni-O distances, reflecting a decrease in the Ni e_g–O $2p$ hybridization concomitant to the gap opening.[2–5] Nickel perovskites with Pr, Nd, Sm, and Eu rare-earth ions present a slight expansion in the orthorhombic structure unit-cell volume across the transition from metal to insulator, without any apparent variation of the crystallographic symmetry, as observed by neutron diffraction.[2] On the other hand, compounds containing small rare-earth ions such as Ho, Y, Er, Tm, Yb, and Lu show a crystallographic symmetry group change, going from orthorhombic to monoclinic symmetry across the metal-insulator transition. This modification has been attributed to charge disproportionation taking place at different sites of Ni, with short (Ni_1) and long (Ni_2) Ni-O bonds.[3] However, recently, it has been proposed that this difference in nickel local environment could reflect the presence of ionic bonding at Jahn-Teller distorted Ni_2 sites and covalent bonding at Ni_1 sites.[6] As a consequence of this symmetry change, a magnetic structure with unequal moments appears at low temperature, as shown by neutron diffraction studies.[3,4,7] Recently, a symmetry change of the unit cell has been identified by electron diffraction, Raman scattering[8] and resonant x-ray scattering[9] on $NdNiO_3$, and by infrared spectroscopy on $EuNiO_3$, $HoNiO_3$, and $YNiO_3$.[10] Also, the possibility of different Ni-O distances in the insulating state of $RNiO_3$, with R=Eu, Nd, and Pr, has been proposed from extended x-ray fine structure (EXAFS) experiments.[11] All these results suggest the existence of an inhomogeneous structure at the local scale in the insulator phase. These nickelates also display large negative isotopic shifts of T_{MI},[12] which indicate that a strong electron-lattice interaction is involved in the metal-insulator transition. Such strong interaction has also been suggested by infrared spectroscopy results.[13] Motivated by the scenario described above, we have studied the local structure around Ni on $PrNiO_3$ at various temperatures below and above the metal-insulator transition by x-ray absorption near edge structure (XANES) using ^{16}O and ^{18}O isotopes. Because XANES is strongly sensitive to the local geometry around the absorbing atomic species, it is an ideal technique to study local symmetry changes, in this case around Ni. Additionally, it has the advantage of being able to probe local structural changes ranging from static distortions up to dynamical changes on the time scale of typical phonons.[14] We present *ab initio* calculations of XANES spectra,[15] which are compared with experimental spectra. The comparison between calculated XANES and experimental spectra leads us to conclude that the observed changes in the XANES across the metal-insulator transition originate in a change in the local symmetry. In Sec. II, we present a brief description of the experimental procedure; results and discussion of the comparison between the calculations and the experimental data are presented in Sec. III. Finally, in Sec. IV, we present a summary and conclusions.

II. EXPERIMENTAL PROCEDURE

$PrNi^{16}O_3$ and $PrNi^{18}O_3$ samples were prepared from the same batch of starting material containing natural oxygen. Then, ^{16}O was replaced by ^{18}O by diffusive means. The procedure is described in Ref. 12. The metal-insulator transition temperature was $T_{MIT}(^{16}O)=128$ K and $T_{MIT}(^{18}O)=136$ K, inferred from differential scanning calorimetry cooling curves, which coincide with the temperatures at which a maximum in the unit cell is achieved, as shown in Ref. 12. Ni *K*-edge XANES experiments were performed at Argonne National Laboratory on beam line 12BM using Si(220) crystals to monochromatice the beam. Powder samples were spread over kapton tape attached to a Cu cold finger, mounted on an aluminum holder on an open-cycle liquid-helium refrigerator. Samples were brought from room temperature to 55 K over a period of 12 h. We note that the temperatures reported are those registered by a thermocouple placed at the cold finger, we estimate that the actual sample temperature could be up 10 K warmer. Hence, the temperatures quoted for the XANES measurements refer to nominal temperatures. Then, the samples stayed at 55 K for another 12 h, and then brought to the lowest measured temperature (105 K) over a period of 1 h. After taking three 30 min scans in $PrNi^{16}O_3$ and three scans at $PrNi^{18}O_3$, the temperature was increased to the next measured temperature over a period of 5 min and there was a lapse of 30 min before initiating the next scan. This procedure was repeated for all temperatures measured in this experiment. Raw XANES data were collected in transmission mode and three individual scans were recorded for each temperature. These scans were averaged for a given temperature to improve the signal-to-noise ratio. The Ni *K*-edge XANES data were calibrated using the first inflection point of a Ni foil. Spectra were normalized using the standard procedure of setting the difference between a polynomial fit to the EXAFS region and another in the pre-eedge region equal to 1 at 8346 eV (Fig. 1).[16]

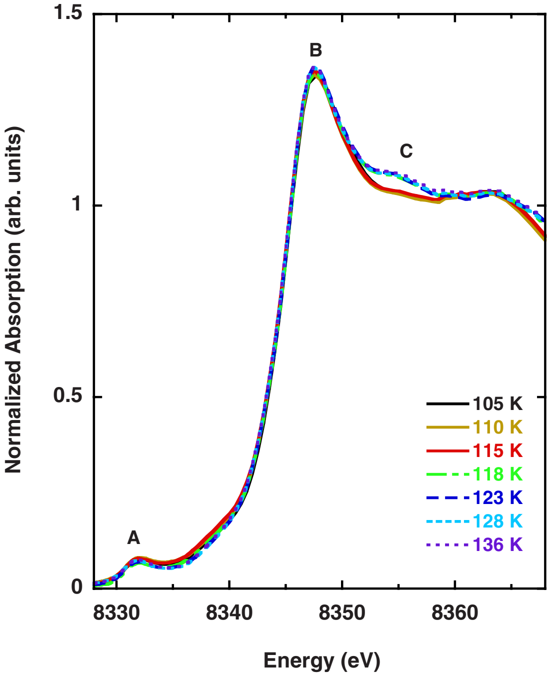

FIG. 1. (Color online) Normalized Ni *K*-edge XANES experimental data at different temperatures above (dashed lines) and below (solid lines) of metal-insulator transition. Quoted temperatures refer to nominal temperatures as explained in the text.

III. RESULTS AND DISCUSSION

Figure 1 shows the Ni *K*-edge XANES spectra of $PrNiO_3$ as a function of temperature. The main change in the absorption cross section across metal insulator is observed in the feature labeled as C around 8350 eV. Additionally, the region after the small peak below the main raise of the edge exhibits a decrease of spectral weight, up to the inflection point of the main rise of the edge, for temperatures above T_{MI}, compared to spectra taken below T_{MI}. The main absorption peak (feature B) exhibits a small increase when the system goes from insulator to metal. The most noticeable change is in feature C, while for temperatures above T_{MI} (in our case, spectra between nominal temperatures between 118 and 136 K), a broad shoulder following the main peak is present; for temperatures below the T_{MI} temperature, this shoulder disappears. These observed changes between the insulating and metallic phases had been previously reported when comparing measurements at 20 and 150 K in this system.[17] The small structure (feature A) is commonly observed in several transition metal oxides and it had been attributed to quadrupolar transitions $1s \rightarrow 3d$.[17,18] However, recent studies in transition metal oxides have shown that almost all spectral weight related to this feature is due to dipolar transitions between metal $1s$ states and hybridized metal $3d$-O $2p$ states.[20] Feature C originates as part of the scattering states described within the x-ray absorption fine structure formalism. The observed changes in the spectra suggest a change in the local atomic structure around the Ni atoms (reflected in the appearance of shoulder C) across the metal insulator transition. However, in order to obtain local atomic and electronic information from the XANES spectra, it is necessary to perform *ab initio* simulations using structural information obtained from other structural techniques. We thus simulated the Ni K-edge XANES using a full multiple-scattering calculation with spherically symmetric self-consistent scattering potentials in a cluster of atoms centered around a Ni atom and with atomic positions given by the crystallographic structure reported by neutron diffraction in the insulator and metallic regime.[2] We performed this calculation using the *ab initio* code FEFF8.[15] The use of this method of calculation has yielded reliable qualitative results in metals and transition metal oxides.[20] It is important to note that the calculation was performed within the one-electron formalism, calculated within the local density approximation, and it ignores effects of electron correlation not included in the self-energy of the photoelectron.[19] Also, the calculation does no take into account quadrupolar transitions. We note that the approximations used in the calculation yield an uncertainty of few eV in the position of the Fermi energy of the system, and thus the energy associated with the rise in the absorption edge. There is also an uncertainty in the overall scale of the absorption cross section due to the estimate of multielectron excitations. Although these uncertainties are not relevant for a qualitative comparison with the experimental spectra, we used an overall shift of the Fermi energy of 6.4 eV, and an overall scale factor of 0.65. The calculation reproduces in a qualitative manner the observed features for temperatures above the T_{MI} (see Fig. 2), including the presence of the “pre-edge” feature A, proving the reliability of the calculation for this system. The comparison to the experimental data shows that the pre-edge peak (feature A) can be explained as originating from a dipole transition, based on the relative intensity of this feature compared to the absorption main peak (B), although a small quadrupole contribution to this peak cannot be ruled out. However, using the average crystallographic structure of the insulator phase, the calculated spectrum is very similar to that above the T_{MI}, specifically the shoulder C is still present in the calculation in disagreement with the experimental spectra. This observation suggests that the changes in the local atomic structure, which determine the XANES spectra, are not reflected in the *average* crystalline structure. This has been documented in other metal oxides, most noticeable $La_{1-x}Sr_xCuO_4$, where the presence of a striped phase with regions of increased tilting of CuO_6 octahedral is observed at low temperatures,[21] although these increased tiltings cannot be inferred from the average crystalline structure. We note that members of the family $RNiO_3$ in which the size of the rare earth is small (X=Y, Ho, Lu, etc.) exhibit a change of crystal symmetry below the T_{MI} transition adopting a monoclinic symmetry group. Raman spectroscopy results[8] and resonant x-ray scattering[9] on $NdNiO_3$ report a breaking of the orthorhombic symmetry at low temperatures. Also, the inference of different Ni-O distances, in EXAFS experiments,[11] suggests that a change in symmetry could occur for all R ions, even Pr, at least at the local level. Following these observations, we calculated the XANES spectrum modifying the symmetry of the local structure for the calculation at low temperature. We assumed a monoclinic space group, $P2_1/n$, with lattice parameters scaled from those in the orthorhombic phase by keeping the same percentage change of the unit cell across the metal-insulator transition.[22] The result of this simulation is compared with the XANES obtained for the orthorhombic phase (see Fig. 3). The simulation was performed by averaging the calculated absorption spectra at Ni_1 and Ni_2 sites, which exhibit different local atomic environments. In this case, the calculated spectra reproduces all observed changes in the experimental measurements (see Fig. 1). The proposed ansatz for the structure leads to a variation of Ni-O distances in a range of ~0.1 Å. We thus conclude that a change of symmetry at the local level occurs in $PrNiO_3$, in agreement with experimental results obtained for other rare earth compounds.[3,4] We note, however, that although XANES is sensitive to a change of symmetry around the absorbing atom, it is not a technique which can provide accurate determination of atomic positions or bond distances. We thus expect that the actual atomic positions might show a difference from the ones used to reproduce the XANES spectra at low temperatures, although exhibiting the change in symmetry. Ideally, high resolution diffraction experiments will show the actual structure, if this is not a dynamical fluctuation outside the time scale probed by the diffraction experiment.[14,23] We note that the proposal of the existence of two kinds of Ni-O bonds in the insulating phase presented in Ref. 6 implies a Ni site with ionic bonding and a Jahn-Teller distortion. Such distortion is consistent with the local structure we have assumed in order to reproduce the XANES spectra, which

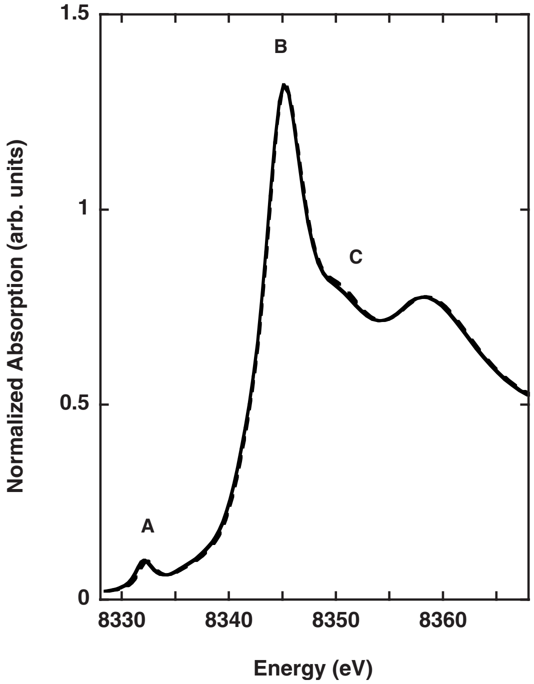

FIG. 2. Ni K-edge XANES simulation using the average crystallographic structure reported by neutron diffraction in the insulator (solid line) and metallic (dashed line) phases.

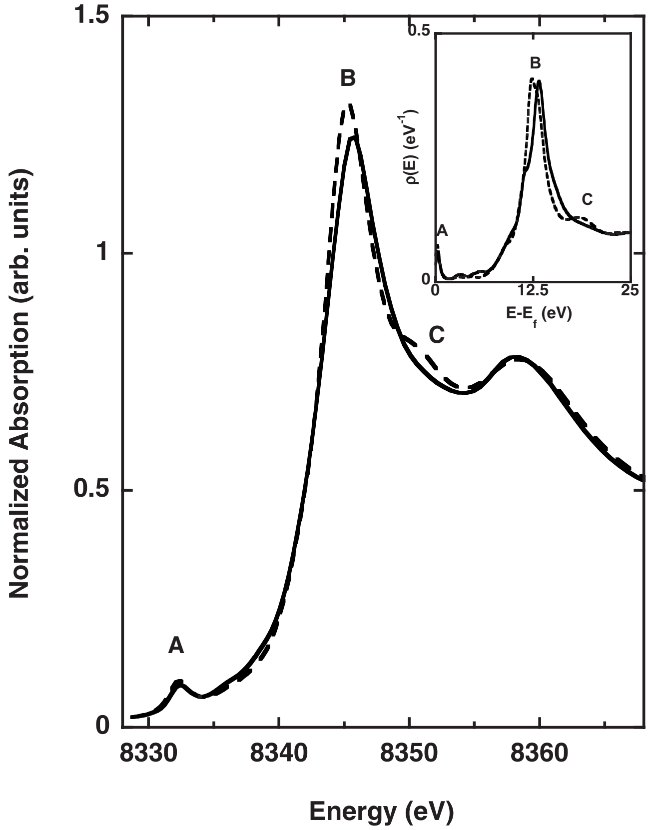

FIG. 3. Ni *K*-edge XANES simulation in the metallic (dashed line) and insulating (solid line) phases using orthorhombic symmetry and monoclinic symmetry groups respectively (dashed line). Insert: Ni *p* density of states as a function of energy, measured from the calculated Fermi level, for the orthorhombic structure (dashed line) and monoclinic structure (solid line).

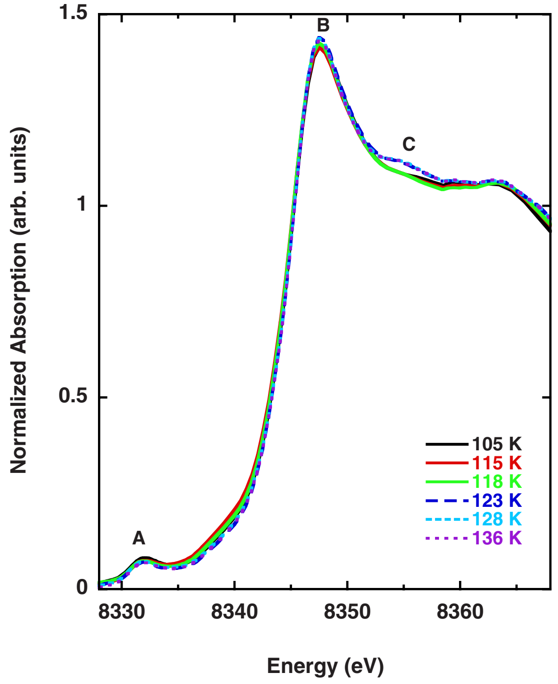

FIG. 4. (Color online) Ni *K*-edge XANES for ^{18}O $PrNiO_3$ at different temperatures above (dashed lines) and below (solid lines) of the metal-insulator transition. Quoted temperatures refer to nominal temperatures as explained in the text.

yields a Ni_2 site with two elongated Ni-O bonds. The Ni *p* projected density of states (*p*-DOS) is shown as an insert of Fig. 3. Although the calculation of the density of states was performed without the presence of the core hole, all features of the calculated XANES appear in the density of states, including feature A, indicating that indeed that feature has a *p* character. The calculation of Ni *d*-DOS exhibits a sharp peak, about 1.5 eV below E_f (not shown). This peak is sharper for the case of Ni_2, indicating more localized states *d* states than for Ni_1 or Ni in the orthorhombic phase. This is consistent with longer Ni-O bonds around that site, yielding less overlap between O 2*p* states and Ni 3*d* states, and a stronger localization of the latter. We note that a quantitative determination of Ni-O distances from EXAFS data is difficult due to the fact that in a monoclinic structure there would be four different Ni-O bond lengths in a range of ~0.1 Å. This leads to strong correlations between the fitting parameters used to fit the EXAFS spectra. Therefore, only the presence of bond lengths Ni-O bonds differing by ~0.1 Å can be inferred for the case of $NdNiO_3$ and $EuNiO_3$ through significant changes in the phase of the isolated Ni-O EXAFS signal, as shown in Ref. 11.

The change in the local structure around Ni implies a coupling between the electronic degrees of freedom (charge and spin) involved in the metal insulator transition and the ions. Such coupling had been originally shown by the large negative oxygen isotope effect on the magnetic and metal insulator transition temperatures in $PrNiO_3$.[12] Given the existence of this lattice-electron coupling, we expected that the change in the local structure around the Ni atoms, probed by the XANES, will show a corresponding change under isotopic substitution. Consequently, we also performed XANES measurements in ^{18}O $PrNiO_3$ across the metal-insulator transition (see Fig. 4). These measurements show the same kind of change observed in the measurements on the ^{16}O sample across the corresponding T_{MI}. The shoulder at C appears with less intensity for temperatures above the corresponding T_{MI}; however, its appearance tracks the change in T_{MI} under isotopic substitution. This result shows that the local atomic structure around Ni, specifically the proposed change in symmetry across T_{MI}, is affected by isotopic substitution. It thus suggests an important role of the electron-lattice interaction at the local level. The fact that the magnitude of this change is smaller than for the ^{16}O sample implies that the nature of the local lattice distortion is dynamical.[24]

IV. SUMMARY AND CONCLUSIONS

XANES measurements at Ni *K*-edge on the $PrNiO_3$ system across metal-insulator transition show a change in the local atomic structure. Modeling of the XANES at Ni *K*-edge shows that observed features are consistent with the orthorhombic structure reported by neutron diffraction for the metallic phase. However, the calculated changes using the same orthorhombic structure for the insulator region are inconsistent with the experimental spectra. Based on our simulations, we conclude that the XANES spectra in the insulator state are consistent with the monoclinic structure observed in other rare earth members of this nickel oxide family. The structure implies the presence of a Ni site with long Ni–O bonds, consistent with a Jahn-Teller distortion. These results indicate that even in the large size rare earth ion compounds of the family RNiO$_3$ a change in the symmetry centered at Ni occurs across the metal insulator transition, at least at the local scale. This change of symmetry implies the presence of an inhomogeneous local atomic structure in the insulating phase, similar to that present in other transition metal oxides, such as high-temperature cuprate superconductors. A metal-insulator transition temperature shift between Ni K-edge XANES of $PrNi^{16}O_3$ and $PrNi^{18}O_3$ is observed indicating a strong electron-lattice interaction at the local level.

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