Charge transfer at very high pressure in NiO

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We use resonant inelastic x-ray scattering to study the electronic structure of nickel oxide, the prototype charge-transfer insulator, as a function of pressure. At ambient pressure, we observe spectral features due to the charge-transfer excitation and the Coulomb correlation energy which progressively smear up to a pressure of 100 GPa. These changes are interpreted as due to increased dispersion of the concerned electronic bands. This opens new perspectives both for the study of electronic structure of correlated materials and for high-pressure research such as a deeper understanding of metal-insulator transitions, as well as the study of deep-earth chemistry.

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Since the early observations of de Boer and Verwey, 1 challenging accepted ideas by showing that partially filled bands could be insulators, the field of strongly correlated electrons has grown rapidly with new materials showing surprising properties. The mechanics of the metal to insulator transition with the variation of a given parameter (for example temperature or pressure) is central to this field. Nickel oxide is the prototype charge-transfer insulator and as such has been widely studied. It is now well established that though the \( U_{d-d} \) correlation energy is relatively high in this compound, the band gap is of the charge-transfer type that is central to this field. Nickel oxide is the prototype charge-transfer insulator and as such has been widely studied. It is now well established that though the \( U_{d-d} \) correlation energy is relatively high in this compound, the band gap is of the charge-transfer type that is primarily \( O \) \( 2p \) to \( Ni \) \( 3d \) character. 2 This gap has been measured to be about 4 eV in magnitude. 3 Several calculations of the electronic structure of NiO exist as this has proved to be a good testing ground for theories due to the influence of strong correlations. In fact, only explicit inclusion of the effects of this strong correlation in sophisticated band-structure calculations could bring these to predict the correct band gap and excitation spectra for this compound. 4 Local cluster models, however, were reasonably successful in predicting them, presumably because they dealt with the effects of correlation in a more direct way. 5

As argued in the well-known pioneering work by Mott, 6 an important parameter that can be varied better understanding of the electronic structure of strongly correlated transition-metal compounds is density, and therefore pressure. However, the variation of pressure either rules out the use of spectroscopic methods or imposes severe constraints on many of them. In this first use of resonant inelastic x-ray scattering (RIXS) under ultrahigh pressure, we measure charge-transfer excitations in NiO up to 1 Mbar. In the coherent second-order RIXS process, an incoming photon is absorbed with the system transiting to an intermediate state. The number of electrons is conserved and the excitation spectrum is measured directly. RIXS has been successfully used 7 to study the electronic structure of Mott insulators. It is also an ideal probe for high-pressure studies, since x-rays can penetrate sample environment, can be focused to small sizes, and can be tuned to a given energy ensuring resonant enhancement of the cross section.

The experiment was performed at beamline ID16 at the European Synchrotron Radiation Facility. The experimental setup was that of a Rowland circle spectrometer using a spherically focusing, elastically bent Si(551) analyzer and a Peltier-cooled Si-diode detector. The scattering plane was horizontal. Undulator radiation monochromatized by a cryogenically cooled Si(111) channel-cut monochromator with a bandwidth of 1.4 eV was focused by a toroidal mirror. The incident-beam intensity was monitored by a Si-diode detector. The sample (polycrystalline powder from Aldrich Chemicals with a nominal Ni content of 76% corresponding to a stoichiometry of Ni\(_{0.97}\)O) was loaded in a symmetrical Mao-Bell cell with 300 \( \mu \)m culet diamonds using a 5-mm-diameter high-strength Be gasket. At the energies used (8.35 keV, around the Ni K edge) and for a 90° scattering geometry, the x-ray transparent Be gasket was a critical part of the experiment. No pressure medium was used permitting us to maximize sample size, the price to pay being nonhydrostaticity. The pressure was determined using ruby fluorescence and diffraction, and the gradient was evaluated. X-rays were incident on the sample through the gasket and slits were used to define the spot size on the sample to 30 \( \mu \)m (vertical) \( \times \) 110 \( \mu \)m (horizontal). This slit size was maintained throughout the experiment as the sample size never became smaller. The measured flux on the sample was 1.3 \( \times \) 10\(^{12} \) photons/s. The total resolution as measured from the full width at half maximum of the peak due to quasielastic scattering was 1.5 eV.

In an earlier study on NiO, Kao \textit{et al}. 8 showed that the RIXS signal measured at a scattering angle of 30° with the momentum transfer along the [001] direction consists of two peaks, centered around 4.9 and 7.8 eV. Our experiment diff-
In Fig. 1, we show our RIXS data at room pressure and temperature. We measure a broad inelastic spectral feature with a marked low-energy shoulder, peaking at 5.3 eV and a peak centered at 8.5 eV, as determined by fits to Gaussian line shapes. The energy loss (4.3 eV) to the edge of the absorption with an arrow showing the choice of incident energy (solid line). The dashed line is a constant-final-state scan (constant energy difference between incident and detected energy) at an energy loss of 5 eV, showing that the strongest resonance corresponds to the quadrupolar prepeak.

FIG. 1. Resonant inelastic x-ray scattering from polycrystalline NiO at ambient pressure with the incident energy tuned to the quadrupolar prepeak in the absorption spectrum. Two structures corresponding to energy losses of 5.3 eV and 8.5 eV are present. Inset: high-resolution partial fluorescence yield spectrum of the Ni K-edge absorption with an arrow showing the choice of incident energy (solid line). The dashed line is a constant-final-state scan (constant energy difference between incident and detected energy) at an energy loss of 5 eV, showing that the strongest resonance corresponds to the quadrupolar prepeak.

The sample and worked at a scattering angle of 90° ~ m. We tuned our incident energy to this resonance with the choice of the energy transfer is maintained while the incident energy is increases from 4 to 5 eV. As pressure is increased, electronic bands increasingly disperse which means that the sharp resonances seen at lower pressures become ill defined as seen by the increasing electronic bandwidth.

FIG. 2. RIXS data as a function of pressure. Bottom dashed line: nonresonant background. As pressure is increased the resonant intensity decreases and the 5.3 and 8.5 eV structures smear out due to the increasing electronic bandwidth. shoulder is the value of the charge-transfer gap in NiO, thus providing a direct measure of this quantity. We associate this feature to the metal-ligand transition leading to a $d^{n+1}$ $L$ excited state, where $d^n$ is the metal ground-state configuration and $L$ is a ligand hole. We associate the peak at 8.5 eV primarily to the metal-metal transitions leading to $d^{n+1}d^{n-1}$ excited states and thus to the correlation energy $U_{d,d}$ related to transport in the $d$ band. Given this sensitivity to the electronic structure of NiO in our measurement we now look for changes introduced by varying the pressure on the sample. In Fig. 2, we show the RIXS data as a function of increasing pressure up to 100 GPa. The data is normalized to the monitor intensity. The dashed line is a measurement of the nonresonant background with the incident energy at 8370 eV, well above the absorption edge. We also show for comparison arbitrarily scaled data (labeled room pressure) measured at ambient pressure outside the pressure cell. As pressure is increased, the resonant inelastic x-ray scattering intensity progressively decreases. Second, the double structure (shoulder and peak) clearly resolved at ambient and lower pressures, smears at pressures above 50 GPa into a poorly defined line shape. By fitting the RIXS data with a sum of three Gaussians to account for the two features mentioned above as well as the intensity at higher energies, this trend can be better understood. The 5.3-eV feature does not shift appreciably as pressure is increased, while its width doubles from 2 to 4 eV. The 8.5-eV peak shifts to above 10 eV up to 50 GPa and then remains constant, while its width also increases from 4 to 5 eV. As pressure is increased, electronic bands increasingly disperse which means that the sharp resonances seen at lower pressures become ill defined as seen by the increasing width of the peaks. In particular, overlap with the anions increases since the lattice parameter changes by about 10% at 100 GPa. Calculations suggest that the shape of the electronic density of states does not change much with pressure but the density of states decreases uniformly and bandwidth increases.10 This is compatible with the behavior changes introduced by varying the pressure on the sample. In Fig. 2, we show the RIXS data as a function of increasing pressure up to 100 GPa. The data is normalized to the monitor intensity. The dashed line is a measurement of the nonresonant background with the incident energy at 8370 eV, well above the absorption edge. 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A recent study has shown. We performed powder diffraction to study structural phase transitions till well above 100 GPa, as a result of structural change. NiO is not known to undergo a significant change in electronic structure due to increased overlap or due to changes in the crystal field. The behavior of the 8.5-eV peak would suggest an initial increase in the d-d Coulomb interaction with pressure. Though this is unexpected, since screening increases with repulsion, we remark that it is limited to lower pressures. The observed trends suggest that a metal-insulator transition would happen due to the closing of the charge-transfer gap as seen in other charge-transfer insulators at lower pressures. It is important to ascertain that this change in electronic structure is associated with band widening due to increased overlap or due to changes in the crystal field consequent to structural change. NiO is known to undergo structural phase transitions till well above 100 GPa, as a recent study has shown. We performed powder diffraction with high-energy x-rays at ambient pressure and at 100 GPa. The diffraction patterns are shown in Fig. 3(a), and are in excellent agreement with the data of Eto et al. Above a pressure of about 50 GPa, we do not observe a significant change in the RIXS signal. However, at higher pressures, changes do occur as observed visually on the sample and as shown by the Ni-K near-edge structure. At 77 GPa, the sample observed through a microscope showed signs of metallic luster, which became clearly defined at 100 GPa. A photograph [Fig. 3(b)] of the sample at 100 GPa shows that the central core reflects light in contrast with the dark ring around it. This luster disappeared when pressure was removed. Preliminary optical reflectivity measurements on the 100-GPa sample show a shift of the 4 eV ambient pressure peak in NiO to 3 eV and a tail extending into the gap causing the metallic luster. It is also possible that the measured pressure gradient could cause a local lowering of symmetry and precipitate changes in electronic structure at pressures lower than expected for the NiO structure. This question could be settled through further measurements using a pressure medium such as He and through calculations that would help to quantify the effect of pressure, as well as that of a gradient on the RIXS signal. In Fig. 4, we show the Ni K-edge measured by using the spectrometer set on the Kβ peak while the incident energy was varied across the edge.
geochemistry, such as the depletion of nickel in earth’s lower mantle.

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