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Experiment title: Effect of lattice distortions in NiO: a high pressure study		Experiment number: HE-2878
Beamline: ID16	**Date of experiment:** from: 19-Nov-2008 to: 26-Nov-2008	**Date of report:** 01-Sep-2009
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Report:
The purpose of this experiment was to see the change in the electronic band structure of NiO as a function of pressure, using resonant inelastic x-ray scattering (RIXS) spectroscopy. The measured signal was the *dd* excitation spectrum. The spectra consist of excitations in an energy-transfer range 0–4 eV, due to transitions between occupied and unoccupied Ni 3d bands, which are partly hybridized with O 2p.

The experiment was performed on ID16 using photon energies at the Ni K edge. The incident beam was monochromated to a bandwidth of 80 meV at 8.3 keV and focused using a toroidal mirror on the sample in a spot of 40×140 μm. The sample was NiO powder enclosed in a diamond anvil cell and a beryllium gasket, using nitrogen as a pressure-transmitting medium. Both ingoing and observed outgoing beams passed through the Be gasket, the scattering angle being 90°. The spectrum of scattered x-rays was analysed using a diced Si(551) analyser crystal and a photon-counting Medipix 2D detector [1]. The spectrometer operated in a Rowland geometry with diameter of 1 m. The total energy resolution was chosen to be 150 meV.

NiO crystallizes in the cubic rock-salt structure but below the Néel temperature ($T_N = 523$ K) it has a small trigonal distortion from the perfect cubic symmetry due to the antiferromagnetic interaction. The cubic crystal field splits the $3d$ orbitals into two braches, e and t_2 sets separated by an energy given by the crystal-field parameter $10Dq$, assuming purely atomic localized levels. There are three clearly visible well-separated dd excitations in this case, one at $10Dq \approx 1$ eV, and two around 1.7 and 3 eV in ambient conditions [2].

The trigonal distortion splits the t_2 levels but not the e in a purely atomic picture. A splitting of the unoccupied e orbitals would be visible in the resonances of the two excitation symmetries. This kind of effect has been indeed observed in a previous experiment performed with a single crystal [2]. Theoretical investigations of the band structure of NiO [3,4] have indeed predicted a nondegeneracy of the e bands already in ambient conditions, with increasing splitting with an increasing pressure. In practice the results show that RIXS can show promise of a k-selective unoccupied-band mapping method.

The measurements were done at $P = 0$, 20 and 55 GPa. The experimental results are shown in Fig. 1. First, we measured the Ni K x-ray absorption spectrum. The left panel in Fig. 1 shows a zoom-up to the pre-edge region in different pressures. The RIXS measurements were done by tuning the incident photon energy around the pre-edge and measuring the spectra of x-rays emitted by the sample. The resulting 2-dimensional maps of the spectra are also shown in Fig. 1. The very intense broad feature starting at energy transfers > 4 eV is the charge transfer band. At lower energy transfers, the 3 distinguishable dd transitions can be observed. They move to higher energy transfers with increasing pressure, with the highest-energy peak merging to the charge-transfer band at 55 GPa. Most important findings are the ones concerning the resonances of the individual excitations: at $P = 0$ GPa the powder average shows only a single resonance but with an increasing pressure the resonances start to split due to an increased splitting of the unoccupied e bands. This is in a good agreement with the theoretical band structure behaviour under pressure [3] and suggests an advanced possibility of **k-selective RIXS [5]** with single crystal samples. A manuscript on these results is under preparation while continuation studies are being planned.

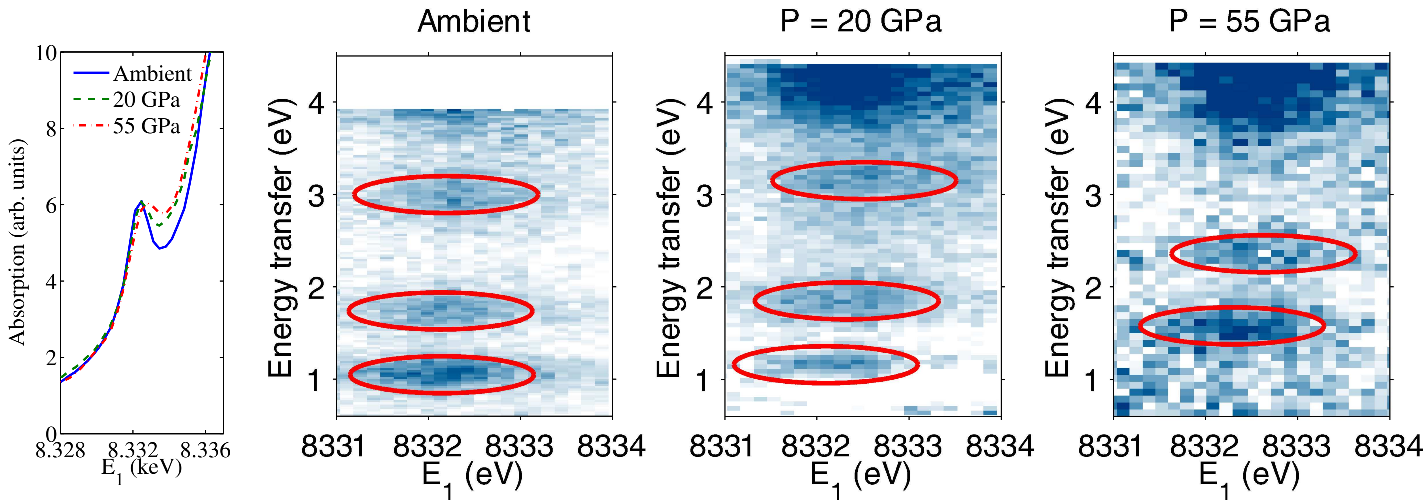

Figure 1. Left: zoom to the pre-edge region of the Ni K edge of NiO in the different pressures. Right: experimental excitation maps as a function of incident-photon energy and energy transfer. The dd excitations are emphasized with ellipses.

[1] Huotari *et al.* Rev. Sci. Instrum. 77, 053102 (2006); [2] Huotari *et al.* Phys. Rev. B 78, 041102 (2008); [3] Zhang *et al.* Phys. Rev. B 74, 054421 (2006); [4] Kuneš *et al.* Phys. Rev. Lett. 99, 156404 (2007); [5] Enkisch *et al.* Phys. Rev. B 60, 8624 (1999)