STUDY OF ELECTRONIC STATES IN 3*d* TRANSITION-METAL OXIDES BY X-RAY RESONANCE MAGNETIC SCATTERING

Transition-metal oxides such as NiO, CoO, and MnO have been recently recognized as charge transfer type insulators of which the band gap exists between the p-band of O^{2-} and the upper Hubbard *d*-band of transition metal M^{2+}. The lower Hubbard band and the *p*-band overlap each other, while the degree of overlap and the energy level of each band differ among NiO, CoO, and MnO. Information regarding the mechanism of the spin state changes of these materials is crucial in the discussion of highly correlated antiferromagnetic insulators on the basis of the charge transfer model. In this context, the *p*-type band of these materials displays interesting magnetic features.

Due to the lack of an effective experimental method, such information of the spin states has never been elucidated. X-ray resonance magnetic scattering is a new spectroscopic method, providing spin resolved information regarding unoccupied states. This method can be applied to antiferromagnetic materials, even though magnetic circular X-ray dichroism or spin resolved photoemission spectroscopy are not applicable for these materials. Moreover, this method enables us to separate the electronic states according to symmetry utilizing polarization dependence of the scattering amplitudes.

The first observation of X-ray resonance magnetic scattering from NiO was reported by Hill *et al.* [1] , introducing the observation of a strong enhancement of magnetic scattering at the energy corresponding to the pre-peak position in the *K*-absorption spectrum. This peak was claimed to be due to the quadrupole resonant magnetic scattering corresponding to the *d*-band, which was also confirmed by Neubeck *et al.* [2]. Furthermore, they

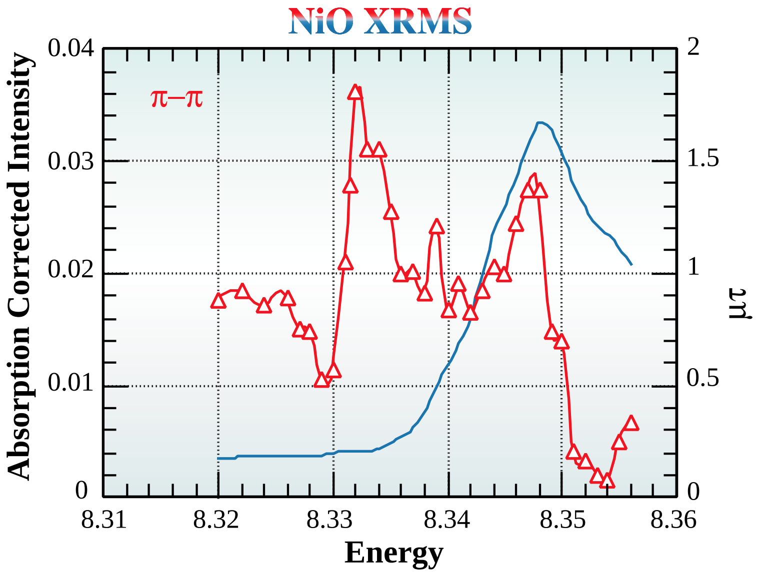

Fig. 1. Energy dependence of the resonance magnetic scattering intensity at the K-absorption edge of nickel. Polarization of the incident beam and scattered beam are in the π–π configuration. Intensities are corrected for the absorption. The K-absorption spectrum is designated by the solid line.

found dipole resonant magnetic scattering at energy corresponding to the main peak position in the K-absorption spectrum, along with an observation of CoO [3], where both dipole and quadrupole resonant magnetic scattering were also reported. The respective origins of the dipole scattering amplitude of NiO and CoO, however, still have not been satisfactorily determined. The 4p-bands of the transition metal in both NiO and CoO are believed to be empty, suggesting no existence of exchange splitting. We planned to investigate the spin polarized spectrum of the vacant states of antiferromagnetic NiO and MnO using polarization analyzed X-ray resonance magnetic scattering. This is the first step in our investigation of the transition metal oxides, toward the observation of the spin polarized spectrum of vacant states in the antiferromagnetic NiO [4].

The experiment was performed at **BL39XU** where the undulator X-ray beam is monochromatized by a Si (111) monochromator. A total reflection mirror is used to suppress higher harmonics. The X-ray beam is highly polarized in π polarization. To make σ polarized incident beam, a diamond phase retarder is used. A π or σ component of the scattered beam was analyzed by an Si (331) analyzer crystal. A sample is a slab-like (111) single T-domain crystal. Both components of the magnetization parallel and perpendicular to the scattering plane are possible to appear, as no magnetic field has been applied.

Rocking curves of a half integer order 5/2 5/2 5/2 reflection are measured in the π–π and the σ–σ polarization configurations at energies near the K-absorption edge. Integrated intensity plots, corrected for absorption, are shown in the figures. The spectrum shown by open triangles in Fig. 1 is measured in the π–π configuration, while the spectrum shown by open triangles in Fig. 2 is measured in the σ–σ configuration. The solid lines

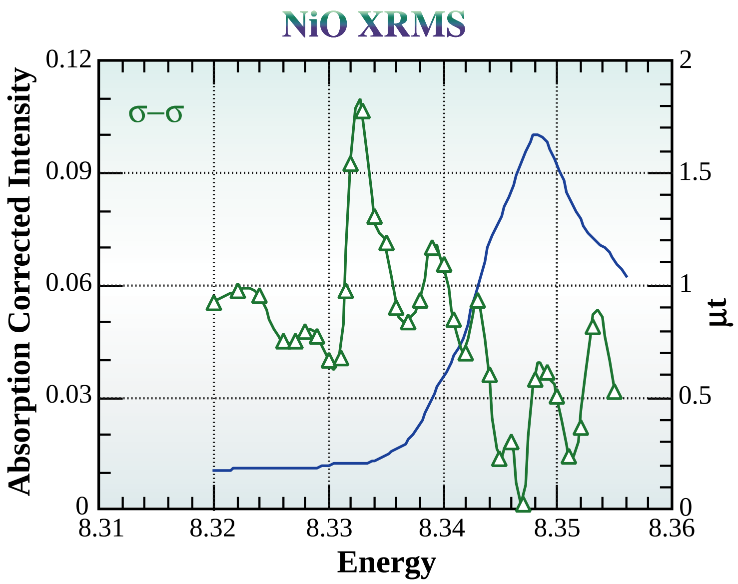

Fig. 2. Energy dependence of the resonance magnetic scattering intensity at the K-absorption edge of nickel. Polarization of the incident beam and scattered beam are in the σ–σ configuration. Intensities are corrected for the absorption. The K-absorption spectrum is designated by the solid line.

in both figures designate absorption spectra measured on NiO powder. We observed a strong intensity enhancement in both resonant magnetic scattering spectrum at 8.332 keV, corresponding to the pre-peak position of the absorption spectrum. Another strong intensity enhancement in the π–π configuration at 8.347 keV, corresponding to the main-peak position of the absorption spectrum, was observed, as well as an anti-phase dip at the same energy in the σ–σ configuration. Interestingly, this anti-phase behavior between the π–π and the σ–σ configurations appears again on the higher energy side of the 4*p* absorption peak. We recognize this phenomenon in Fig. 3, where the spectrum indicated by open triangles is a difference spectrum between π–π configuration and σ–σ configuration after being scaled at the maximum. An anti-phase oscillatory behavior in the difference spectrum suggests the existence of some other mechanism beyond the simple 4*p* polarization model. At the pre-peak position, the peak widths of the π–π configuration and the σ–σ configuration spectra interestingly appear to differ, where higher energy side of the π–π configuration spectrum is wider than that of the σ–σ configuration spectrum. A small hump in the difference spectrum at the pre-edge position in Fig. 3 indicates this fact. Our immediate future direction is to proceed to the measurement of MnO. A comparison of the spectra between NiO and MnO is highly expected.

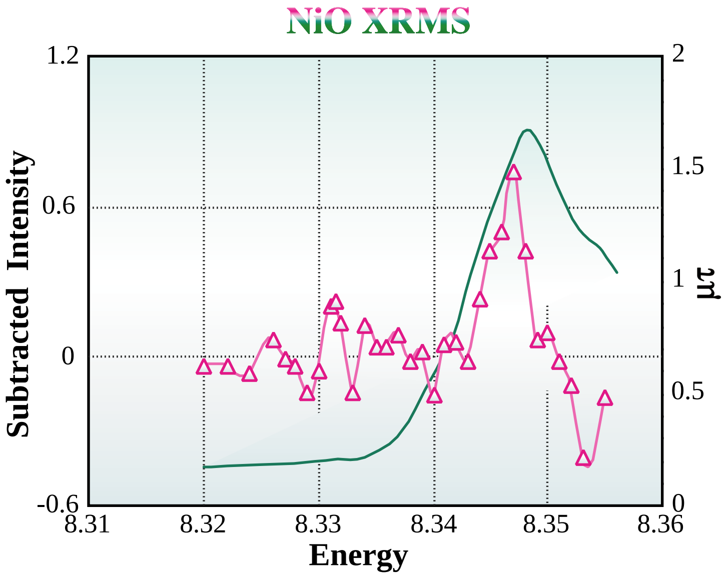

Fig. 3. A difference spectrum between the π–π configuration and the σ–σ configuration, after the intensity had been scaled at the maximum. Large p-type polarization appears at the region, which coincides with the main absorption peak. The spectrum is bipolar, while the absorption is unipoler type. A small hump can be seen at the slightly high energy side of the pre-edge absorption peak.

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