

## Resonant Soft X-Ray Emission Spectroscopy of NiO across the Ni $L_{2,3}$ Thresholds

Hirofumi ISHII<sup>1,\*</sup>, Yoichi ISHIWATA<sup>1</sup>, Ritsuko EGUCHI<sup>1</sup>, Yoshihisa HARADA<sup>2</sup>,  
Masamitsu WATANABE<sup>2</sup>, Ashish CHAINANI<sup>1,3</sup> and Shik SHIN<sup>1,2</sup>

<sup>1</sup>*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581*

<sup>2</sup>*Institute of Physical and Chemical Research(RIKEN), Sayo-gun, Hyogo 679-5143*

<sup>3</sup>*Institute for Plasma Research, Bhat, Gandhinagar-382 428, India*

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We study the electronic structure of NiO using resonant soft X-ray emission spectroscopy across the Ni  $L_{2,3}$  thresholds. We observe inelastic (Raman) features within 10 eV of the elastic peak energy. At the  $L_3$  resonance, the features within 4 eV are enhanced and can be directly assigned to the  $d$ - $d$  multiplets of NiO, in correspondence to features observed in optical absorption spectra. Resonance enhancements of the triplet and singlet states resolved in energy confirm a spin-flip transition. Charge-transfer (CT) excitations are also clearly identified by resonance enhancement at photon energies corresponding to the satellites observed in the Ni  $L_{2,3}$  X-ray absorption spectra.

KEYWORDS: resonant soft X-ray emission spectroscopy,  $d$ - $d$  excitation, charge-transfer excitation, transition metal, NiO, Raman

### §1. Introduction

Electronic structure of transition metal compounds remains a very interesting topic of research even after decades of research due to the discovery of exotic properties such as superconductivity and giant magnetoresistance (GMR). One-electron band theory predicts that partially filled  $d$ -electron compounds such as divalent NiO should be metallic, in stark contrast to its well-known properties of a large band gap antiferromagnetic insulator. The introduction of the concept of strong electron correlation by Mott in 1949 at least qualitatively explains the insulating gap in terms of a half-filled band in NiO.<sup>1)</sup> A more complete picture relating the delicate tuning of electronic structure in transition metal compounds by the relative strengths of the Coulomb correlation energy versus charge transfer energy is provided by the Zaanen-Sawatzky-Allen (ZSA) generalized theoretical phase diagram.<sup>2)</sup> Further complications such as bandwidth control, crystal field effects, orbital ordering, etc. enhance the field of transition metal compounds for developing new properties of materials. While the concept of strong on-site Coulomb correlations in transition metal compounds is indispensable, determination of its magnitude is no easy task. While the band gap may be associated with the energy required to remove an electron from the valence band and add it to the conduction band, for a ground state  $d^n$  configuration the energy corresponds to the  $d^n + d^n \rightarrow d^{n-1} + d^{n+1}$  relating the energy difference to the on-site Coulomb interaction,  $U_{dd}$ . Although recent sophisticated band structure calculations obtain a small gap for NiO, an experimentally determined intrinsic gap yields a value of 4.3 eV. The problem is more general and relates to the class of insu-

lating transition metal compounds expected to be metals by band theory. Band-theory calculations of the Ni dihalides predict metallic behavior or at most a small gap, whereas the optical measurements suggest a large band gap decreasing with decreasing electronegativity of the anions. Further, cluster calculations on NiO and NiCl<sub>2</sub> suggest that the band gap is better defined as a charge transfer gap rather than a  $d$ - $d$  gap, as in the ZSA phase diagram. Thus, in the charge transfer insulator NiO, the eight electrons in the partially filled  $3d$  shell of the Ni<sup>2+</sup> are localized. In contrast to the free ion, the degeneracy of the  $d$  state is partially lifted; the  $t_{2g}$  and  $e_g$  states are energetically separated by the crystal field splitting arising from the six surrounding O<sup>2-</sup> ligand ions. The ground possesses a spin triplet  ${}^3A_{2g}$  ( $t_{2g}^6 e_g^2$ ) symmetry, hybridization with O  $2p$  states result in substantial charge transfer character and NiO is described as a linear combination of  $d^8$ ,  $d^9 \underline{L}$  and  $d^{10} \underline{L}^2$  states. Several triplet and singlet excited states exist within  $\sim 3$  eV of the ground state. Dipole transitions also become weakly allowed for the  $d$ - $d$  transitions at the Ni<sup>2+</sup> ion because of ion-lattice interactions and have been identified in optical spectroscopy. While core-level XPS as well as valence and conduction band measurements have been carried out in detail and confirm the charge-transfer character of NiO,<sup>3,4)</sup> recent theoretical work indicate band structure effects in the core-level XPS of NiO and two independent relaxation processes involving valence band Ni  $d$  state of either pure or hybridized character.<sup>5)</sup> In this work, we study the electronic structure of NiO using soft X-ray emission spectroscopy (SXES) which does not have the problem of core-hole effects as in XPS, and also is more bulk-sensitive.

Due to the advent of third generation synchrotron

\*E-mail: ishii@issp.u-tokyo.ac.jp

sources, resonant soft X-ray emission spectroscopy (RXES) is now possible with the required energy resolution and intensity to probe  $d$ - $d$  excitations and charge-transfer (CT) excitations. Recent work has indeed shown that  $d$ - $d$  and charge-transfer excitations can be identified in inelastic x-ray emission spectra in systems like MnO,<sup>6)</sup> Sr<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub>,<sup>7)</sup> TiO<sub>2</sub>,<sup>8)</sup> etc. The importance of RXES is growing and the role of the intermediate state is under examination. Our results provide clear evidence of inelastic features in NiO resolved into the  $d$ - $d$  multiplets of NiO, confirm the spin-flip transition and the charge transfer excitations.

## §2. Experiment

Soft X-ray emission measurements were performed at undulator beamline BL-2C of the Photon Factory (PF).<sup>9)</sup> The SXES spectrometer uses the Rowland-circle geometry in which input slit, spherical grating, and multichannel detector lie on the focal circle.<sup>10)</sup> The total resolution of the SXES experiment was 0.7 eV corresponding to a  $E/\Delta E \approx 1000$ . The incident angle of the polarized light on the sample was about 40°. The X-ray absorption spectrum (XAS) was obtained at the same beamline by using the total electron yield (TEY) mode as measured by the drain current of the sample. The sample was single-crystal of NiO and the measurements were carried out at room temperature. The base pressure of the vacuum chamber was about  $1 \times 10^{-8}$  Pa.

## §3. Results and Discussion

Figure 1(a) shows the X-ray absorption spectrum (XAS) across the Ni  $L_{2,3}$  thresholds as a function of incident photon energy. The two groups of spectral features around 853 eV and 870 eV are due to the spin-orbit split  $L_3$  and  $L_2$  levels, respectively. The number labeled on the spectrum correspond to photon energies at which the XES measurements were obtained and relate to the various structures as discussed below. In the  $L_3$  region, we observed four features (Nos. 4, 5, 6 and 7). From an analysis in terms of the Anderson impurity model, it is known that features 4 and 5 originate in the multiplets of the  $3d^8$  initial state and features 6 and 7 are due to the charge-transfer state  $3d^9L$ .<sup>11)</sup> A similar assignment can be made to features labeled 11 and 12 in the XAS spectrum due to the  $3d^8$  multiplets at the  $L_2$  threshold with charge transfer excitations at higher energy but which exhibit very weak intensity.

Figure 1(b) shows the resonant soft X-ray XES (RXES) of NiO obtained at energies labeled in Fig. 1(a). We first discuss the spectrum obtained at the highest incident photon energy 882.4 eV (labeled No. 13). This energy is far above the  $L_3$  and  $L_2$  absorption edges, resulting in two main fluorescence structures which correspond to the refill of  $2p_{3/2}$  (851.4 eV) and  $2p_{1/2}$  (869.0 eV) holes, which vertical dot lines in Fig. 1(b) indicate respectively. A weak structure around 853 eV is also observed. This feature is not observed at lower photon energies, but only for excitation energies larger than or equal to the  $L_2$  absorption peak labeled No. 11 (869.8 eV). Since this structure can be observed only after creation of

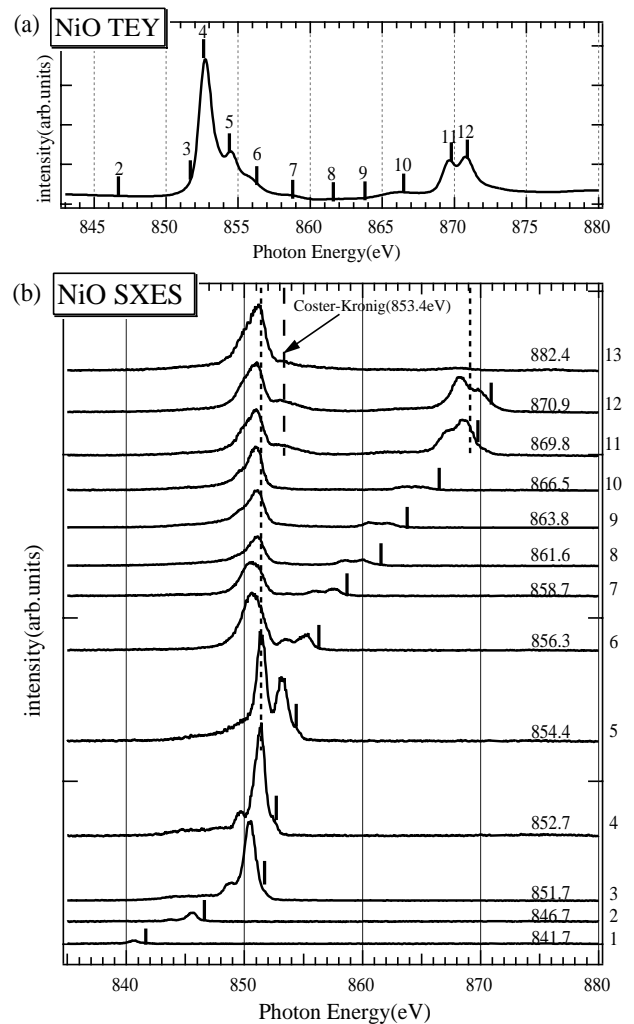


Fig. 1. (a) NiO  $L_{2,3}$  X-ray absorption spectrum. (b) The SXES spectra of NiO across  $L_{2,3}$  absorption edge. The number labeled beside the right axis stand for the excitation energy corresponding to the number obtained in (a).

the  $2p_{1/2}$  hole, this structure is assigned to the Coster-Kronig decay structure<sup>12,13)</sup> of the  $2p_{1/2}$  hole of the kind:  $2p_{1/2} \rightarrow 2p_{3/2}$ . The weakness of the fluorescence intensity of the  $2p_{1/2}$  feature compared to the relative intensity in the absorption spectrum is due to the increase of the Coster-Kronig decay channel.

Next we discuss the RXES obtained with the lowest photon energies used in the present experiment. Starting with the photon energies below the  $L_3$  threshold, we see a weak feature tracking the incident photon energy, which is due to the normal Raman process. The vertical tick marks in the figure correspond to the photon energy measured. A strong enhancement and clear structures are seen when the incident photon energy is 852.7 eV (No. 4) and this corresponds to the  $L_3$  absorption peak. A similar enhancement in intensities is also observed for the  $L_2$  absorption peak at 869.8 eV (No. 11). The assignment of such structure is well understood when we plot the XES spectra as a function of the loss energy or the Raman shift, as shown in Fig. 2. The Raman shift is derived from the emission spectra by subtracting the energy of the incident photons from the energy of the

emitted photons and plotted on a loss scale. At the  $L_3$  threshold (No. 4), we see a clear three peak structure in the spectrum. The small peak at 0 loss energy corresponds to the elastic recombination peak, with features corresponding to inelastic Raman shifts at constant loss energy when the photon energy is changed. Prominent Raman structures at 1.1 eV (A) with a shoulder at 1.6 eV (B) and another feature at 3.0 eV (C), as well as broad weak features between 4–10 eV are observed. Comparing with the XAS spectrum also plotted with the incident photon energy on a vertical scale in the same figure, we understand that the features (A)–(C) originate in the  $3d^8$  initial state. Feature (A) is strongly enhanced at a photon energy of 852.7 eV while on increasing the incident energy to 854.4 eV (No. 5) feature (A) is suppressed and feature (C) is enhanced. This change in intensity of the Raman features indicates that the lowest energy feature (A) is dominated by the spin triplet state and feature (C) is dominated by the spin singlet state. This implies that feature (C) is derived from a spin flip transition as was calculated by Braicovich *et al.*<sup>14</sup> and de Groot *et al.*<sup>15</sup> The shoulder (B) is also more clear in the spectrum No. 5 and suggests a singlet state. This is consistent with the multiplet structure and has been measured from optical spectroscopy by Newman and Chrenko,<sup>16</sup> and is also shown in Fig. 2 for comparison. On increas-

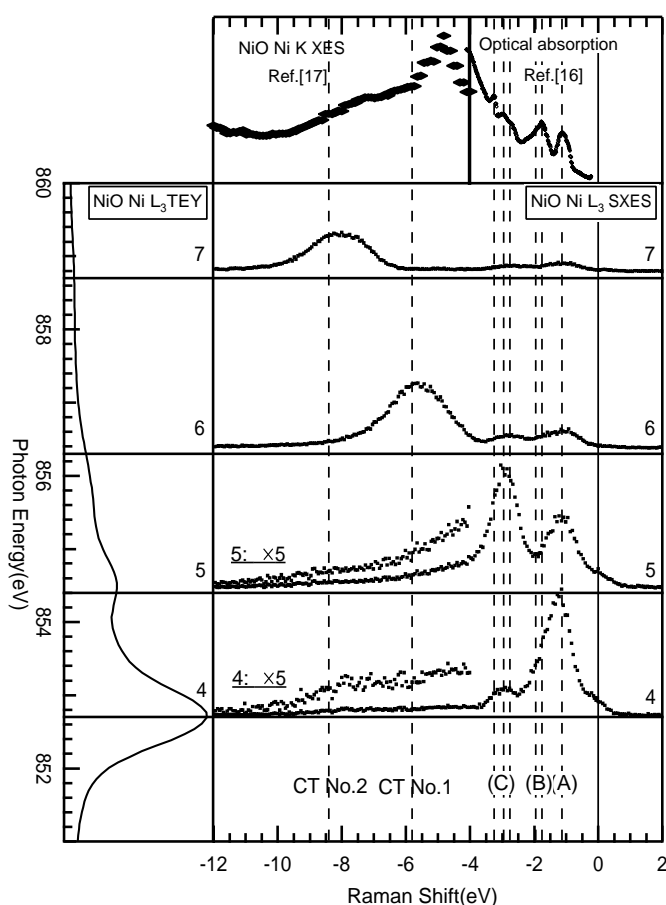


Fig. 2. The Raman spectra at Ni  $L_3$  absorption region. The labeled beside the left axis stand for the excitation energy corresponding to the letters in Fig. 1(a). The dotted lines indicate inelastic structures of RSEXES spectrum.

ing the incident photon energy to the satellites (No. 6 and No. 7) seen in the XAS spectrum originating in the charge-transfer initial states of  $3d^9\bar{L}$  character, we observe inelastic features at 5.8 eV and 8.4 eV enhanced in the spectra. This indicates the CT character of features seen in XES and are marked CT No. 1 and CT No. 2 in Fig. 2. This is consistent with the Ni  $K$ -edge XES study and for comparison we show the CT excitations measured in the Ni  $K$ -edge XES by Kao *et al.*<sup>17</sup> The validity of CT interpretation of the Ni  $K$ -edge XES satellite features has been supported by comparing the energy position and width of the features and resonance effect they exhibit. In the present case, the observed inelastic Raman structure also show the same behavior. Since the measurements show broad features for the CT satellites which include the fluorescence features (see Fig. 1 dotted line), the higher resolution used in the present study enable us to correctly find the CT energies ( $\sim 5.8$  and  $\sim 8.4$  eV). This is in good agreement with photoemission compared to ( $K$ )-edge XES, though a discrepancy of  $\sim 1$  eV for the energy position of CT No. 1 satellite exists, most probably due to the differences arising from the selection rule.

Summarizing, we show in Fig. 3 a schematic diagram of the Ni  $L$ -edge SXES process. The ground state of NiO can be described as a superposition of the two principal components  $3d^8$  and  $3d^9\bar{L}$ . The energy of the  $3d^9\bar{L}$  state is higher than the  $3d^8$  state with the charge-transfer energy,  $\Delta$ . These initial states give rise to the intermediate state with a core-hole in the  $L_{2,3}$  levels. On deexcitation we obtain the charge neutral final states  $3d^9\bar{L}$  and  $3d^8$ . The intermediate state results in a rearrangement of the  $d$  electrons with intra-atomic  $d$ - $d$  transitions as shown in Fig. 3(b). These transitions result in a triplet dominated and a spin-flipped singlet dominated loss feature within 3eV of the elastic peak in RXES as seen in Fig. 2.

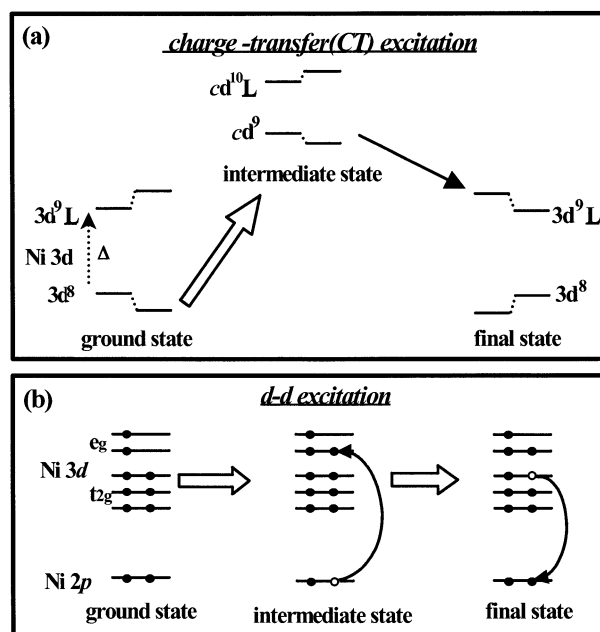


Fig. 3. Schematic diagram of (a) charge-transfer (CT) transition and (b)  $d$ - $d$  transition of NiO.

#### §4. Conclusion

In conclusion, resonant soft x-ray emission is found to be an efficient tool to study the  $d$ - $d$  transitions as well as charge-transfer excitations in strongly correlated NiO. The results are consistent with a spin-flip transition in the manifold of  $d$ - $d$  excitations, and confirm the role of charge transfer in describing the electronic structure of NiO.

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