Resonant X-ray emission spectra of $K_2Ni(CN)_4.H_2O$ at the Ni *K*-edge

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Resonant X-ray emission spectra were measured at the Ni K-edge for a planar low-spin nickel complex $K_2Ni(CN)_4.H_2O$. In the Ni K_β emission spectra, a resonant X-ray Raman scattering was observed in the pre-edge region, showing linear energy dispersion of the emitted photon with the incident photon energy. No energy loss features corresponding to the ligand-to-metal charge-transfer (LMCT) was identified. The LMCT feature is characteristic of strongly correlated systems such as NiO; therefore, the LMCT effect proves to be significantly suppressed. This is consistent considering strong covalent character between low-lying π* ligand and metal 3d (occupied) orbitals in low-spin nickel complexes.

Keywords: resonant X-ray emission; inelastic scattering; low-spin Ni complex; Ni K-edge; charge transfer.

1. Introduction

Recently resonant X-ray emission, or resonant inelastic X-ray scattering (RIXS), has become very attractive to investigate electronic structure of transition metal compounds, as well as X-ray absorption and photoelectron spectroscopy. One of its characteristics is that the resonant X-ray emission spectrum can give direct information on electron correlation effects such as LMCT, which are essential to describe the electronic state of transition metal oxides and halides (Kao et al., 1996; Hill et al., 1998; Shoji et al., 1999).

On the other hand, transition metal compounds with strong π-bonding such as a planar low-spin complex $K_2Ni(CN)_4.H_2O$ show strong covalent interaction between low-lying π* ligand orbitals and metal 3d (occupied) atomic orbitals (Hatsui et al., 1998; Takata et al., 1998; Takata et al., 1999). In the ground state, π back donation is as important as strong σ donation from ligand to metal. We can expect that the strong covalency hybridization and ligand field should enhance excitations to unoccupied ligand orbitals, resulting in LMCT satellites weakened. In order to know directly whether the correlation effect is small or not in the π-bonding system, resonant X-ray emission spectra of $K_2Ni(CN)_4.H_2O$ at the Ni K-edge are discussed.

2. Experimental

The experiments were performed at BL-7C of the Photon Factory with a Si (111) double crystal monochromator. As a sample $K_2Ni(CN)_4.H_2O$, we did not use single crystals but used a pellet of powder sample to avoid polarization dependence in X-ray absorption and emission spectra. The near-edge (XANES) spectra at the Ni K-edge were measured in the transmission mode. The energy spread of the incident beam was about 1.7 eV. X-ray emission was observed at a 90° scattering angle in the vertical plane by using a cylindrically bent Ge (444) crystal for the energy range around the Ni K_β fluorescence line. The analyzed X-rays were detected by a position-sensitive proportional counter (Iwazumi et al., 1997). The total energy resolution was 2.3eV around the Ni K_β line.

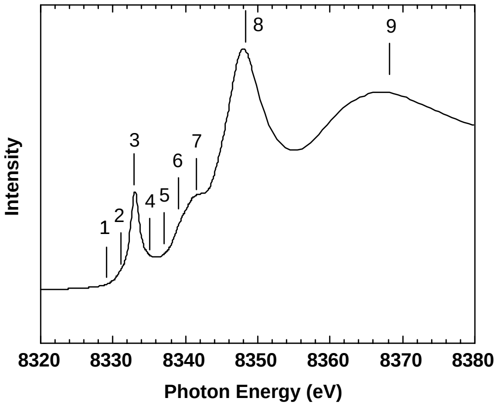

Figure 1
Ni K-XANES spectra of powder $K_2Ni(CN)_4.H_2O$.

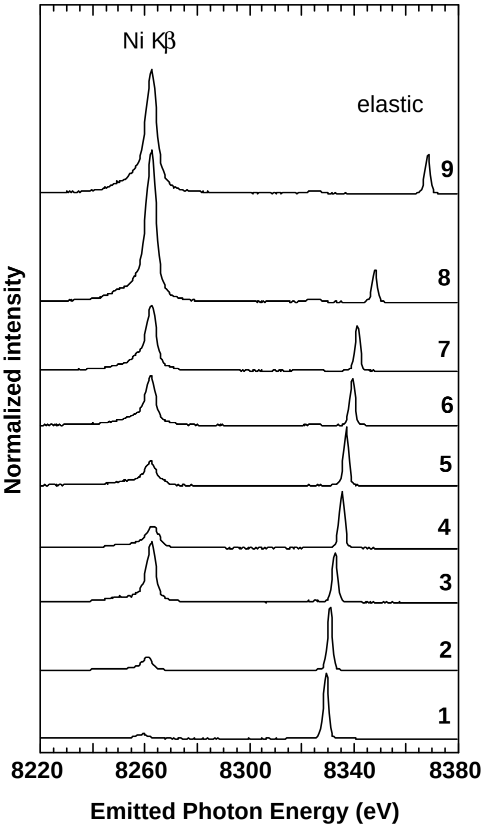

Figure 2
Resonant Ni K_β emission and elastic scattering spectra of $K_2Ni(CN)_4.H_2O$ obtained with the incident photon energies marked in Fig. 1. The intensity was normalized by the integrated intensity of the incident beam.

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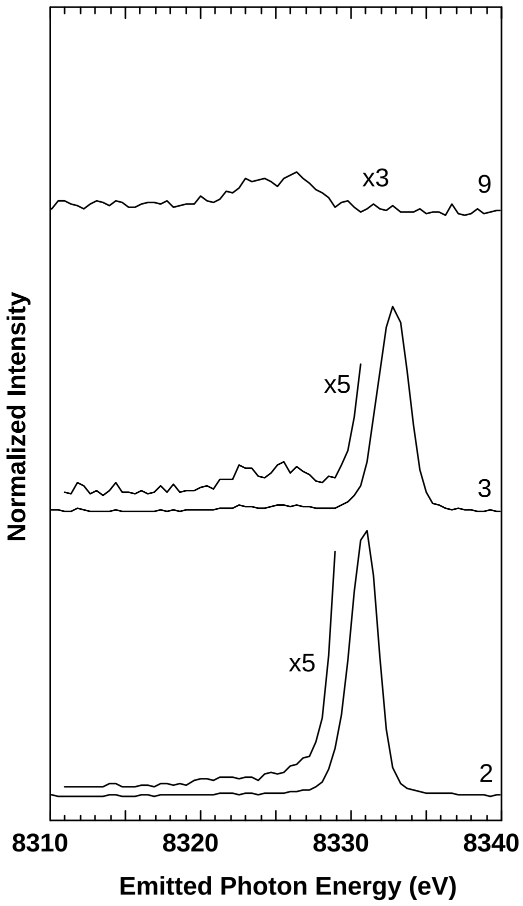

Figure 3
Elastic scattering spectra measured at the excitation energies (2) and (3) and the normal X-ray emission spectrum (9).

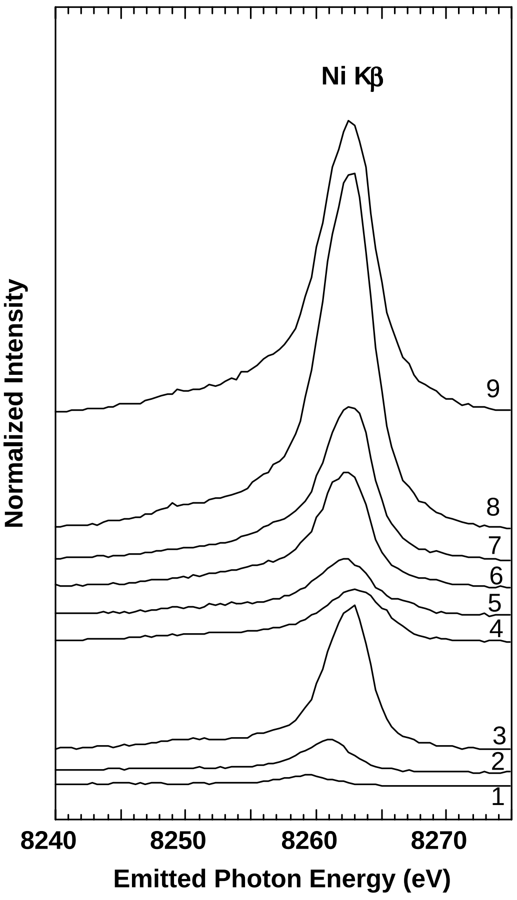

Figure 4
Excitation energy dependence of the Ni K_β peak.

3. Results and discussion

Figure 1 shows Ni K-XANES spectra of $K_2Ni(CN)_4.H_2O$. A weak shoulder 2 is assigned to a quadrupole transition to b_{1g}* (Ni 3_{dx2-y2}*-L_{x2-y2}). Peaks 3 and 7 are assigned to dipole transitions to a_{2u}*(Ni $4p_z$*+L_z*) and a_{2u}*(Ni $4p_z$*-L_z*), respectively (Kosugi et al., 1986), where L_z* means an unoccupied π (p_z) ligand orbital.

Figure 2 shows overview of X-ray emission spectra measured at the incident photon energies marked in Fig. 1. The intensity was normalized by the integrated intensity of the incident beam. In contrast to the elastic scattering peaks above 8330eV, the intensity of Ni K_β lines is enhanced by the resonant excitations. The elastic peaks measured in the pre-edge region (2 and 3) and above the Ni K-edge (9) are enlarged in Fig. 3. If there are some LMCT states, a satellite structure should be observed with energy loss of several eV, and show linear dispersion with the incident photon energy, as observed in NiO (Kao et al., 1996) and nickel halides (Shoji et al., 1999). At the quadrupole transition (2), no corresponding structure is clearly observed. At the dipole transition (3), two weak satellites appear but still exist at the same energies even at the normal emission (9); i. e., they do not show the linear dispersion. These satellites are assigned to the valence →Ni 1s transition. These results clearly indicate that the LMCT effect is negligibly small.

Figure 4 shows excitation-energy dependence of the Ni K_β peak. In NiO and nickel halides (Shoji et al., 1999), two weak shoulder structures are observed due to the mixing of the LMCT states. On the other hand, in $K_2Ni(CN)_4.H_2O$, no noticeable shoulder feature is observed and the K_β peak is considerably narrow in width. This also indicates a very weak LMCT effect in this compound. In the pre-edge region (1-5), the emitted photon energy disperses linearly with the incident photon energy. This is characteristic of resonant X-ray Raman scattering.

4. Summary

Resonant X-ray emission spectra of a planar low-spin nickel complex $K_2Ni(CN)_4.H_2O$ were measured at the Ni K-edge. No structure originating from LMCT states is observed around either the elastic scattering or the Ni K_β emission peaks. This is a direct experimental evidence for negligibly small electron correlation in the present π-bonding system. It can be concluded that covalent interaction between low-lying π* ligand orbitals and metal 3d (occupied) atomic orbitals governs electronic states as previously pointed out (Hatsui et al., 1998; Takata et al., 1999)

References

Kao, C.C., Caliebe, W.A.L., Hastings, J.B. & Gillet, J-M. (1996). *Phys. Rev.* **B54**, 16361-16364.

Hatsui, T., Takata, Y. & Kosugi, N. (1998). *Chem. Phys. Lett.* **284**, 320-324.

Hill, J.P., Kao, C.C., Caliebe, W.A.L., Matsubara, M., Kotani, A., Peng, J.L. & Greene, R.I. (1998). *Phys. Rev. Lett.* **80**, 4967-4980.

Iwazumi, T., Kobayashi, K., Kishimoto, S., Nakamura, T., Nanao, S., Osawa, D., Katano, R. & Isozumi, Y. (1997). *Phys. Rev.* **B56**, R14267-14270.

Kosugi, N., Yokoyama, T. & Kuroda, H. (1986). *Chem. Phys*. **104**, 449-453.

Shoji, H., Kobayashi, K., Iwazumi, T., Katano, R., Isozumi, Y., Kishimoto, S. & Nanao, S. (1999). *Jpn. J. Appl. Phys.* **Sup.38**, 592-595.

Takata, Y., Nakamura, M. & Kosugi, N. (1998). *Chem. Phys. Lett.* **287**, 35-39.

Takata, Y., Hatsui, T. & Kosugi, N. (1999). *J. Electron Spectrosc.* **101-103**, 443-447.

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