molecules and clusters

Li K-edge spectra of lithium halides

J. Tsuji[a), K. Kojima[b), S. Ikeda[c) H. Nakamatsu[d), T. Mukoyama[d) and K. Taniguchi[a)

[a]*Division of Electronics and Applied Physics, Osaka Electro-Communication University, 18-8 Hatsucho, Neyagawa, Osaka 572-8530, Japan,* [b]*Faculty of Science and Engineering, Ritsumeikan University, 1-1-1 Nozihigashi, Kusatsu, Shiga 525-8577, Japan,* [c]*Research Organization of Science and Engineering, Ritsumeikan University, 1-1-1 Nozihigashi Kusatsu, Shiga 525-5577, Japan,* [d]*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

We measured the Li K-edge spectra of lithium halides by means of total electron yield method (TEY), using the soft x-ray Beam Line 2 (BL2) of the compact synchrotron radiation facility at Ritsmeikan University in Japan. In lithium halides, the spectra have a sharp peak at about 60eV and a broad peak at the higher energy side. Various peak structures that appear in the absorption spectra are assigned to the corresponding Li-1s to valence band free orbitals transitions, which have been calculated by the Discrete Variational (DV)-Xα molecular orbital calculation method.

Keywords: Li K spectra; total electron yield; DV-Xα calculation

1. Introduction

X-ray emission and absorption spectroscopy are very useful techniques for the study of valence band structure. Especially, x-ray absorption spectroscopy can provide information of the unoccupied levels in the valence band as follows: valence band state, molecular Rydberg state, shape resonance state, free electron state and multiple electron excitation. Each state is characterized by its peak width, energy and asymmetry, and is affected by the chemical conditions.

Recently, light elements such as lithium and boron compounds and high molecular compounds including C, N and O have been investigated by means of x-ray spectroscopy in various fields of material science. Lithium compounds are generally used in lithium batteries, lithium glasses and other materials. However, there are few reports about Li-K absorption spectra (see for example, Sonntag, 1974; Kunz *et al.*, 1974; Peterson, 1975). Therefore, it is interesting to investigate the chemical bond condition of lithium compounds by comparing the experimental and the theoretical spectra.

In this work, the Li K-edge spectra of lithium halides measured by TEY are discussed with the theoretical spectrum calculated by DV-Xα molecular orbital calculation. Using the experimental spectra of lithium halides, the origin of each peak of the spectra is discussed by the wave function of the theoretical spectrum. Some differences are observed between experimental and theoretical spectra, but the overall agreement is well.

2. Experiment

We measured Li K-edge spectra using BL2 at the compact synchrotron radiation facility located in Ritsumeikan University in Japan. The storage ring is operated at 575 MeV and beam current of about 300 mA. BL2 is composed of pre-mirror and monochromator.
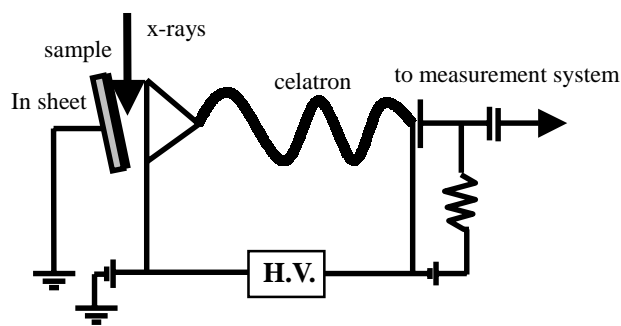
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*CELATRON is kind of electronmultiplier made by Murata Co.

Figure 1
The schematic illustration of sample room

The grazing incidence monochromator is using a concave grating of the modified Vodar type (Taniguchi, 1984). The entrance slit and concave grating are fixed, while the exit slit moves mechanically by keeping the position of each of the three elements on the Rowland circle (Tsuji *et al.*, 1997; Taniguchi, 1984). The concave grating (1200 lines/mm) is used in order to get monochromatic beam of the synchrotron radiation in the energy range between 50 eV and 600 eV. Li K-edge spectra are obtained by means of TEY method. The emitted photoelectron are captured by a CELATRON* detector, which is set at nearly parallel position to the sample (see Fig. 1). All spectra are calibrated by the energy of the first sharp peak of LiF (61.9 eV (Sonntag, 1974)).

3. Results

The Li K-edge spectra of lithium halides shows mainly a strong and sharp peak corresponding to the core excitation, and several fine structure features on the higher energy side (see Fig. 2). The spectrum of LiF agrees well with the result of previous works. Sonntag (1974) pointed out that the K-edge absorption of the lithium atom begins with the 1s to the 2p band excitation (the weak peak at 54 eV) and reaches its maximum at 61.9 eV. Menzel *et al.* (1973) and Kunz *et al.* (1973) calculated the imaginary part of the dielectric function (ε_2) for LiF, and compared their results to previous experimental absorption spectra reported by Brown *et al.* (1970) and Hansel *et al.* (1968). By their calculation, the weak absorption peak at about 54 eV and the peak of 61.9 eV were reproduced, however the structure in the higher energy side was not.

The decay mechanism of the core exciton has been studied by various methods (see, Aita *et al.*, 1981; Haensel *et al.*, 1969; Sugawara *et al.*, 1979; Arakawa *et al.*, 1976) and the first sharp peak of the absorption spectra for the lithium halides was attributed to the core exciton. However, there are very few theoretical calculation spectra that agree well with the experimental ones.

Previous X-ray Absorption Near Edge Structure (XANES) and X-ray Photoelectron Spectroscopy (XPS) spectra showed that the energy position of the Li K-edge depends on the electronegativity of the binding atom in the lithium compounds. This fact can be observed in the present result too. The peak position for the LiF, LiCl, LiBr and LiI-2H$_2$O is shifted toward lower energies as the electronegativity of the binding atom (F, Cl, Br and I respectively) decreases. This peak positions is 61.9 eV for LiF, 60.8 eV for LiCl, 60.5 eV for LiBr and 60.1 eV for LiI-2H$_2$O, respectively.

Besides the core excitation peak situated at 61.9 eV (marked as (a) in Fig. 2), we can observe higher energy features for all of the lithium halides (marked as (b) in Fig.2), situated at 69 eV for LiF, at 68.2 eV for LiCl, at 68 eV and at 65.6 eV for LiI-2H$_2$O. We can also observe the Br $M_{4,5}$-edge situated at 77 eV for LiBr which is
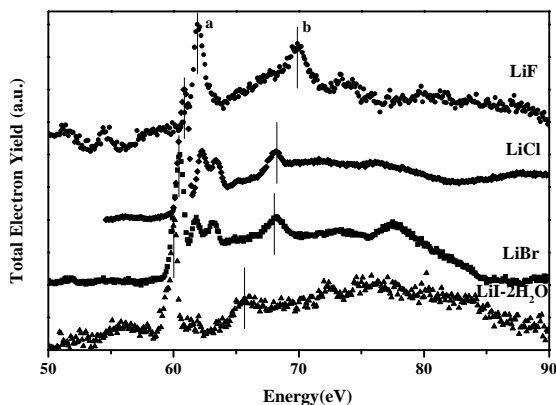
Figure 2
Li K-edge spectra of various lithium halides

however not taken into discussion in the present work.

4. Calculation

The obtained experimental of lithium halides are compared in the present work to the theoretical spectra obtained by DV-Xα molecular orbital calculation (Adachi *et al.*, 1978). $(LiX_6Li_{12}X_8Li_6Li_{24})^{29+}$ cluster (X=F, Cl, Br) was used in the calculation. The crystal structure of LiX is NaCl-type. The length of the *a*-axis for LiF is 0.40173 nm. The details of the x-ray absorption spectrum are described by Nakamatsu (Nakamatsu *et al.*, 1994; Nakamatsu, 1995; Nakamatsu, 2000). The atomic basis function set used in this calculation is from 1s to 3d for all atoms. All obtained peaks are convoluted by a Lorentzian distribution having the Full Width of Half Maximum (FWHM) of 1 eV. The energy axis has been shifted so that the strongest peak agrees with first peak of the experimental spectrum. The bulk state is approximated by embedding the $(X_{24}Li_{12}X_{24}Li_8)^{28-}$ cluster in the surrounding of a $(LiX_6Li_{12}X_8Li_6Li_{24})^{29+}$ cluster. For the embedding cluster, only the potential is used in the calculations, and the wave function are not updated (Nakamatsu *et al.*, 1986).

5. Calculation and discussion

Comparison between the measurement and the theoretical spectra for LiX (X=F, Cl, Br) is shown in Fig. 3. In Fig. 3, there are some difference points, however general features agree well. Figure 3(1) is shown the measurement and the theoretical Li K-edge spectrum of LiF. In the measurement spectrum the first peak is sharp, and the wide structure is shown in the higher energy side. The first peak is also similarly sharp in the theoretical spectrum and the structure in the higher energy side is reproduced by the many small peaks. The energy region of the structure in the higher energy side agrees almost, however the intensity of it is different from comparison with the measurement and the theoretical spectrum. Figure 3(2) is shown the measurement and theoretical Li K- edge spectrum of LiCl and Figure 3(3) is shown those of LiBr. The first peak is sharp as well as it of LiF for both measurement spectra. However, unlike LiF, we can observe the two small peaks in the higher energy side of the first peak. Wave-function and the potential cross section for (1) LiF, (2) LiCl and (3) LiBr are shown in Fig. 4. The figures which described the bottom of each figure are the potential cross section of the cluster used for the calculation. Besides, it is a figure of the wave function at each peak that is sealed in Fig. 3. The number written in each wave function is correspondent to the energy value of the theoretical spectrum and the number written in the width is the magnification which made (a) in the standard in order to observe the
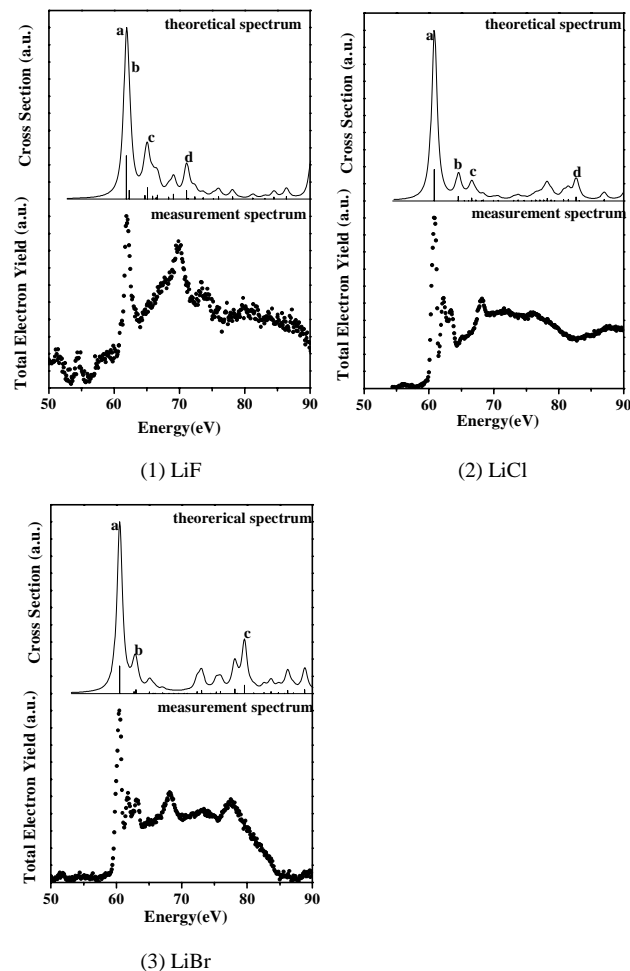

(1) LiF

(2) LiCl

(3) LiBr

Figure 3
Comparison with measurement and theoretical spectra for LiF, LiCl and LiBr

wave function more in detail. For (1) LiF, the intensity is very strong for the wave function on (a), and the characteristic form has been done. It seems to be closing the electron which was excited from lithium this in the potential of the fluorine. Therefore, in the spectrum, the intensity is the strongest and it is proven that the peak is due to core exciton. Generally, by cooling the sample at the liquid nitrogen temperature, exciton peak of alkali halide is observed by the measurement at the visible light region. However, in this case though the measurement is executed ordinary-temperature, it is possible to confirm the exciton peak. It is generated as a result of the interaction at the valence band level, but in this case, the electron of the inner shell is excited in unoccupied level, and the excited electron and hole seemed to cause core exciton by the interaction. Therefore in wave function the excited electron is observed in order to closing by potential barrier of the fluorine. This corresponds to resonance at the absorption spectrum. Afterwards, the intensity of wave function weakens with continuing with (b), (c) and (d). The intensity and shape resemble well each other on wave function of (b) and (c). In wave function of (d), though the shape of wave function near the center resembles other wave function well, the amplitude reaches to the distance. The shape of this wave function resembles very well the amplitude of EXAFS (Extended X- ray Absorption Fine Structure). In short, though the first sharp peak is due to core exciton, it is observed that the component which correspond to the excitation to the continuum state with going to the high energy side, is mixed. In next for (2) LiCl, it is observed that it confines it to the inside where wave function of (a) which is a first
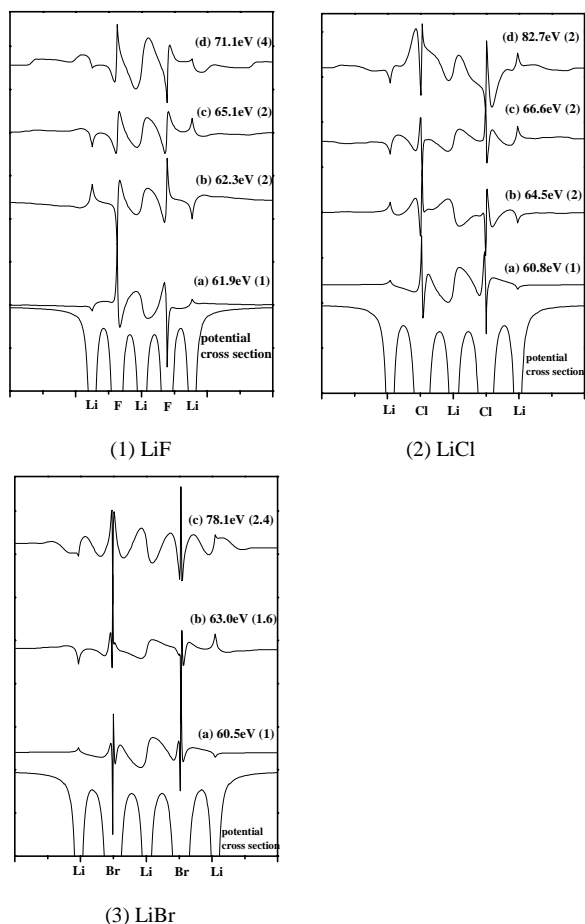
(1) LiF

(2) LiCl

(3) LiBr

Figure 4
Wave functions and the potential cross section for LiF, LiCl and LiBr

sharp peak is the potential of chlorine and bases it on core exciton. The shape of wave function of (b) and (c) resemble that of (a), but it is also observed that the amplitude of EXAFS has been mixed. In (d), the amplitude of EXAFS reaches to the distance. At last for (3) LiBr, the shape of wave function of (a) resembles that of (1) LiF and (2) LiCl. Similarly wave function of (a), the shape resembles the amplitude of EXAFS.

Finally, the theoretical spectra do not agree with the measurement spectra very well. Especially, in theoretical spectra for LiCl and LiBr, two peaks at 62eV and 63eV in the measurement spectra was not reproduced. It is considered that next two points are causes on this fact. First point is for the potential selection on the calculation. In case of lithium, the occupied level is only 1s and 2s, in addition, the occupied level is only 1s in the bonding state. Therefore the depth of the well potential shallows very much in comparison with other. As a result, it is difficult to sense the potential of lithium for the potential of other atom. In the calculation for solid, it is important point to not consider to influence from other atom. In next step, more adequate selection of the potential is necessitated. Secondary point is for the background. In all measurement spectra, the background intensity generally rises from the first sharp peak to about 15 or 20eV. However, in theoretical spectra the complicated structure is not observed. In this case, all measurement spectra are obtained by means of TEY. It is well known, the probability which release Auger electron increases in light element. In addition, the probability of shake-up in decay process also increases. Especially, since the distance between sample and detector is short, these secondary electrons are taken all in the detector, and the background

of the whole spectrum may rise as the results. This problem may be resolved by means of partial electron yield method. By improving two points, there seems to be the better coincidence on experimental spectrum and theoretical spectrum.

In making the lithium compound to be the new function material, in the twenty-first century, it will seem to shoulder the important role. Therefore, in addition, collection of basic data and elucidation of the electronic structure in the lithium compound will be advanced in future, and it is considered that application of the real material to the evaluation is necessary.

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