Satellite free F Kα from CaF_2 and SrF_2

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INTRODUCTION

A characteristic X-ray is emitted from an atom whose inner shell electron has been ionized by bombardment of electrons, ions and photons with sufficient energies. The fine structure of the characteristic X-ray resulted from a transition between an inner shell and a valence band has been utilized to understand a partial density of state of the valence band which is responsible for revealing various types of physical and chemical properties of atom-aggregates. However, under the excitation conditions mentioned above, multiply ionized states are produced together with a singly ionized state, which emit X-rays with higher energies, named satellites, than the energy of the characteristic X-ray from the latter state. Coexistence of these two kinds of X-rays make explanation of the fine structure complicated and ambiguous.

Monochromatized synchrotron radiations can well be used to eliminate the satellites emitted from the multiply ionized states[1]. In this report we compare observed satellite free F Kα emissions with the partial density of states estimated from the DV-Xα molecular orbital calculations[2]. Here CaF_2 and SrF_2 were employed for investigating the partial density of state of occupied F 2p in the valence bands.

EXPERIMENTAL RESULTS

F Kα emission spectra of CaF_2 and SrF_2 shown in Fig. 1(a) and (b) were measured using a grating monochrometer at B.L.8. Excitation energies were 704 and 703 eV for CaF_2 and SrF_2, respectively, which were chosen, referring to a series of excitation-energy dependent F Kα spectra emitted from CaF_2[3], from the following stand point; photon energies to be large enough for F K shell single ionization but too small for K^1L^n multiple ionization. Here K^1L^n denotes a state with one and n vacancies in K and L shells, respectively. Energy calibration for the reported emission spectra was obtained by assuming the energy of K^1L^0 of F Kα from CaF_2 to be 677.2 eV[4].

The F Kα peaks of CaF_2 and SrF_2 can be deconvoluted into two components with 1.8 eV in FWHM, whose centroid energies, their energy separations and relative intensities are summarized on table 1.
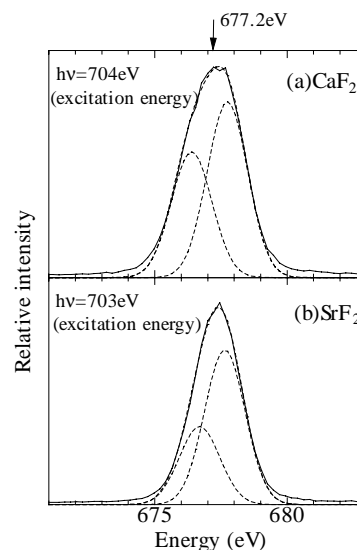

Fig.1 Observed F Kα emission spectra free from doubly ionized satellites, which are emitted from CaF_2 (a) and SrF_2 (b).

Table 1 Molecular orbital components of F Kα emitted, and theoretically estimated from CaF_2 and SrF_2.

		Observed	Calculated	MO
CaF_2	Centroid Energies	676.4 eV 677.7	Relative	$30t_2$ $33t_2$
	Peak separation	1.3 eV	1.4 eV	
	Relative Intensities	42 % 58	41 % 59	$30t_2$ $33t_2$
SrF_2	Centroid Energies	676.7 eV 677.6	Relative	$51t_2$ $53t_2$ $54 t_2$
	Peak separation	0.9 eV	1.0 eV	
	Relative Intensities	34 % 66	37 % 4 59	$51t_2$ $53t_2$ $54 t_2$

MOLECULAR ORBITAL CALCULATIONS AND DISCUSSIONS

Molecular Orbital (MO) calculations at the ground state were performed using the discrete-variational (DV)-Xα method[2]. The basis functions for CaF_2 and SrF_2 were 1s-3p for F, 1s-4p for Ca and 1s-5p for Sr. Sample points of 10000 for numerical integration were distributed three-dimensionally in a manner described elsewhere[2]. A diameter and depth of the potential to confine wave functions were chosen to be $0.67a_0$ and –3.0 Hartree, respectively, where a_0 is an interatomic distance between F and Ca or Sr atoms. In the present study, a cluster model of $(F^- M^{2+}_4 F^-_6 F^-_{12} M^{2+}_{12})^{13+}$ with Td symmetry was employed, as shown in Fig. 2.
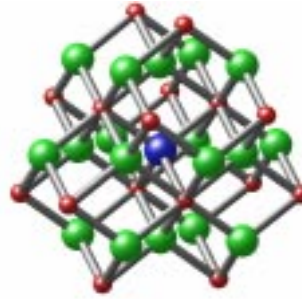
Fig. 2 A cluster model $(F^- M^{2+}_4 F^-_6 F^-_{12} M^{2+}_{12})^{13+}$ for CaF_2 and SrF_2, where M denotes Ca and Sr. A central F^- is surrounded by four M^{2+} as the first neighbors, six F^- as the second, twelve F^- as the third, and twelve M^{2+} as the fourth neighbors.

Calculated F 2p partial density of states (PDOS) for CaF_2 and SrF_2 are shown in Fig. 3 (a) and (b), respectively, which are responsible for F Kα emissions if assuming the dipole approximation for the Kα transition to be used. Here two and three components of PDOSs for Caf_2 and SrF_2, respectively, were convoluted using FWHM of 1.8 eV, and are drawn by full lines, where relative intensities and their energy separations between two main components are summarized on Table 1.

The calculated PDOSs of F 2p for CaF_2 and SrF_2 reproduce the F Kα spectra of the fluorides observed here satisfactorily. In addition, the above PDOSs can well be used to explain shapes of

photoelectron spectra of F 2p and F Kα emission spectra already reported[5,6] for CaF_2 and SrF_2, though the latter are contaminated with the doubly ionized K^1L^1 satellites.
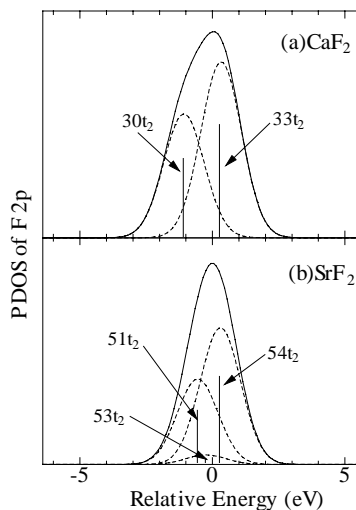

Fig. 3 Calculated F Kα emission spectra emitted from CaF_2 (a) and SrF_2 (b).

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