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Mn $L\alpha,\beta$ and F $K\alpha$ resonant X-ray fluorescence spectroscopy of MnF_2

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Mn $L\alpha,\beta$ and F $K\alpha_{1,2}$ (K–$L_{3,2}$) X-ray fluorescence spectra of MnF_2 were measured when the excitation X-ray energy was higher and lower than the threshold energies. Monochromated synchrotron radiation was used for primary excitation. The resonance fluorescence of Mn $L\beta$ and the multiply ionized F $K\alpha_{3,4}$ satellites (KL–L^2) were observed.

Keywords: X-ray fluorescence; multiple ionization satellite; resonance fluorescence; threshold excitation; Raman scattering.

1. Introduction

MnF_2 solid was selected to measure the threshold excitation X-ray fluorescence spectra. It was chosen because the Mn L X-ray characteristic lines are 50–60 eV from the F K line and thus can be measured in the same window of the position-sensitive X-ray detector. Since the MnF_2 solid has a $3d\uparrow^5$ electron configuration in the ground state, the $2p\downarrow \rightarrow 3d\downarrow \rightarrow 2p\downarrow$ resonance X-ray fluorescence process was expected using the empty Mn $3d\downarrow$ level. The X-ray fluorescence spectra of F are also interesting. The F $K\alpha$ X-ray fluorescence spectra have been measured by many researchers for various compounds and solids as the $K\alpha$ (K–$L_{2,3}$) X-ray fluorescence lines are accompanied by strong $K\alpha_{3,4}$ Wentzel–Druyvesteyn-type satellites (KL–L^2), *i.e.* shake-off satellites; also the chemical effect on the intensity of the $K\alpha_{3,4}$ satellites is remarkable compared with that of other elements. O'Bryan & Skinner (1940) reported the chemical effect on the intensity of the $K\alpha_{3,4}$ satellite. In the present report, both the resonance X-ray fluorescence of Mn and the shake-off satellites of F are reported for a solid powder sample of MnF_2 excited by synchrotron radiation.

2. Experimental

High-purity MnF_2 ($\geq$98%) was obtained in powder form from Soekawa Chemicals Co. Ltd, Japan. The powder was fixed on the sample holder by double-sided carbon adhesive tape (electric conductive), commonly used in electron microscopes.

The X-ray absorption and fluorescence spectra were measured on undulator beamline BL19B in the Photon Factory at the High Energy Accelerator Research Organization (formerly the National Laboratory for High Energy Physics), Tsukuba, Japan. The electron-storage ring was operated at 3.0 GeV and the ring current was between 210 and 160 mA during the measurement. No corrections were made for the change of the ring current during measurement. A grating monochromator, VLM19, designed by Fujisawa *et al.* (1996), was used for monochromatization.

X-ray absorption spectra were measured by the total electron-yield method by recording the sample electric-drain current (Fig. 1); one channel was 1 s with a 0.5 eV step. The ring current was 195–194 mA during this measurement. The X-ray absorption spectra were measured in a similar manner to that described for ScF_3 by Umeda *et al.* (1996). The absorption peaks at 690–694 eV are due to F $1s\downarrow$ –$t_{2g}\downarrow$ and $1s\downarrow$–$e_g\downarrow$ electron transitions. The Mn L absorption spectrum (635–660 eV) has fine structures.

The X-ray fluorescence spectra were measured by an X-ray fluorescence grating spectrometer (radius 10 m and line density 2400 lines mm^{-1}) designed by Shin, Agui, Fujisawa *et al.* (1995). The spectra were recorded by a position-sensitive detector; it took 30 min to 5 h to measure one spectrum, depending on the X-ray intensity. X-ray fluorescence spectra were measured under similar conditions to those reported by Shin (1995), Shin, Agui, Watanabe *et al.* (1995), Tezuka *et al.* (1996) and Agui *et al.* (1997). The vacuum of the chamber was less than 10^{-7} Pa. Photon energy was calibrated using the F $K\alpha$ maximum at 677 eV (White & Johnson, 1970).

3. Results and discussion

A representative X-ray absorption spectrum of MnF_2 is shown in Fig. 1. The arrows in Fig. 1 indicate the incident X-ray energy for fluorescent excitation. Fig. 2 shows the Mn $L\alpha,\beta$ X-ray fluorescence spectra excited at (*a*) 637.2, (*b*) 652.5 and (*c*) 655.5 eV. These spectra were obtained by (*a*) 76, (*b*) 36 and (*c*) 50 min accumulation using a position-sensitive detector. The number of channels between 620 and 670 eV was 440. Spectrum (*a*) in Fig. 2 was obtained below the L_2 threshold energy. Thus only the $L\alpha$ is observed. Spectrum (*b*) was measured at L_2 threshold excitation; thus the resonance X-ray fluorescence of $2p_{1/2}\downarrow \rightarrow 3d\downarrow \rightarrow 2p_{1/2}\downarrow$ is strong. The intensity of $L\beta$ is stronger than that of $L\alpha$ because of the resonance fluorescence or scattering, though the statistical ratio of $L\beta/L\alpha$ is 0.5. Spectrum (*c*) was excited by the photons of energy 5 eV higher than that of the L_2 threshold energy, where the intensity ratio observed was $L\beta/L\alpha$ = 0.5, which equals the statistical ratio.

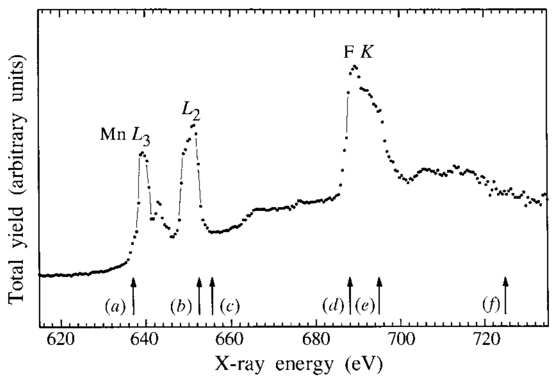

Figure 1
The Mn L and F K absorption spectrum measured by the total electron-yield method for MnF_2. Arrows (*a*)–(*f*) indicate the excitation energies for the measurements of the spectra in Figs. 2 and 3.

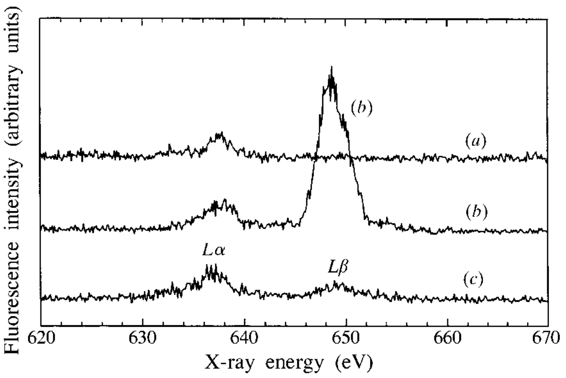

Figure 2
The measured Mn $L\alpha,\beta$ X-ray fluorescence spectra excited at (*a*) 637.2, (*b*) 652.5 and (*c*) 655.5 eV incident X-ray energy.

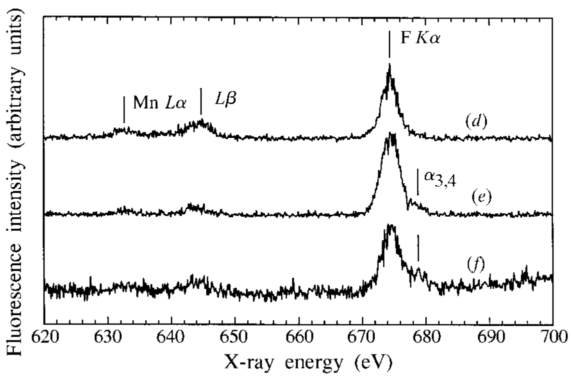

Figure 3
The measured F $K\alpha$ X-ray fluorescence spectra excited at (*d*) 688, (*e*) 695 and (*f*) 725 eV incident X-ray energy. The accumulation time was 30 min for 688 and 695 eV excitation, and 5 h for 725 eV excitation.

Fig. 3 shows the measured F $K\alpha$ X-ray fluorescence spectra excited at (*d*) 688, (*e*) 695 and (*f*) 725 eV. These spectra are raw data, but numerically processed spectra have been reported (Kawai *et al.*, 1998), where the spectra have been displayed after 500 iterations of five-point Savitzky–Golay (Savitzky & Golay, 1964) smoothing, background subtraction and normalization with respect to the peak maximum. It took 5 h to take the spectrum at 725 eV excitation. Thus the background of the 725 eV spectrum was relatively higher than for the other spectra. Spectra (*e*) and (*f*) in Fig. 3 have Wentzel–Druyvesteyn-type $K\alpha_{3,4}$ (KL–L^2) satellites. The intensity of the difference spectrum (*f*)–(*d*) relative to the intensity of spectrum (*d*) is 39.9%. Thus, the double-to-single ionization probability ratio $P(KL)/P(K)$ is 0.40, where $P(KL)$ denotes the KL double ionization probability and $P(K)$ the single ionization probability. It is interesting to note that the intensity ratio of Mn $L\beta/L\alpha > 1$ for F K threshold excitations, though the reason for this is not clear.

In summary, we have measured the Mn L and F K absorption spectrum of MnF_2 using monochromated undulator radiation. Mn $L\alpha,\beta$ and F $K\alpha$ X-ray fluorescence spectra at threshold excitation were also measured. The $L\beta$ spectral intensity was resonantly enhanced because of the $2p_{1/2}\downarrow \rightarrow 3d\downarrow \rightarrow 2p_{1/2}\downarrow$ transition. The KL satellite intensity in F $K\alpha$ X-ray fluorescence spectra is 40% of the single ionization X-ray line. Detailed analysis of F and Mn spectra will be presented by Kawai *et al.* (1998) and Yamamoto *et al.* (1998).

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