

Materials Science : Electronic & Magnetic Properties

EXTENDED SPIN-POLARIZED X-RAY ABSORPTION NEAR-EDGE SPECTRA OF MnO

Spin-polarized XANES (SPXANES) gives a direct approach to resolve the spin dependence of excited electronic states of non-ferromagnetic materials [1]. It is based on the assumption that one can separate the $K\beta_{1,3}$ ($3p \rightarrow 1s$) emission spectrum into an internally referenced spin-up part and a spin-down part [2], and hence one can achieve a local-spin selectivity in the K -edge XANES by measuring the emission from either the main (spin-down, $K\beta_{1,3}$) or satellite (spin-up, $K\beta'$) bands as a function of incident X-ray energy.

At beamline **BL47XU**, X-ray emission in the Mn $K\beta$ region of MnO powder was measured at room temperature using a multicrystal spectrometer [3]. The radiation was horizontally dispersed and vertically focused with five cylindrically bent Ge (440) crystals having a 550 mm radius of curvature. Analyzed X-rays from different crystals were focused on different vertical positions of a two-dimensional position-sensitive proportional counter. The overall energy resolution was 1.4 eV.

Figure 1(a) shows a $K\beta_{1,3}$ (spin-down)- and $K\beta'$ (spin-up)-emission contour map of MnO [3,4], where the abscissa (ω_1) and the ordinate (ω_2) are excitation and emission energies, respectively. Here, the $1s \rightarrow 3d$ resonant excitation appears as an island,

and the existence of two prominent ridges extending parallel to the abscissa, indicated by broken lines, is evident. The energy ω_2 of each ridge is the same as that of regular $K\beta_{1,3}$ and $K\beta'$ emissions. In addition, three ridges stretching diagonally (constant energy loss), also indicated by broken lines, are also conspicuous.

By traversing the contour map along a constant ω_2 axis, one obtains an excitation spectrum for the constant final state energy, which is equivalent to measuring excitation spectra while monitoring the part of fluorescence spectra, the conventional method of observing SPXANES [1]. Shown in Fig. 1(b) are two such excitation spectra obtained along the lines $\omega_2 = 6491$ eV ($K\beta_{1,3}$ peak) and $\omega_2 = 6476$ eV ($K\beta'$ peak), which are essentially the same as the SPXANES reported previously [1]. Here, non-vanishing components were noted in the energy region of $1s \rightarrow 3d$ transition not only in the spin-down polarized spectrum but also in the spin-up spectrum. Since all five $3d$ -electrons of Mn^{2+} in MnO are known to be spin-up, the transition is forbidden from Hund's rule in the latter spectrum. This casts some doubts on the validity of the underlying assumption of the conventional SPXANES method.

The $K\beta$ -contour map, shown in Fig. 1(a), can be analyzed using the following equation based on the Kramers-Heisenberg formula [4]

$$\frac{d\sigma(\omega_1)}{d\omega_2} \propto \int \frac{(\Omega_{1s} + \omega) \{ (dg_{1s}^{up}/d\omega)f^{up} + (dg_{1s}^{down}/d\omega)f^{down} \}}{(\Omega_{1s} + \omega - \omega_1)^2 + \Gamma_{1s}^2 / 4\hbar^2} d\omega \quad (1)$$

Here, $\hbar\omega$ is the energy of the excited electron in the intermediate state, and Γ_{1s} is the widths of the $1s$ levels, the energy of which is represented by $\hbar\Omega_{1s}$. $dg_{1s}^{up}/d\omega$ and $dg_{1s}^{down}/d\omega$ are spin-dependent oscillator strength distributions for spin-up and spin-down $1s$ electrons, respectively. The shape of the $K\beta$ -emission spectra is determined also by final-state effects, such as lifetimes and multiplet structures. In equation (1), they are taken into consideration by functions f^{up} and f^{down} .

In Fig. 2(a), $K\beta$ -emission spectra observed at the excitation energies indicated are shown by solid lines. Calculated $K\beta$ -spectra by using equation (1) and by assuming that the two spectra in Fig. 1(b) represent $dg_{1s}^{up}/d\omega$ and $dg_{1s}^{down}/d\omega$ are also shown in Fig. 2(a) by broken lines. Agreements between the observed and calculated spectra are not very good, in particular

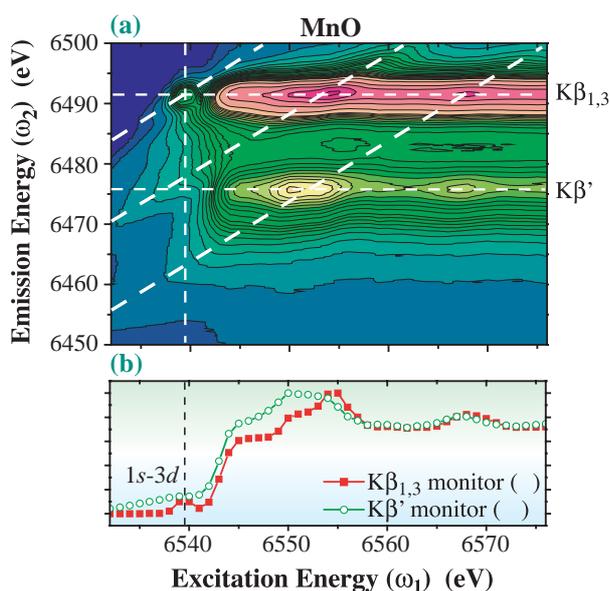


Fig. 1. (a) A $K\beta$ -contour map of MnO; emission intensities as functions of excitation (ω_1) and emission (ω_2) energies are plotted. Two horizontal and three diagonal ridges are indicated by broken lines. (b) Cross sections of the map at $\omega_2 = 6476$ eV (solid squares) and $\omega_2 = 6491$ eV (open circles).

below the absorption edge excitation. This result reveals that the two spectra of Fig. 1(b) do not well represent the $dg_{1s}/d\omega$'s. Subsequently, by modifying $dg_{1s}^{up}/d\omega$ and $dg_{1s}^{down}/d\omega$, similar calculations were repeated by trial and error until satisfactory agreements were reached. The 'best-fit' $dg_{1s}/d\omega$'s thus obtained are shown in Fig. 2(b).

In Fig. 2(a), best-fit calculated RIXS spectra at each excitation energy are shown by circles. The calculated spectra almost completely overlap the observed ones at every spectrum. It must be stressed that a single set of $dg_{1s}^{up}/d\omega$ and $dg_{1s}^{down}/d\omega$ has been employed to generate all the emission spectra, in spite of the fact that observed spectra vary enormously with excitation energy.

The best-fit $dg_{1s}^{up}/d\omega$ and $dg_{1s}^{down}/d\omega$ are

considerably different from the excitation spectra obtained by monitoring $K\beta'$ or $K\beta_{1,3}$ in Fig. 1(b). Major features are labeled; $1s \rightarrow 3d$ (pre-edge peak), A and B (shoulders), C and E (peaks), and D (valley), which well correspond to those in the spectra calculated by Soldatov *et al.* [5]. It is evident that $1s \rightarrow 3d$ transition is completely missing in the $dg_{1s}^{up}/d\omega$, as is expected from Hund's rule. It is immediately understood from Fig. 1(a) that the non-vanishing intensity apparent in the $K\beta'$ excitation spectrum is due to the diagonal component that originates from the main peak of the $K\beta_{1,3}$ ridge.

The present results indicate that analyses of emission maps in terms of the Kramers-Heisenberg equation (eq. (1)) are crucially important for a correct determination of SPXANES.

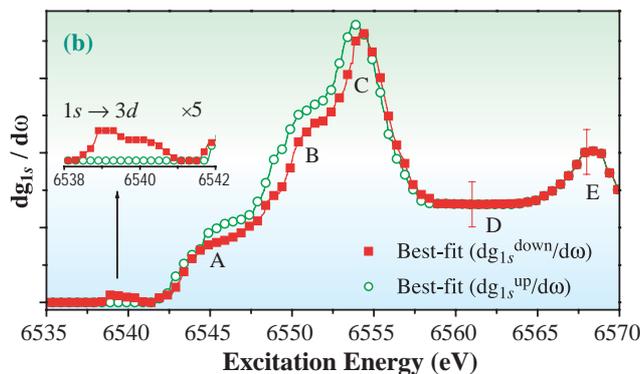
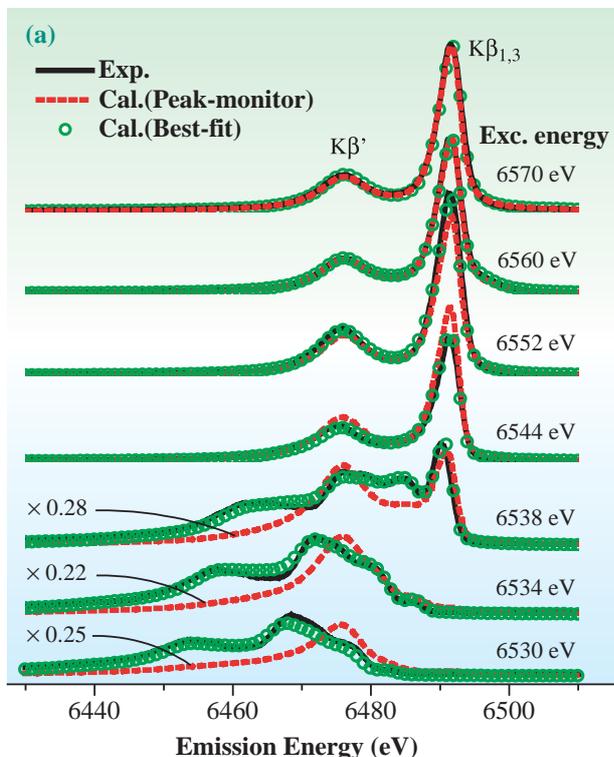


Fig. 2. (a) Comparisons of the observed $K\beta$ -emission spectra of MnO ('Exp.') with calculated ones by the best-fit $dg_{1s}^{up}/d\omega$ and $dg_{1s}^{down}/d\omega$ ('Best-fit'). Also shown are calculated emission profiles using the excitation spectra shown in Fig. 1(b) ('Peak-monitor'). (b) The SPXANES profiles obtained by the analysis using equation (1) for MnO [4].

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References

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