Electronic structure of KNbO₃: Nb $M_{4,5}$ x-ray-fluorescence measurements

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We present synchrotron based soft x-ray emission (XES) measurements (Nb $L\beta_{2,15}$, Nb $L\gamma_1$, Nb M_3, Nb $M_{4,5}$, O $K\alpha$) and theoretical calculations of x-ray emission spectra of KNbO₃. The obtained results are compared with x-ray photoemission spectroscopy valence-band measurements and band-structure calculations. The Nb $M_{4,5}$ emission spectra show strong dispersion and by tuning the exciting synchrotron radiation through the Nb 3d threshold ($E_{exc}=206.5$–240.6 eV), we identify contributions to the valence emission from the decay of both holes, $3d_{5/2}$ and $3d_{3/2}$. It is also shown that it is generally possible to measure $M_3(4d5s\rightarrow3p_{3/2})$ x-ray emission spectra of 4d metals in order to study the distribution of 4d valence-band states. [S0163-1829(99)03331-7]

Mixed oxides of perovskite-type structure, depending on their composition, give rise to a variety of electric, magnetic, and optical effects. Among these perovskite oxides, potassium niobate provides multiple electro-optical, and catalytic applications,[1] making the study of its electronic structure very important.

The electronic structure of KNbO₃ has been extensively studied by means of band-structure calculation schemes beginning with the empirical parameter-adjusting schemes[2,3] and followed by first-principles self-consistent treatments.[4,5] Later, the focus of interest in this ferroelectric compound shifted toward fine estimations of the spatial electron density distribution, total energy as a function of atomic displacements,[6,7] electrostatic polarization,[8] and the lattice dynamics.[9,10] In terms of the experimental techniques appropriate for the analysis of the electronic states distribution in the valence band, very few studies have been done apart from the photoelectron spectroscopy measurements.[5,11,12] These experiments were usually interpreted by comparing the measurements with the calculated total density of states in the valence band. However, these conventional experimental techniques for the study of dielectric materials are limited due to sample-charging effects. It has been shown

that some momentum-resolved information regarding the valence-band dispersion can be extracted from soft x-ray resonant inelastic spectra (XRIS).[13–17] This method is not affected by charging of the sample during irradiation and seems to be a promising tool for the study of dielectrics.

X-ray emission spectroscopy can provide important additional experimental information such as the spatial and energetic distribution of electronic states in the compound. The dipole selection rules govern the transitions from different core states and there is a need for calculations of the corresponding transfer probabilities from first principles, based on a computed band structure. In the present paper, we calculated the partial density of states (DOS) and several x-ray emission spectra of KNbO₃ by the all-electron full-potential linearized augmented plane-wave method (FLAPW).[18] Due to the large size of the basis of augmented plane waves, this method allows a practical description of the electronic states up to relatively high energies in the conduction band, which is important for analyzing the trends in the x-ray absorption and the resonance x-ray emission intensities.[19] The experimental lattice constant $a=7.553$ a.u. was used, and the atomic sphere radii were set to 1.95 a.u. (K), 1.85 a.u. (Nb), and 1.65 a.u. (O). The lattice was assumed to be an ideal

cubic perovskite because the effect of ferroelectric distortion on the DOS is known to be negligible considering the comparison to experimentally broadened spectra. The exchange correlation has been treated within the local density approximation, according to the prescription by Perdew and Wang.[20] The valence-band states have been treated semirelativistically, the core states with a fully relativistic treatment. The DOS and emission spectra were calculated using the tetrahedron method, for the $12 \times 12 \times 12$ divisions of the whole Brillouin zone. Whereas our calculated partial and total DOS agree with previous calculations, the calculated x-ray emission (and absorption) spectra, including the energy dependence of the dipole transition-matrix elements present, to our knowledge, new information. We utilize our calculated results to understand the trends in our resonant x-ray emission spectra.

The soft-x-ray fluorescence experiments were performed at Beamline 8.0 of the Advanced Light Source at Lawrence Berkeley Laboratory. The undulator beamline is equipped with a spherical grating monochromator[21] and the resolving power was set to $E/\Delta E = 500$ for our experiments. The fluorescence end station with a Rowland circle grating spectrometer provides a resolving power of about 300 at 200 eV. The x-ray photoemission spectroscopy (XPS) measurements were obtained using a Perkin Elmer PHI 5600ci Multitechnique System with monochromatized Al $K\alpha$ radiation [bandwidth of 0.3 eV full width at half maximum (FWHM)]. In order to obtain clean surfaces for the XPS measurements, the $KNbO_3$ single crystal was cleaved under UHV conditions. The x-ray Nb $L\beta_{2,15}$ and Nb $L\gamma_1$ fluorescence spectra were obtained by a Stearat spectrometer.[22] A quartz crystal ($d=0.334$ nm) curved to $R=500$ cm was used as a dispersive element to analyze the photons. X-ray emission spectra were detected by a flow proportional counter by scanning along the Rowland circle with an energy resolution of ±0.2 eV.

In Figs. 1(a) and 1(b) the Nb $M_{4,5}$ emission spectra of $KNbO_3$ are shown for various excitation energies near the Nb $3d$ threshold. Four features are observed and labeled A through D. The most dramatic changes in the shape of the fine structure of Nb $M_{4,5}$ emission spectra are found for excitation energies between 206.5 and 212.3 eV where new features D and B appear with changes in excitation energy. It is suggested in Ref. 23 that in Nb $M_{4,5}$ emission only reveals the M_5 ($3d_{5/2}$) emission features because the M_4 ($3d_{3/2}$) is filled by radiationless transition. Therefore, it was unexpected when we found the excitation energy dependence of Nb $M_{4,5}$ to be distorted by the spin-orbit splitting of the Nb $3d$ levels and not revealing the band dispersion.

Figure 2 displays a full calculation of the Nb $M_{4,5}$ emission spectra based on the Nb $5p$ and Nb $4f$ DOS modulated by the transition probabilities. In the calculation, the resulting spectrum has been simulated by shifting the two identical contributions by the value of the spin-orbit splitting in the Nb $3d$ shell, which amounted, according to our full-electron calculation, to 2.88 eV. These two contributions, corresponding to individual M_4 and M_5 spectra, were then summed up with relative weights of 2:3. It is found that the contribution of the Nb $4f$ states to the emission is negligible and only $5p \rightarrow 3d$ transitions are important for the interpretation of Nb $M_{4,5}$ x-ray emission (XES). The O $2s$ states contribute to the Nb M_5 XES due to the O $2s$-Nb $5p$ hybridization. The corre-
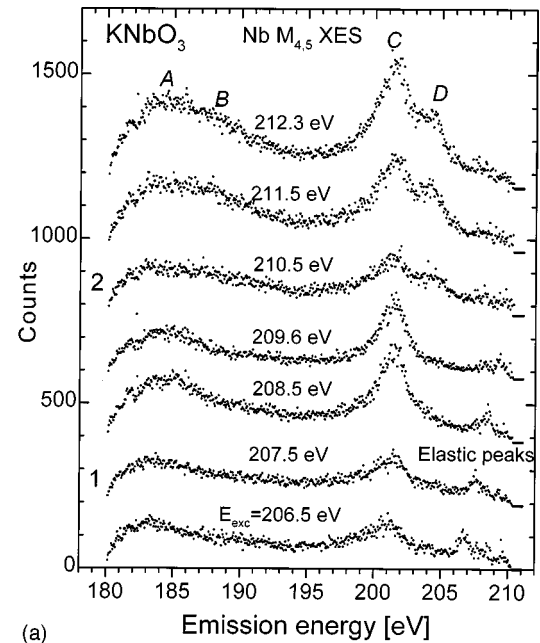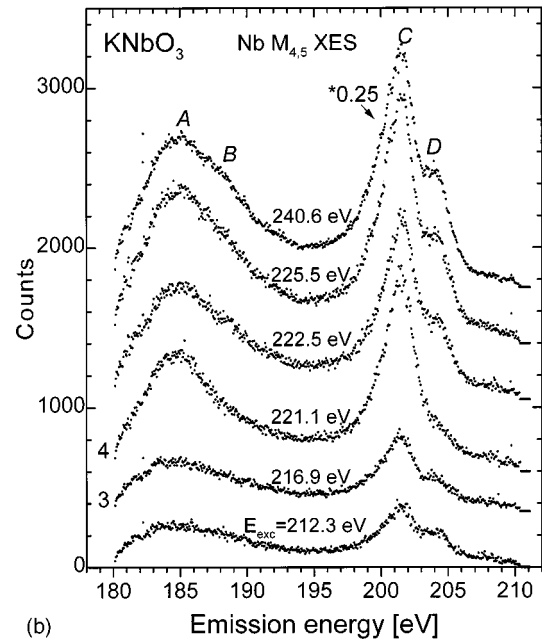
FIG. 1. Nb $M_{4,5}$ emission spectra of $KNbO_3$. The excitation energy is tuned through the Nb $3d$ threshold from 206.5 to 212.3 eV [Fig. 1(a)] and from 212.3 to 240.6 eV [Fig. 1(b)]. The numbers 1 through 4 refer to selected photon energies (Fig. 3): the onset of the Nb $3d_{5/2}$ and $3d_{3/2}$ and excitation of Nb $3d$ into vacant Nb $5p$ states.

sponding features in the Nb M_4 and M_5 XES near -16 and -13 eV are broadened in the experimental spectra but still recognizable in Fig. 1 as A and B. Peaks C and D are due to the emission from the spin-orbit splitting involving the hybridization O $2p$-Nb $5p$.

Going back to the discussion of energy dependence of the Nb $M_{4,5}$ emission spectra in $KNbO_3$ (Fig. 1), we note that according to our XPS measurements the Nb M_5 ($3d_{5/2}$) and Nb M_4 ($3d_{3/2}$) binding energies are 207.2 and 210 eV, respectively (relative to the vacuum level). Conclusively, the emission features in the spectra excited between 206.5 and 209.6 eV are generated by the refill of the Nb M_5 ($3d_{5/2}$)
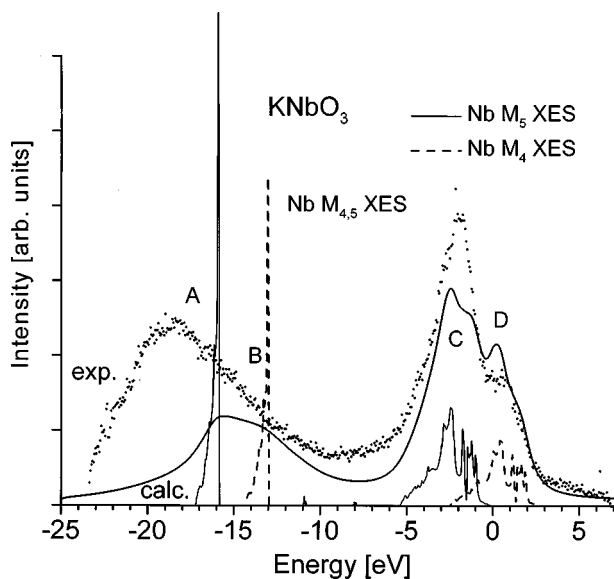
FIG. 2. Calculated Nb $M_{4,5}$ XES of KNbO$_3$ broadened for instrumental distortion (0.2 eV), core level lifetime (0.35 eV) and valence lifetime (2.0 eV). The contributions of unbroadened M_5 and M_4 spectra are also shown.

hole as excitation of Nb M_4 is not possible below 210 eV. In the excitation energy range between 210.5 and 216.9 eV additional features B and D appear as a result of contributing transitions to Nb M_4 $(3d_{3/2})$. The sharp increase in intensity in the emission spectra at excitation energies from 216.9 to 221.1 eV can be attributed to the threshold of the $3d \rightarrow 5p$ absorption. This is illustrated by the calculated Nb M_4-absorption spectrum in Fig. 3. The $3d \rightarrow 5p$ absorption starts to contribute at an excitation energy of about 218 eV. The onset for the $3d$-$4f$ absorption occurs around 235 eV. The strong enhancements of the emission (see Fig. 1) occur when the excitation energy exceeds the M_5 threshold (E_{exc} = 208.5 eV, M_4 threshold (E_{exc} = 211.5 eV), the $3d$-$5p$ threshold (E_{exc} = 221.1 eV) and the $3d$-$4f$ threshold (E_{exc} = 240.6 eV) as displayed in the partial fluorescence yield (PFY) spectrum (Fig. 3). We note that the spectrum excited at the $3d$-$4f$ threshold (E_{exc} = 240.6 eV) is divided by a factor of four in order to display all spectra on the same scale.[24]

The emission spectrum corresponding to the excitation energy of 221.1 eV in Fig. 1 exhibits, as compared with that for E_{exc} = 216.9 eV, strongly enhanced M_5 but relatively unchanged M_4 intensity. Therefore, this specific selective excitation of Nb M_5 XES can be also used to receive experimental information about the Nb $5p$ DOS undistorted by overlapping with Nb M_4 XES. Starting from E_{exc} = 222.5 eV, the resonant emission gets enhanced for the M_4 component as well, so that the original shape of the spectrum (for smaller excitation energies) is roughly restored, but with much higher intensity. Apart from Nb $M_{4,5}$, some other XES measurements can be useful to collect complementary information about the distribution of electronic states of the Nb site. In Fig. 4, Nb $L\beta_{2,15}$ $(4d_{5/3,3/2} \rightarrow 2p_{3/2}$ transition) and Nb $L\gamma_1$ $(4d_{3/2} \rightarrow 2p_{1/2}$ transition) spectra are shown and exhibit some differences in the fine structure reflecting exactly the differences in Nb $4d_{5/2,3/2}$ and Nb $4d_{3/2}$ DOS distribution in the valence band of KNbO$_3$.
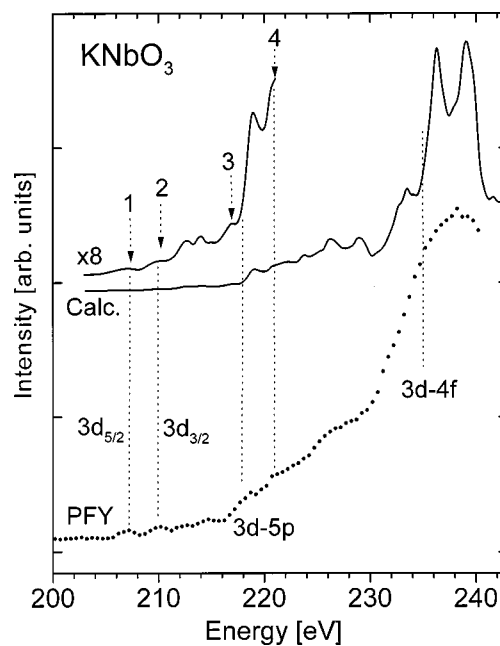

FIG. 3. Calculated absorption (calc.) and measured partial fluorescence yield (PFY) at the Nb $3d$ threshold. Vertical lines indicate the onset of the $3d_{5/2}$ and $3d_{3/2}$ excitation, the excitation of $3d$ electrons into vacant Nb $5p$ states and into unoccupied $4f$ states. The arrows indicate selected excitation energies at which XES spectra were taken and the numbers refer to the numbers in Figs. 1(a) and 1(b).

The present Nb M_3 spectrum in Fig. 4 may be considered as new because this spectrum is not listed in the Beardeen tables,[25] nor in the last systematic study of the ultrasoft XES in $4d$ transition metals.[26] The present Nb $M_{2,3}$ spectra lie in a convenient energy region for the synchrotron study, and their
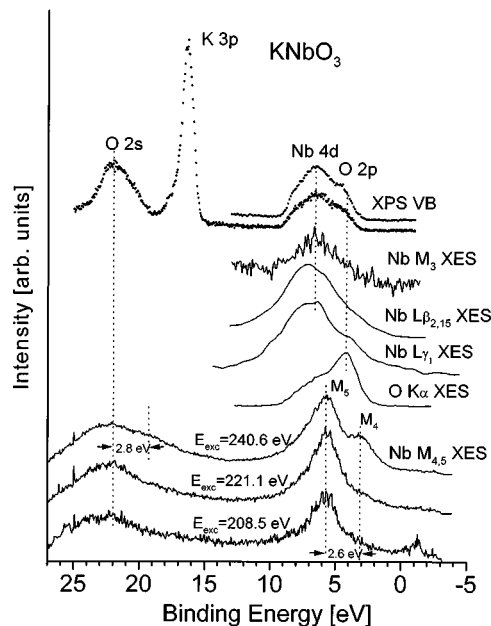

FIG. 4. The result of fluorescent measurement of Nb M_3 (E_{exc} = 410 eV), O $K\alpha$ (E_{exc} = 540 eV), Nb $L\beta_{2,15}$ (E_{exc} = 8000 eV) and Nb $L\gamma_1$ (E_{exc} = 8000 eV) x-ray emission spectra of KNbO$_3$.

two components are well separated by $\sim$15 eV. The obtained result is shown in Fig. 4 (upper panel) for the counting time of 20 min. The Nb M_3 XES of $KNbO_3$ was found to have extremely low intensity, but is generally suitable for the study of the valence band.

To summarize, we have measured soft x-ray emission spectra excited through the Nb $3d$ threshold. The spectra show dependence on excitation energy and are explained by the calculations (based on DOS and full band-structure calculations). The changes in the spectra occur at the $3d_{5/2,3/2}$, $3d$-$5p$, and $3d$-$4f$ thresholds of the absorption. Tuning the excitation energy to the corresponding thresholds of the absorption spectrum allows us to attribute contribu-tions from the decay of the $3d_{5/2}$ holes (peaks C and A) and the $3d_{3/2}$ holes (peaks D and B) via valence emission. The overlap of these two spectra complicates the analysis of the excitation energy dependent trends in the resonant emission, which otherwise would be able to provide key information about band dispersion, as shown by studies of other materials.[13,14]

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