Soft-X-Ray Emission Insulators: Spectator versus Normal Emission

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We investigate the excitation energy dependence of the boron K soft-x-ray emission of B_2O_3 and hexagonal-BN using synchrotron radiation. When exciting into the core exciton state the spectra are shifted to lower energy by 1.5 and 1.8 eV, respectively. This shift is found to be a result of phonon relaxation and differences in initial- and final-state electronic screening.

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The soft-x-ray absorption (SXA) spectra of many insulators are similar in that they contain a very intense and narrow feature at threshold. This feature is due to the core exciton state, a localized state in which the excited electron screens the core hole. Occupation of the exciton state generally results in higher kinetic-energy Auger electrons [1–3]. This result has been explained in terms of final-state electronic screening [1–3]. Soft-x-ray emission (SXE) competes with the Auger process. In this Letter we present and discuss boron K SXE (B K SXE) spectra of B_2O_3 and hexagonal-BN (h-BN) for different excitation energies near the absorption threshold. We find that occupation of the exciton state lowers the SXE energy. This result cannot be explained in terms of final-state screening alone. We describe these energy shifts in terms of initial- and final-state electronic screening and phonon relaxation effects. This more complete discussion is also applicable for Auger emission.

The measurements were performed on the University of Tennessee (UT) and National Institute of Standards and Technology (NIST) beam line located at the National Synchrotron Light Source. The monochromator [4] consists of a toroidal mirror, a fixed variable-line-spaced grating, and a scanning mirror. A resolution of 1 eV was chosen for the monochromator in order to enhance the flux onto the sample. The SXE was measured on the UT-NIST SXE spectrometer [5], consisting of a toroidal grating and a position-sensitive detector capable of scanning along the Rowland circle defined by an entrance slit and the grating. The resolution of the SXE spectrometer was 0.4 eV. Data collection times were typically 2 h for the spectra shown. Samples used were polycrystalline, the B_2O_3 was cleaved and the h-BN was scraped with a clean razor blade immediately prior to vacuum insertion.

In order to describe the different SXE processes we borrow terminology used to describe Auger emission [1–3]. When a core exciton is formed, the core hole can radiatively decay by spectator emission or by direct recombination. In direct recombination (also referred to as exciton emission), the electron excited to the exciton state recombines with the core hole. In spectator emission, the core hole is filled by a valence electron rather than by the excitonic electron. When the core hole is created and filled without an electron in the exciton state, the radiative decay is termed normal SXE.

To assist in understanding the results, it is important to consider the absorption behavior of an insulator. When the excitation energy is set at threshold the exciton state is occupied and only spectator and direct recombination are possible. At excitation energies above this threshold normal emission takes place. If the photon excitation energy is increased beyond the absorption threshold, by an amount equal to the energy gap, a second threshold is reached. At this second threshold it is energetically possible to occupy the exciton state by either a shakeup event or by electron-electron scattering. Since electron-electron scattering can be faster than SXE, either of these two mechanisms can result in occupation of the exciton state before SXE takes place. Therefore, above this second threshold, both direct recombination and spectator SXE are possible. Between the two thresholds only normal SXE is possible. This description ignores electron-phonon scattering into the exciton state, which we assume to be unimportant.

The B K SXE of B_2O_3, obtained for different photon excitation energies near threshold, are shown in Fig. 1. The spectra consist of a main peak near 180 eV, associated with boron p-type states, and a smaller peak near 168 eV, associated with O $2s$ states. There is also a very weak double-humped structure near 193 eV which has been identified as the core exciton. These photon excited spectra are very different from the published B K SXE of B_2O_3 [6], obtained by electron excitation. To understand this we have investigated the SXE from B_2O_3 with elec-

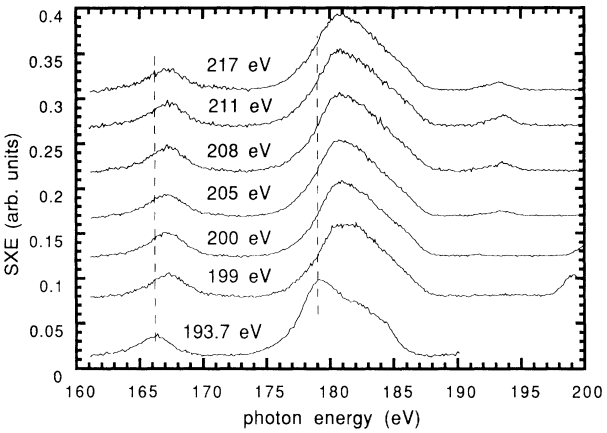

FIG. 1. B K SXE from B_2O_3 for different photon excitation energies.

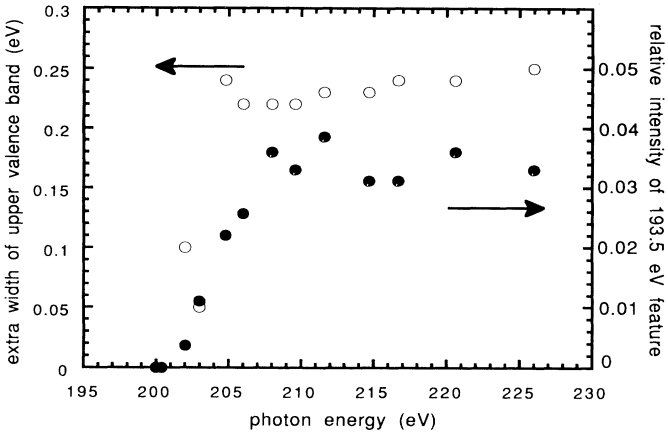

FIG. 2. Comparison of the relative intensity of 193.5 eV emission feature, ●, with broadening of the upper valence band, ○, for B K SXE of B_2O_3. Second absorption threshold is located at 200.7 eV.

tron excitation (2 μA at 1 keV) and have determined that this difference is due to electron beam damage. The electron-excited spectra changed over a period of ten minutes from looking similar to the photon-excited spectra to looking similar to published electron-excited spectra.

The B K absorption threshold in B_2O_3 is found to be 193.7 eV (similar to published SXA results in Ref. [6] and this excitation energy gives the spectator SXE spectra, Fig. 1. This spectrum also contains a very large peak at 193.7 eV due to elastic scattering and direct radiative recombination. This peak has been omitted from Fig. 1 for clarity. At photon excitation energies between 195 and 200 eV the SXE remains fairly constant but has shifted to higher energies relative to the spectator SXE. We identify the SXE at these excitation energies as normal SXE. As the photon excitation energy is increased past 200 eV a very weak emission peak at 191.5 eV appears and stays constant in intensity relative to the main SXE peak with increasing photon excitation energy. At excitation energies above 202 eV a second peak, at 193.5 eV, appears and grows in relative intensity with excitation energy up to 210 eV. The width of the main emission peak also increases on the low-energy side above excitation energies of 202 eV.

We identify the emission peak at 193.5 eV as direct recombination of the core exciton. This is reasonable since the emission energy is very close to the absorption energy of the exciton, 193.7 eV. The small shift may be explained by phonon relaxation; however, the experimental uncertainty is too large to say anything quantitative about this. The second threshold occurs at 202 eV, consistent with a band gap of ≈ 7.0 eV [7]. Its existence is demonstrated in Fig. 2, which plots the relative magnitude of the exciton peak at 193.5 eV to the main SXE spectrum, and the excess broadening of the main SXE spectra at excitation energies above 202 eV. Above this threshold spectator emission and direct recombination are again possible. Spectator emission accounts for the low-energy widening of the valence emission spectra while direct recombination accounts for the emission at 193.5 eV. The appearance of the second threshold near a photon energy equal to the absorption threshold plus the band gap supports the assumption of ignoring phonon scattering of the excited electron into the exciton state.

Using these ideas the branching ratio for radiative decay of the B K exciton can be determined. Linear combinations of the normal and spectator SXE spectra were compared to the SXE spectra taken above 210 eV excitation energy. From these comparisons it was determined that $(12 \pm 4)\%$ of the valence SXE feature was due to spectator emission. The relative intensity of the exciton peak to the intensity of the two main emission peaks is 0.033 ± 0.003. The branching ratio for radiative decay of the core exciton is thus $0.033/0.12 = 0.28 \pm 0.1$, if the branching ratio is defined as the probability of direct recombination relative to the probability of spectator decay. This analysis ignores self-absorption effects, making the value a lower bound.

The identity of the weak emission feature at 191.5 eV is unclear. This peak along with the exciton peak have been observed in electron-beam-excited data [6]. The 191.5-eV peak has been attributed to phonon ringing [6]. This is clearly not the case since the 191.5-eV emission feature appears at excitation energies where the exciton emission feature does not. The 191.5-eV peak is most likely due to a lattice defect or impurity associated with some small fraction of the excited atoms.

Similar measurements were made on the B K SXE of h-BN, Fig. 3. The h-BN SXE spectra consist of the main emission peak near 180 eV, due primarily to boron p states, a weaker peak near 170 eV, due primarily to nitrogen $2s$ states, and two weak features at 189.8 and 191.5 eV. Qualitatively, the excitation energy dependence of the h-BN SXE is similar to that of B_2O_3. Above the exciton absorption energy, 191.5 eV, the emission spectra

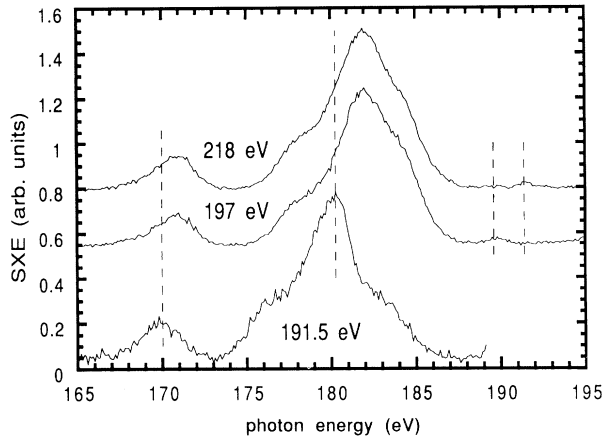

FIG. 3. B K SXE from h-BN for different photon excitation energies.

shifts to higher energies. At 196 eV excitation energy the emission peak at 189.8 eV appears. This peak grows in relative intensity up to 197 eV excitation energy and then diminishes, reaching a constant intensity at 210 eV excitation energy. At 200 eV excitation energy the emission peak at 191.5 eV appears. This peak grows in relative intensity as the excitation energy is increased, until 212 eV where its relative intensity remains constant. The main emission peak is widened on the low-energy side for excitation energies above 200 eV. We identify the 191.5-eV emission peak as the core exciton and determine its branching ratio for radiative decay to be 0.08 ± 0.03. The 191.5-eV emission feature and the exciton feature have been observed in electron beam excited data and together have been interpreted as phonon ringing [8]. Again this is clearly not the case since the 189.8-eV peak appears in the absence of the 191.5-eV peak for an excitation energy of 197 eV, Fig. 3.

The spectator emission spectra are compared to the normal emission spectra for both B_2O_3 and h-BN in Fig. 4. The spectator spectra have been shifted 1.5 and 1.8 eV for B_2O_3 and h-BN, respectively, in order to align the main emission feature. These shifts will be referred to as the spectator shifts. The relative intensities across the normal and spectator spectra are different after accounting for the spectator shift. It is also apparent, Fig. 4, that the lower valence emission feature has been shifted too much. The actual spectator shift for the low-energy peaks are 0.7 and 1.0 eV for B_2O_3 and h-BN, respectively. The spectator shifts will be discussed in terms of electronic screening and phonon relaxation. As a result of limited space a discussion on the different spectator shifts observed for the upper and lower valence bands will be presented elsewhere. The difference in shape will be discussed in terms of phonon relaxation energies and core hole lifetimes.

The initial state for spectator SXE has an electron in the exciton state. The final state for spectator SXE does not have a core hole and thus the core exciton state is not

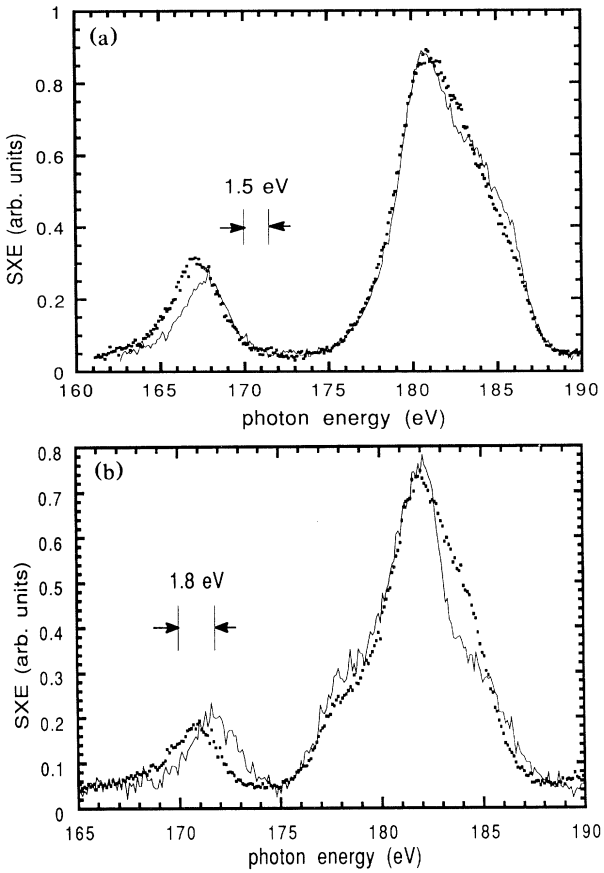

FIG. 4. (a) Comparison of B K spectator, solid line, and normal, points, SXE for B_2O_3. The spectator SXE has been shifted 1.5 eV to higher energies. (b) Comparison of B K spectator, solid line, and normal, points, SXE for h-BN. The spectator SXE has been shifted 1.8 eV to higher energies.

an eigenstate. One possible final state is a valence exciton which is due to the presence of the valence hole. The change in energy for the spectator electron during the SXE event would be $\Phi_{core} - \Phi_{val}$, where Φ_{core} is the binding energy of the core exciton and Φ_{val} is the binding energy of the valence exciton. In normal SXE the exciton states are not occupied in either the initial or final states. Since $\Phi_{core} > \Phi_{val}$, electronic screening shifts the spectator SXE to lower energies relative to normal SXE. Other final states, i.e., electron in conduction band, would result in satellites or broadening in the spectator SXE. We were unable to identify any such features in our data.

The magnitude and direction of the spectator shift is consistent with electronic screening effects; however, previous work suggests that phonon relaxation effects would also contribute to a shift. Phonon relaxation in SXE is well understood theoretically [9,10]. Briefly, phonon relaxation is important in SXE when the phonon relaxation rate is similar to or greater than the core hole decay rate. When the phonon relaxation rate is much greater than the core hole decay rate the SXE spectra is shifted to

lower energies by an amount equal to twice the phonon relaxation energy (Σ_{ph}). When the phonon relaxation rate is similar to the core hole decay rate the SXE is shifted by an amount less than $2\Sigma_{ph}$.

Phonon relaxation should affect both spectator and normal SXE. O'Brien *et al.* [11] have measured the phonon effects for a number of insulators. They found that Σ_{ph} is generally much lower for core electron transitions involving core exciton states than for core electron transitions involving conduction band states. This suggests, everything else being equal, that phonon relaxation should shift the normal SXE towards lower energies relative to the spectator SXE (opposite to what is observed). On the other hand, a screened core hole has a longer lifetime than an unscreened core hole [12]. This suggests, everything else being equal, that phonon relaxation would more effectively shift the spectator SXE towards lower energies, consistent with our observation. It is therefore difficult to make a general prediction on the direction of the spectator shift due to phonon relaxation. Comparison of SXE energies to photoemission energies of h-BN by Barth, Kunz, and Zimkina [13] and of other insulators by O'Brien *et al.* [14] show that the phonon relaxation in normal SXE for insulators is on the order of 1.0 eV. The magnitude of these relaxation energies suggests that phonon relaxation effects should not be ignored in a complete analysis of the spectator shift.

The main emission peaks of both B_2O_3 and h-BN contain sharper features in the spectator spectra, Fig. 4. Recently, Ma *et al.* [15] have discussed momentum conservation effects on SXE for excitation energies near threshold. These effects will be important when phonon coupling is weak. In insulators such as B_2O_3 and h-BN the phonon coupling is very strong and we expect any momentum conservation effects to be minor. Also, the 1-eV resolution of our excitation source would tend to reduce any momentum conservation effects. Phonon broadening is proportional to Σ_{ph} so normal SXE should have more phonon broadening than spectator SXE. Also, the shorter core hole lifetime associated with normal emission would broaden the normal SXE spectra when compared to the spectator SXE. An estimate of the magnitude for these two effects combined can be obtained by comparing the FWHM of the B *K* photoemission peak of BN (experimental broadening removed), 1.5 eV [13], to the FWHM of the exciton absorption peak, 0.4 eV [13].

The spectator shift for the Auger process should also be discussed in terms of initial- and final-state electronic screening and phonon relaxation. The only difference is that the binding energy of the trion state [1–3] (spectator electron screening the two hole final state) would replace the valence exciton binding energy. Unfortunately, we are not aware of any appropriate Auger work on either h-BN or B_2O_3. However, resonant Auger emission studies have been performed on other insulators. Ichikawa *et al.* [1] investigated LiF, LiBr, and LiCl, Kamada *et al.* [2] investigated NaCl and NaBr, and Tiedje *et al.* [3] investigated CaF_2. Each of the Auger spectator shifts was found to be towards higher kinetic energies. These shifts to higher kinetic energies for the spectator Auger electrons were each discussed in terms of the final-state screening of the two valence holes by the spectator electron [1–3]. It is impossible for a model based only on final-state screening to predict spectator shifts to lower energies as observed for the B_2O_3 and h-BN SXE. Any discussion of spectator shifts in either Auger or SXE must include both initial- and final-state electronic screening and phonon relaxation effects as outlined above. Only with this more complete analysis can both positive and negative spectator shifts be predicted.

In summary, we have investigated the SXE of B_2O_3 and h-BN using different photon excitation energies near threshold. From these spectra we were able to obtain both spectator and normal SXE spectra. Using these and the SXE from the core exciton state we determined the branching ratio for radiative decay of the core excitons. The spectator shifts in B_2O_3 and h-BN were discussed in terms of electronic screening and phonon relaxation. Finally, the differences in phonon relaxation energies and core hole lifetimes were used to explain the existence of sharper features in the spectator SXE spectra.

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