PHYSICAL REVIEW B VOLUME 36, NUMBER 17 15 DECEMBER 1987-I

Anisotropy of BN and Be x-ray-emission bands

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(Received 22 June 1987)

We present measurements of the K emission spectra of hexagonal Be and BN (h-Be and h-BN). The anisotropy of the emission allows us to separate the bands into their σ and π components, enabling us to demonstrate the unambiguous π character of the B core exciton. We find that the exciton presents a double-peaked structure which we attribute to phonon ringing. For the first time we are able to separate into π and σ components the doubly ionized K emission bands of B and N in h-BN and of Be in h-Be, revealing the effect of the spectator core hole on the shape of the density of states. Such an effect is in qualitative agreement with the final-state rule, although the local p density of states is distorted more than has previously been reported.

I. INTRODUCTION

Anisotropic emission of characteristic x-rays of noncubic crystals has been recognized in recent years as a very powerful tool for providing detailed information about electronic structure.[1] Among the most anisotropic crystals is hexagonal boron nitride (h-BN), a layered compound isoelectronic to graphite, whose highly symmetric crystal structure and strong anisotropic character made it the subject of extensive theoretical and experimental studies. A double-peaked core exciton in the boron K emission spectrum was first reported by Fomichev in 1968.[2] The polarization character of that exciton has since then been a subject of controversy. Using a textured h-BN sample, Borovskiy *et al.*[3] reported its occurrence for both normal and parallel polarizations, but with a downwards shift in energy in the former polarization. Davies *et al.*,[4] using polarized synchrotron radiation, reported a prominent absorption peak at 192 eV near the boron K threshold, which they ascribed to a core exciton constructed mostly of π-like wave functions, but with a small admixture of σ-like wave functions because its intensity is not completely extinguished for $\mathbf{E}\perp\mathbf{c}$. Their interpretation was theoretically substantiated by Robertson,[5] who interpreted the σ-π mixing as being caused by the delocalized character of the exciton in $\mathbf{k}$ space. On the other hand, Leapman *et al.*,[6] using electron-energy-loss spectroscopy, showed that the exciton was entirely of π polarization, in agreement with the conclusion reached by Barth *et al.*,[7] who disregarded the weak structure seen in their s-polarized photoyield spectra as due to imperfect orientation of the crystal layers. It may indeed be that sample texture is a decisive factor in many of the experimentally determined properties of h-BN. Following a careful characterization of our sample, we report in this paper the investigation of the orientational dependence of the B core exciton in h-BN as seen in the boron K soft-x-ray emission (SXE) spectrum.

The polarized K emission spectrum of hexagonal Be (h-Be) has been measured by Brümmer *et al.*[8] The size of the observed anisotropy is a source of disagreement between the experiment and the various existing theoretical models.[9,10] Employing a different procedure of analysis than has been previously used, we measure the angle-dependent K emission band of h-Be, obtaining a different result, which we compare with a recent calculation.

In addition, we report the first experimental evidence of the anisotropic character of the K doubly ionized high-energy satellites of B and N (in h-BN) and of Be (in h-Be), revealing the effect of the spectator core hole on the shape of the density of states.

II. EXPERIMENTAL METHOD AND SAMPLE CHARACTERIZATION

The spectrograph used in this work has been described elsewhere.[11] Briefly, the sample is excited with an electron beam and the emitted x rays dispersed by a grazing-incidence toroidal diffraction grating. The detector is a phosphor-coated position-sensitive photodiode array. The calibration accuracy in the energy range of interest and the instrument resolution are approximately 0.14 and 0.18 eV for B, 0.27 and 0.6 eV for N, and 0.1 and 0.15 eV for Be, respectively. A rotatable sample holder allowed the take-off angle measured from the sample normal to be varied between 0° and 80° without breaking vacuum. The pressure in the sample chamber was maintained in the low-10^{-9}-Torr range. The excitation electron-beam energy was varied between 1.0 and 3.0 keV, while the current was maintained at 1.0 mA.

In the absence of available single crystals of BN, we used a compressed annealed pyrolytic boron nitride sample. We determined its crystallographic texture using Schulz's reflection method.[12] The pole figures of the (001) reflection were measured using a Siemens texture goniometer and filtered Cu $K\alpha$ radiation. The results were compared to those obtained for highly oriented pyrolytic graphite (HOPG), and indicated very good c-axis alignment of the hexagonal crystallites (mosaic spread less than 2°).[13]

The Be(0001) sample was etched initially with HCl, then cleaned at 10^{-5} Torr by extensive argon-ion milling-annealing cycles prior to data acquisition.

III. RESULTS AND DISCUSSION

Emission from h-BN and h-Be is anisotropic, with σ and π valence electrons contributing differently to the emission spectrum at any given angle. Here we shall assume that one π electron ($2P_z$) is available to contribute to the emission, while two ($2P_x$, $2P_y$) of the σ electrons can contribute. If θ is the take-off angle measured from the c axis, the σ-emission intensity in the dipole approximation can be expressed as a function of the energy E and angle θ as

$$I_\sigma(E,\theta)=I_\sigma(E)\left[\frac{1+\cos^2\theta}{2}\right],$$

where $I_\sigma(E)$ is the σ-band transition density of states (TDOS). The π-emission intensity, on the other hand, is

$$I_\pi(E,\theta)=I_\pi(E)\sin^2\theta\ ,$$

$I_\pi(E)$ being the corresponding TDOS. Suppose we carry out measurements of the spectrum for various values of θ. We then have, at each energy, a series of measured intensities which are a linear combination of σ and π contributions varying with angle according to

$$I(E,\theta)=I_\sigma(E)\left[\frac{1+\cos^2\theta}{2}\right]+I_\pi(E)\sin^2\theta\ . \quad (1)$$

It is then a simple matter to evaluate I_σ and I_π using a linear least-squares fit to the data at each energy. This algorithm differs from that used previously[8,14] to separate SXE spectra into σ and π components. The differences and their implications will be discussed below.

A. Boron nitride

Figure 1 shows a series of measurements of the boron K emission of h-BN for different take-off angles, normalized to the same area in the energy range 165–195 eV. The dominant feature with a peak near 182 eV is the fundamental boron K emission band. The peak at 171 eV is formed mainly as a result of the effect of the N $2s$ orbitals on the B density of states and represents bonding B $2p$ electrons hybridized with N $2s$ states. The feature above the top of the valence band is ascribed to the radiative decay of a core exciton. We have discussed the presence of exciton emission in a separate publication.[15]

In all measurements just above a core threshold where the absorption coefficient may be large, and varying with energy, the possibility of distortion of the measured emission spectrum by self-absorption must be considered. We correct our data for self-absorption using the absorption data of Davies *et al.*[4] and an algorithm developed by Crisp.[16] Figure 2 shows the B π and σ subbands obtained according to Eq. (1) and after a correction for self-absorption has been applied. The intensity is divided by E^3 to yield a TDOS (in the one-electron approximation) and expressed in density of states (DOS) units by normalizing the area under the π and σ intensity curves to one and two electrons, respectively. The simplest approach to interpreting x-ray emission spectra

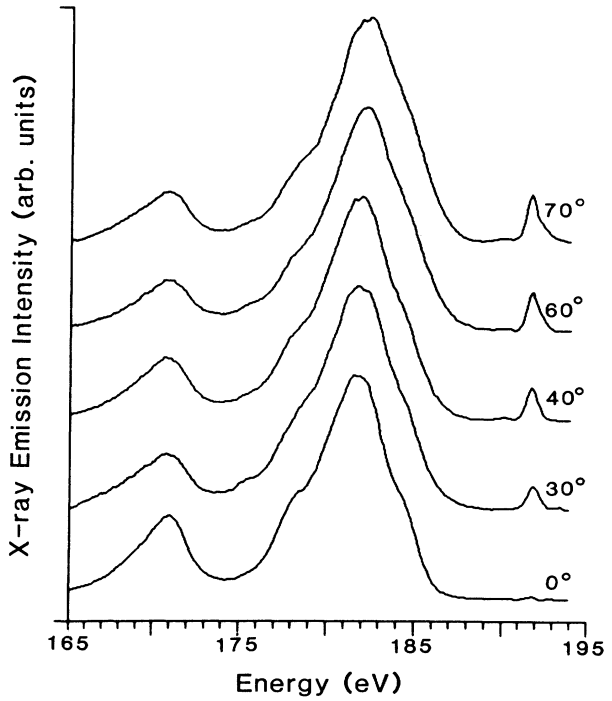

FIG. 1. B K x-ray emission band in BN measured at 0°, 30°, 40°, 60°, and 70° take-off angle.

is within the one-electron approximation where many-particle processes are ignored. Both bands shown in Fig. 2 exhibit a low-energy tail that extends several tens of eV below the bottom of the bands, and which is characteristic of a shake-up process often referred to as "radiative Auger."[17] This is a two or more electron process where the inner core hole decays by the simultaneous emission of a photon and the excitation of valence electrons into the conduction band, depriving the emitted photon of some of its energy, and consequently resulting in the low-energy tail invariably observed in x-ray emis-

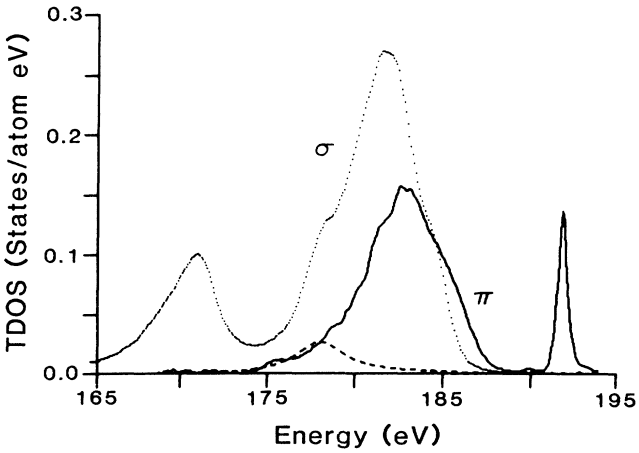

FIG. 2. σ (points) and π (solid line) subbands of B K emission band in BN, and "radiative Auger" (dashed line) contribution to π subband. Intensity is expressed in density-of-states units.

sion spectra. The dashed line underlying the π band in Fig. 2 is our estimate of the radiative Auger contribution obtained using a simple model of this process[18] and which must be subtracted from the spectrum in order to reveal the shape of the one-electron x-ray emission band. In the past, the most commonly used procedure in deriving the σ and π bands from x-ray emission data has been to assume that the bottom of the valence emission band is entirely of σ character so that two spectra obtained at different take-off angles can be normalized to match in amplitude at the bottom of the band. Then the π band is generated from the difference curve of the two normalized spectra. Such an approach ignores, of course, the effect of radiative Auger processes which cause π-like intensity to extend to very low energies. We tested such an algorithm and found that failure to account for this effect in deriving the σ and π subbands in that way will result in overweighting the σ band,[3,14] and will produce an artificial departure from the nominal 2:1 ratio.

Another source of discrepancy with previous emission measurements[3,19] is the anisotropic character of the B core exciton. This core exciton presents a double-peaked structure similar to that reported for another boron compound, B_2O_3.[2,20] It does not appear at all in the σ polarization, thereby indicating its unambiguous π character. In previous emission measurements, a textured BN sample was used by Borovskiy *et al.*,[3] while Tegeler *et al.*[14] attempted to obtain well-oriented samples by rubbing BN powder onto scratched aluminum plates. The degree of orientation of the crystallites in the samples were determined to be 0.47 (Ref. 3) and 0.9 (Ref. 14), versus 1.0 for an ideal single crystal. We believe discrepancies with these measurements are due to misorientation in textured samples. In fact, spectra we have taken on various samples which were not as well aligned, as determined by our sample characterization procedure, exhibited the double-humped exciton for both polarizations, demonstrating that misalignment will indeed account for the feature not vanishing near $\theta=0°$ as observed previously. Our π polarization assignment for the exciton is consistent with band-structure calculations according to which the lowest unoccupied band is of π character localized mainly near B atoms.[21]

The simplest explanation of the exciton double-humped structure attributes it to phonon ringing, an effect predicted by Mahan,[22] and observed in B_2O_3.[20] Mahan showed that a phonon-broadened transition can give rise to a double-peaked emission spectrum where the two peaks are separated by about $4S\hbar\omega$, twice the Stokes shift, where S is the usual linear phonon coupling constant and ω the phonon frequency. This occurs only when the phonon decay rate is very small, as for a local mode.[20] In the linear phonon coupling model, the width of the exciton as seen in absorption dictates the choice of the coupling constant. A linear coupling of an optical transition to the lattice vibrational degrees of freedom[23] will result in a Gaussian broadening of the absorption line with a standard deviation σ given by

$$\sigma^2=S(\hbar\omega)^2\coth(\hbar\omega/2kT)\ .$$

By fitting the absorption data of Davies *et al.*,[4] we find

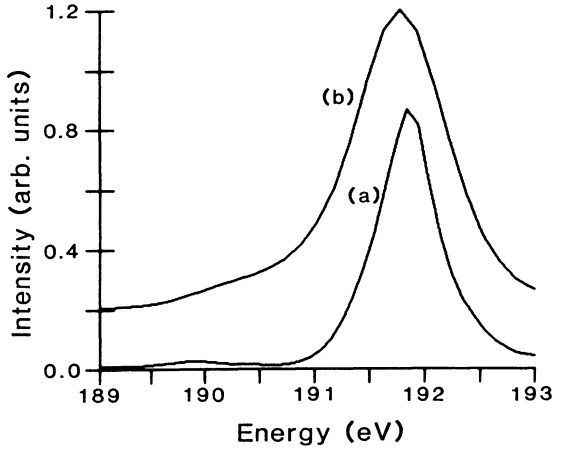

FIG. 3. (a) B core exciton in BN as seen in emission. (b) Mahan model fit to exciton region for $\omega=0.15$ eV, $S=3.5$, and $\gamma=0.12$ eV.

$\sigma=0.28$ eV. Choosing $\omega=0.15$ eV, which compares favorably with the longitudinal-optical phonon frequency of h-BN,[24] we find an S value of 3.5. This yields $4S\hbar\omega=2.1$ eV, in very good agreement with our measured value of 2.0 eV for the separation of the two emission exciton peaks. Figure 3(a) shows an expanded view of the exciton emission region and Fig. 3(b) the evaluation of the Mahan model using the above parameters. The inverse Auger lifetime is taken to be 0.12 eV. With these optimally chosen parameters we obtain only qualitative agreement between experiment and the phonon ringing model as shown in Fig. 3. Such a model, qualitatively if not quantitatively, accounts for the unusual double-peaked exciton, implying a very small phonon decay rate for those phonons that couple to the core transition. We tried to improve our fit to the data by incorporating anharmonic effects in the same phenomenological way as we did for B_2O_3 and Li, where those effects

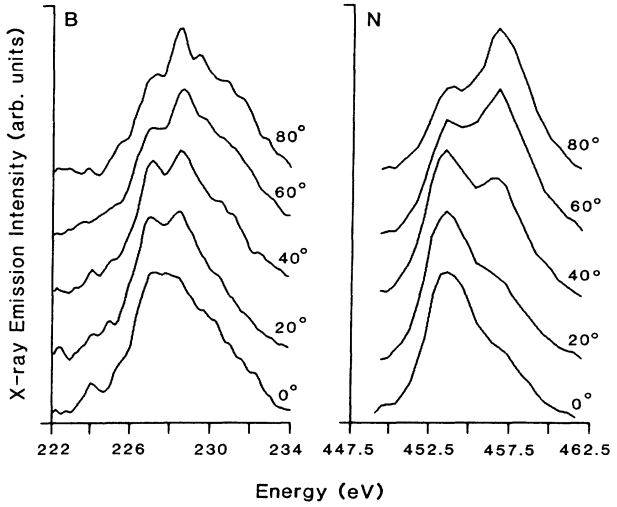

FIG. 4. B and N satellite bands measured at 0°, 20°, 40°, 60°, and 80° take-off angle, and normalized to the same area.

were found to be important.[20] We evaluated the Mahan model for a series of values of ω, and tried to reproduce our data by patching together an envelope of these shapes with ω increasing monotonically with E. However, our attempts to do any better than the results shown in Fig. 3 failed. It proved impossible to match the low minimum between peaks and still produce a low-energy shoulder with any combination of parameters. Proper theoretical treatment of anharmonic effects through a systematic reevaluation of the model[22,25] beyond the harmonic approximation may account for the quantitative discrepancy between the model and the experiment.

Radiative decay of doubly ionized core holes from noncubic solids is also expected to be anisotropic.[26] We observe the B and N doubly ionized high-energy satellites in h-BN at 228 and 456 eV, respectively. The B high-energy satellite has been previously reported at 231.9 eV by Hayasi.[27] A simple atomic argument equivalent to using a screening factor of $\frac{1}{2}$ for the 1s shell for estimating the energy of the N double core hole satellite places it halfway between the energies of the 1s states of N and O.[28] This estimate provides an upper limit of 467 eV, about 10 eV above the observed value. A lower limit, on the other hand, can be obtained by using a slightly different atomic model developed by Hayasi.[29] This estimate places the peak at 440 eV. These two estimates bracket our measured energy, supporting the identification of this feature as the N double core hole satellite.

Figure 4 shows a series of measurements of the (B and N) K high-energy satellite emission spectra for different take-off angles normalized to the same area. The strong dependence of the shape of the peak region of both B and N emission bands upon the take-off angle demonstrates the most pronounced anisotropic effect observed to date for high-energy satellite emission bands. Figure 5 shows their corresponding σ and π subbands obtained using a linear least-squares fit of the intensities measured at different angles at each point in energy according to Eq. (1), normalized to the same area as their corresponding parents, and superimposed on the main σ and π bands. The B σ and π satellites are normalized to the same area as their corresponding main bands over the energy region 175–190 eV, thereby disregarding the N 2s orbital and B core exciton contributions to the main B K emission band. The satellite subbands have been

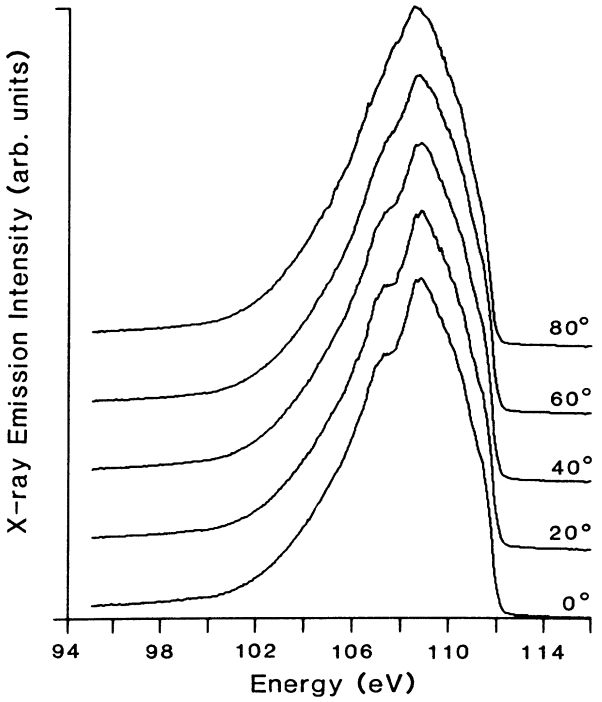

FIG. 6. Be K x-ray emission band in he-Be measured at 0°, 20°, 40°, 60°, and 80° take-off angle.

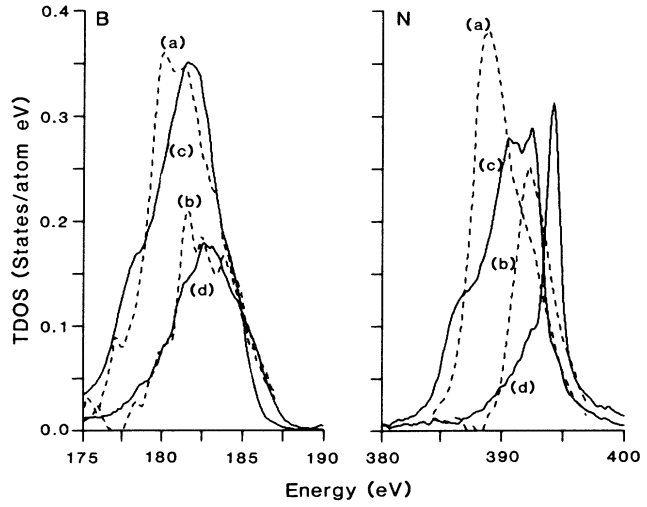

FIG. 5. B and N satellites and parents σ and π subbands in BN. Satellite bands are shifted down in energy by 47.0 eV (B) and 64.7 eV (N), and normalized to the area of their corresponding parents. (a) Satellite σ band, (b) satellite π band, (c) main σ band, and (d) main π band. Intensity is expressed in density-of-states units.

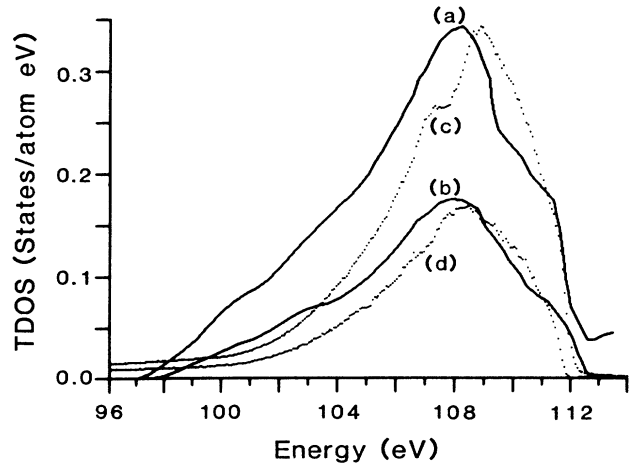

FIG. 7. σ and π components of the Be K emission band. (a) σ theory (after Ref. 10), (b) π theory (after Ref. 10), (c) σ experiment, and (d) π experiment. Intensity is expressed in density-of-states units.

shifted down in energy by 47.0 and 64.7 eV for B and N, respectively. The intensity of the π band at the peak is smaller than that of the σ band for both the B and N high-energy satellites. This contrasts with the respective parent bands where the intensity distribution of the π band relative to that of the σ band is much narrower for nitrogen than for boron, reflecting the fact that the π electrons are localized on the nitrogen atom. In addition, strength from the top part of the N K high-energy satellite σ and π bands has been pulled down towards the bottom of the band, unlike their corresponding main bands where the intensity of both the σ and π bands is concentrated in the upper part of the valence band. This represents a striking example of the effect of the spectator core hole. This point will be developed below. This effect is less dramatic for boron.

B. Hexagonal beryllium

Beryllium has a hexagonal-close-packed (hcp) crystal structure with a closed electronic shell $(1s)^2(2s)^2$ configuration. The $2s$ and $2p$ bands hybridize in the solid state, and similarly to B and N in BN, transitions from the P_z-like states of the valence band into the $1s$ states are polarized parallel to the c axis of the crystal (z direction), giving rise to the π band, whereas the σ band is formed by those radiative transitions of the $P_{x,y}$ electrons into $1s$ states that are polarized perpendicular to the c axis. Figure 6 shows our measurements of the Be K emission band for take-off angles between 0° and 80° in increments of 20°, normalized to the same area. The variation of the shape of these spectra as a function of the take-off angle, in addition to a systematic shift of their first moment, reflect the polarization dependence of the h-Be K emission band. This anisotropy is less pronounced than for those materials that exhibit a layered structure of hexagonal arrays of atoms such as graphite and boron nitride. The first indication of the anisotropic behavior in the h-Be K emission band was found by Brümmer *et al.*,[8] who measured the anisotropic emission using the property that a surface cut parallel to the c axis emits two σ components for e⊥c and (one σ and one π) components for e∥c. Their immediate motivation for carrying out such measurements was the x-ray diffraction measurements of structure amplitudes of Brown[30] and the band calculation of Inoue and Yamashita[31] predicting the existence of bonding charges between Be atoms along the c axis. They normalized their spectra by scaling them in overall amplitude to best match in the lower- and higher-energy regions. Under these conditions and other assumptions relating to the excitation conditions and the grating reflection power, they generated a pure π spectrum by simply subtracting the σ component from the spectrum obtained in the e∥c configuration. Then the additional intensity in the π band as compared to the σ band led them to confirm the existence of p-like localized charges along the c axis. The shapes of the σ and π bands were later found to be in good agreement with theoretical predictions by Rennert *et al.*[9] As described above, the radiative Auger intensity on the low-energy side, as well as the fact that the high-energy edges for both configurations do not match, make the entire algorithm not suitable in determining the correct π:σ intensity ratio. The Be K σ and π bands obtained in the present work using Eq. (1) are shown in Fig. 7. Shown for comparison are the calculated σ and π subbands as obtained by Angonoa *et al.*[10] using a density-of-states expansion technique. The intensity of the experimental bands is expressed in DOS units as explained above. The theoretical bands are normalized to the same peak height as the experimental σ band. We note the fairly good agreement between our assumed and their calculated σ to π band intensity ratio.

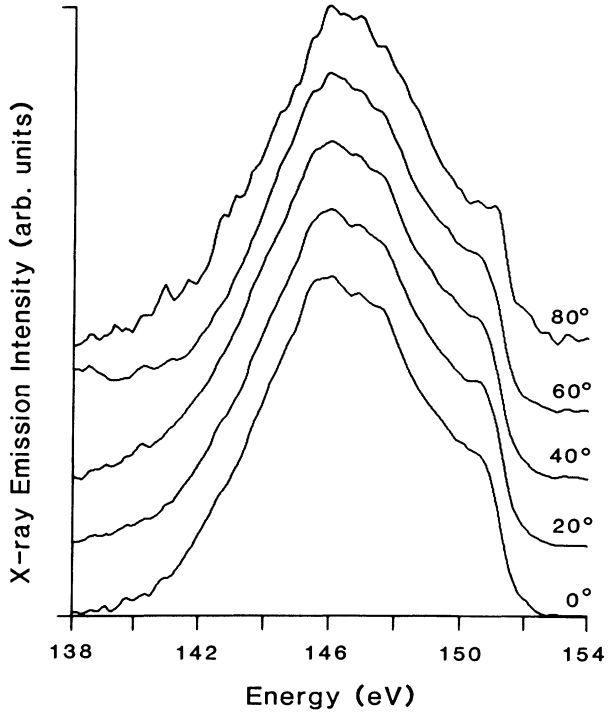

FIG. 8. Be satellite bands measured at 0°, 20°, 40°, 60°, and 80° take-off angle, and normalized to same area.

Figure 8 shows the angular dependence of the Be doubly ionized high-energy satellite and Fig. 9 the corresponding π and σ subbands, obtained using Eq. (1) as described above, shifted down in energy by 39.4 eV, normalized to the same area as their corresponding parents, and superimposed on the main σ and π bands of Be. The significant change in the shape of the doubly ionized satellite σ and π bands as compared to those of the main band reflects the effect of the initial extra core hole on the TDOS. The extra core hole enhances the low-energy part of the band in an attempt to form an exciton, in the same way it does in an absorption process. By contrast, it has been shown theoretically that the shape of the local p DOS remains essentially unchanged upon introduction of a core hole, so that one might expect the spectral shapes of the main and satellite K emission bands to be quite similar, with some broadening of the satellite due to the shorter lifetime of the doubly ionized state.[32] This result finds support in the early Li and Be satellite emission band measurements by Catterall and Trotter.[33] However, as already pointed out by Sagawa,[34] and as

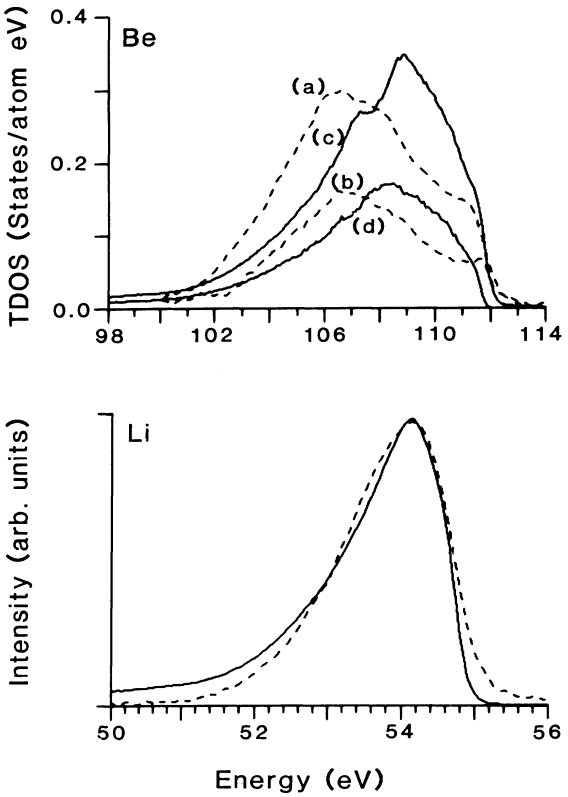

FIG. 9. Top: Satellite and parent σ and π subbands of Be. Satellite bands are shifted down in energy by 39.4 eV and normalized to the area of their corresponding parents. (a) Satellite σ band, (b) satellite π band, (c) main σ band, and (d) main π band. Intensity is expressed in density-of-states units. Bottom: Satellite (dashed line) and parent (solid line) K emission bands of Li. Satellite band is shifted down in energy by 29.0 eV and normalized to the same area as the main band.

shown in Fig. 9, we find that while the parent and satellite bands look quite similar in the case of Li, the shape of the Be K satellite, on the other hand, is significantly altered compared to that of the main band. The implication is that in the case of Be, the influence of the spectator core hole on the local p DOS is more important than had previously been thought. In fact, such distortion qualitatively resembles that experienced by the $L_{2,3}$ high-energy satellite of Na as a result of the strong influence of the core hole on the local s DOS.[31]

We can qualitatively understand this difference as follows: The distortion of the TDOS depends on how well the conduction electrons screen the core hole. For p waves, this can be roughly estimated by the product of the Thomas-Fermi screening length (l_{TF}) and the Fermi wave vector (k_F). For $k_F l_{TF} \ll 1$ the screening is nearly complete and little distortion of the TDOS is expected. For Li and Be, the two products are 0.68 and 0.89, respectively, suggesting that in Be the core hole is less well screened, so we expect more distortion in that case.

IV. CONCLUSION

We have shown how the anisotropy of some solids influences the x-ray emission spectra. This has made it possible to determine the following.

(a) The unambiguous π character of the double-peaked B K emission core exciton in h-BN. We ascribe the origin of the double-peaked structure to phonon ringing. Because the presently available theory does not describe its shape well, we suggest that a proper theoretical treatment including anharmonic effects may account for the quantitative discrepancy with the experimental data.

(b) The separation of the doubly ionized B and N (in h-BN) and Be (in h-Be) K emission bands into their σ and π components revealing the effect of the spectator core hole on the shape of the p TDOS. Such an effect is qualitatively reasonable but has not yet received quantitative theoretical attention.

ACKNOWLEDGMENTS

We are grateful to A. W. Moore of Union Carbide and B. Addis of Cornell University for respectively providing the BN and Be samples. We are indebted to Wolfgang Ruch of the Materials Science Department at the University of Virginia for his help in characterizing the BN sample. We would also like to thank the other members of our group, D. Carson, D. Husk, P. Livins, P. Bruhwiler, C. Tarrio, and J. Nithianandam, for helpful suggestions and discussions. This work was supported in part by National Science Foundation Grant No. DMR-85-15684.

[1]See, for example, the extensive review article by G. Dräger and O. Brümmer in Phys. Status Solidi B **124**, 11 (1984), and references therein.

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