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1998 J. Phys.: Condens. Matter 10 2181

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Local deformation in hexagonal boron nitride crystal near the B K-shell π -excitation

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Received 9 June 1997, in final form 4 November 1997

Abstract. Theoretical and experimental studies of the B K-shell absorption near the π -excitation in hexagonal boron nitride were carried out. The absorption spectrum over the interval 191.5–193.5 eV was analysed in the framework of the quasi-atomic model with respect to its molecular simulation and for the features of its recombination. Our analysis points to the appearance of local deformations in the crystal lattice around a core-excited atom which are mainly created by the breaking of the ground-state symmetry due to out-of-plane displacements of core-excited boron atoms in a basal plane (0.16 Å). The comparison with the experimental B K-shell absorption spectra for the metastable incoherent phase BN and defect-containing BN crystals supports this polaron mechanism. Methods for the description of the x-ray absorption in solids taking into account the related atomic rearrangement are discussed.

1. Introduction

Long-living high-energy excitations in solids are of particular interest for investigations of the atomic dynamics accompanying them. Experimental studies of x-ray absorption, fluorescence and emission spectra as well as the polarization and orientation dependences of the x-ray reflectivity near the B K edge in hexagonal boron nitride (h-BN) crystal [1–11] provide evidence of the appearance of a well resolved, intense and narrow absorption line at 191.8 eV. In the high-energy part of the B K emission, an intense and complex band attributed to the radiative decay of this excitation is observed. Its shape is strongly deformed and shifted downward by about 0.50 eV [12] (or ~ 0.44 eV, according to [2]) relative to the absorption peak [2, 12–15]. The electron–phonon interaction is regarded as the main cause of this difference. Within the Born–Oppenheimer approximation and the two-step *absorption-followed-by-emission* model, this red shift and the phonon sideband for the emission line are expected due to the accompanying phonon excitation [16, 17]. In the framework of Mahan’s model of incomplete phonon relaxation [18], the authors of references [12, 15] have succeeded in explaining qualitatively the doublet structure of the emission line. It is important to account for the anharmonicity effects in a purely phenomenological way to analyse the experimental and theoretical spectra [12]. The investigations of the K-shell excitations in graphite and diamond give results in good accordance with this model and demonstrate a strong vibronic coupling and the appearance of a very extended phonon sideband, indicating a large displacement of the core-excited atom from its equivalence position in the ground state and its Jahn–Teller distortion [16].

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In this contribution, we report on experimental and theoretical investigations of B K-shell excitations in h-BN, and reveal changes in the x-ray absorption due to the local deformation of the crystal structure and discuss the x-ray absorption π -resonance structure (XA π S) in this context. We show that the XA π S can be rationalized assuming the existence of defect sites in the crystal due to out-of-plane displacements of boron atoms in the basal plane. As regards the possibility of the creation of the defect sites owing to the relaxation after the π -excitation of the crystal, the coupling of absorption and recombination processes makes them observable in the XA π S.

2. Experimental procedure

The x-ray absorption measurement of a powdered BN sample was performed on the beamline BN0 of the synchrotron radiation laboratory at the Bonn electron stretcher and accelerator ELSA. ELSA was operated at 2.3 GeV in the storage-ring mode with an average current of 30 mA. The synchrotron radiation was monochromatized using the high-energy toroidal grating monochromator (TGM). The TGM is equipped with ion-etched, Au-coated gratings with 600, 1200 and 2400 lines mm^{-1} providing highly resolved monochromatized synchrotron radiation in the energy ranges 50–120 eV, 100–240 eV and 200–480 eV, respectively. The energy resolution ($E/\Delta E$) at the B K edge (≈ 200 eV, 1200 lines mm^{-1}) was better than 800 which is sufficient for investigating the electronic structure of B in solids with a natural linewidth of the B K-core level of about 0.2–0.3 eV. To obtain this resolution, the slit widths were adjusted to $0.25 \times 1.2 \mu\text{m}^2$ (entrance slit) and $0.5 \times 1.20 \mu\text{m}^2$ (exit slit), respectively. The influence of second-order N K XANES features on the line shape was found to play an unimportant role ($<1\%$) [19].

The absorption spectra reported here were recorded in the electron-yield mode using a channeltron (Galileo) as the electron detector. The energy calibration of the TGM was controlled by monitoring the position of the absorption maximum of NaNO_3 (405.7 eV). The determination of the energy positions of the absorption features and the analysis of the π -resonance structure were performed using a least-squares fitting routine.

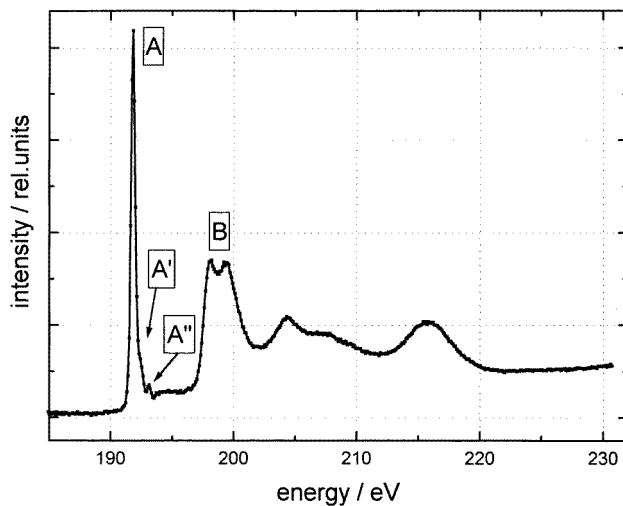


Figure 1. The B K-shell XANES of h-BN measured in the total-electron-yield mode.

3. Results and discussion

The B K-shell absorption spectrum of h-BN is displayed in figure 1. The absorption peak A at 191.8 eV and line B at 199 eV, the natures of which have been discussed in many studies [1, 3, 4, 8, 20], dominate its spectral dependence. The peak A is assigned as a transition from the B 1s level to a strongly localized atom-like $2p(a_2'')$ state oriented normally to the basal plane (xy). It originates from the splitting of an intense atomic B $1s^{-1}2p$ resonance by the essentially anisotropic surroundings. Recently, detailed investigations of the K-shell absorption in BN allotropes [20] have revealed the weakness of chemical effects on the excitation, which can be treated as a 'pure' atom-like π -component. This means that the radial and angular deformations of the B $2p_z$ function due to the impact of the surroundings can be ignored. The B $2p_{xy}$ functions responsible for the doubly degenerate σ -component (B) are, in contrast, strongly deformed by the surroundings and converted into a quasi-discrete state located above the edge [20].

The analysis of the low-lying excitation (A) in figure 1 shows that (i) its full width at half-maximum (FWHM) amounts to ~ 0.32 eV (for comparison, 0.37 eV in [20]), which is typical for an atomic x-ray transition in a solid and supports the conclusions [20] regarding its atomic origin and the nonbonding character of the relevant a_2'' MO and (ii) there is an additional structure consisting of a shoulder A' centred at 192.4 eV and a peak A'' at 193.1 eV. This structure was earlier registered in experimental studies [7, 20].

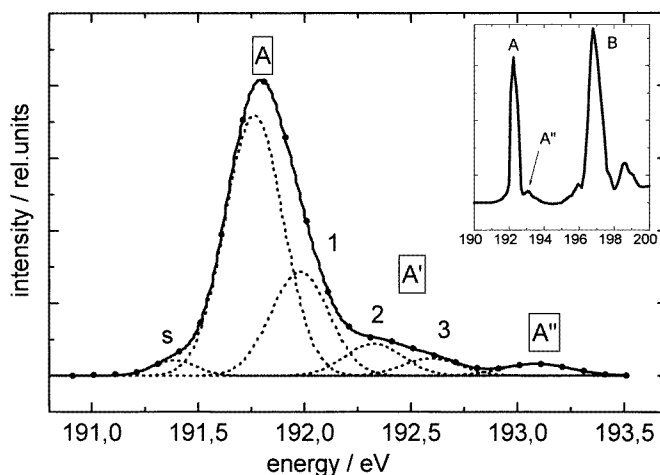


Figure 2. The B K-shell XA π S of h-BN. Its spectral deconvolution is shown by dotted lines. Inset: the XA π S region of BCl₃ [21].

To examine the XA π S, its spectral deconvolution is plotted in figure 2. We used Gaussians of equal width (representing first of all the instrumental bandwidth) but different intensities and positions. The number of Gaussians was varied too. There is a set of nearly equidistant discrete peaks 1, 2 and 3 lying at +0.26, 0.61 and 0.86 eV above the main transition, and an isolated peak at 193.1 eV as well as a peak s below the main transition. The experimental FWHM of the peak at 193.1 eV coincides precisely with the main excitation. The area of the high-energy satellites (1–3, A'') is approximately ten times larger than that of the low-energy one. The recognized XA π S is an argument against the conventional picture of Gaussian broadening of the x-ray transition in a solid with standard

deviation $\sigma = [S(\omega) \cotan(\omega/kT)]^{1/2}$ where the coupling constant S is equal to the mean number of photons created in the transition.

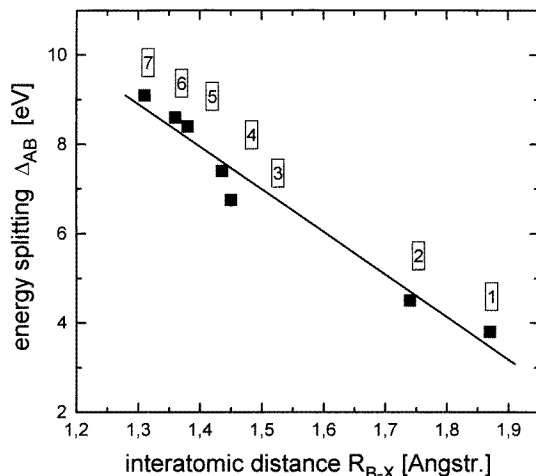


Figure 3. The $\Delta_{AB}(R_{B-X})$ dependence of the energy splitting between the main π - and σ -resonances in B K-shell spectra, i.e. the dependence on the interatomic distance between a B atom and its nearest neighbours X: (1) BBr_3 ($\Delta = 3.8$, $R = 1.87$); (2) BCl_3 (4.5, 1.74); (3) h-BN (6.75, 1.45); (4) $\text{B}_3\text{N}_3\text{H}_6$ (7.4, 1.436); (5) B_2O_3 (8.4, 1.38); (6) borate, BO_3^{3-} (8.6, 1.36); (7) BF_3 (9.1, 1.31). For very large R , both the π - and σ -excitations convert into a parent B $1s^{-1}2p$ resonance.

According to reference [20], the potential of a core-excited atom and its nearest neighbours (X) dominates the spectral dependence of the photoabsorption in h-BN near the B K edge and describes the energy positions and intensities of the two main excitations in figure 1. Thus, the A and B absorption lines can be considered as being strongly localized within the planar $[\text{BN}_3]$ fragment in the crystal. This conclusion is confirmed by the analysis of the splitting Δ_{AB} of the B $1s^{-1}2p$ resonance in the long row of chemical compounds containing free molecules (BF_3 , BCl_3 and BBr_3) [21] and solids (amorphous B_2O_3 , borates, h-BN) [20]. The smooth and continuous dependence of Δ_{AB} on the interatomic distance R_{BX} is shown in figure 3. This experimentally obtained dependence indicates unambiguously both the strong localization of these excitations within the $[\text{BX}_3]$ fragments and their relation to a parent atomic $1s^{-1}2p$ resonance, enabling a molecular BHal_3 simulation and a molecular-orbital treatment to be carried out.

The localized nature of the wave functions of the initial and final states of the x-ray transition offers an approach to study how the crystal structure rearranges itself, modifies its symmetry, and how it relaxes in the vicinity of the excited atom. By comparing with the B K-shell excitations in free BF_3 , BCl_3 and BBr_3 molecules [21], the molecular origin not only of the A and B resonances but also of the peak A'' in h-BN can be furthermore revealed, since there exist similar features at ~ 0.8 eV above the main excitation in BCl_3 and ~ 0.7 eV in BBr_3 , respectively. As an example, the XA π S of the BCl_3 molecule taken from [21] is inserted in figure 2. Both the quasi-atomic calculations for h-BN [20] and the *ab initio* MO calculations [21–23] of the B K-shell excitations in the BHal_3 molecules taking into account Rydberg states indicate that one cannot assign the A'' peak as a single-electron transition at fixed molecular geometry. Thus, the A'' peak at 193.1 eV in h-BN can be regarded as a *quasi-molecular* feature, the origin of which remains unclear. Ishiguro *et al*

[21] have suggested that it is related to molecular dissociation.

Quasi-molecular simulation is a useful tool for the description of electronic excitations in solids [20, 24, 25] but not vibrational effects in them, excepting, perhaps, the Jahn–Teller distortions. In view of the strong spatial localization of the π -excitation in h-BN, we can put forward the suggestion that its molecular modelling can be extended to atomic dynamics near the core-excited atom in the crystal. For molecules, such as ethylene and benzene [26], the inner-shell excitations provide compelling evidence that the ground-state symmetry is broken and the internuclear potentials are modified according to their ground-state values. Therefore, the above-mentioned features of the B K absorption and emission can be regarded as the result of local atomic rearrangement near to the π -excited atom. This supposition correlates with the strong influence of vibronic coupling on the decay of this excitation [16] and with the effect of anharmonicity on the vibrations [15] accompanying it. Since the shape of the relevant emission band indicates the existence of very highly excited harmonic-oscillator states, roughly 2 eV above the bottom of the potential well [16], the harmonic approximation is certainly of limited applicability. Its correction has to include not only a cubic term in the lattice coordinates, but also asymmetric forces which can be especially important for excited quasi-two-dimensional systems. Then the relaxation (electronic decay and atomic rearrangement) of the x-ray excitation in h-BN can be approximately described as occurring within the $[\text{BN}_3]$ fragment. As a result it acquires molecular properties. Similarly to the case of molecular dissociation, the core-excited atoms leave their regular positions and make it possible to create defects in the lattice. This supposition correlates with the features of x-ray emission from B_2O_3 and h-BN, associated with some small fraction of a lattice defect or impurities of boron atoms [14].

To describe the relaxation, the methods developed to establish the core-level decay of molecular species (see, e.g., reference [27, 28]) can be applied. Then, the two timescales characterizing electronic (t_e) and atomic (t_a) relaxations near the core-excited atom can be introduced. There exist well known molecular examples where one or the other timescale is short enough to dominate the decay spectrum [27, 28]. However, for a lot of cases, a delicate balance between the two processes is required to describe experimental data [27]. So, the emission spectra become more complicated, as they include both molecular and atomic contributions.

As for the π -excitation in h-BN, the time t_e is rather large and the rearrangement of atoms in the vicinity of the core-excited atom cannot be ignored. Since the bulk excitations dominate the B K-emission band, their atomic relaxation rearranges the atomic configuration of the surroundings (incomplete dissociation). With respect to the molecular (BF_3) dynamics near the B $1s^{-1}2p(a_2'')$ excitation [29, 30] characterized by the strong enhancement of the B^+ -ion yield, the appearance of out-of-plane displacements of core-excited boron atoms in h-BN seems to be rather reasonable. In particular, a transition from its planar $[\text{BN}_3]$ (ground state, D_{3h}) configuration to a pyramidal one (C_{3v}) is expected. Then, the B K-emission band at 191.3 eV can be assigned as a mixture of the B $1s^{-1}$ radiative decays occurring in the planar and pyramidal $[\text{BN}_3]$ configurations. Its downward shift and characteristic shape originates from both the incomplete phonon relaxation [12] and the breaking of the ground-state symmetry of core-excited B atoms in the crystal. Such a pyramidally deformed $[\text{B}^*\text{N}_3]$ configuration (like planarly compressed ones) can be regarded as a small-radius polaron accompanying the B K-shell excitation in the crystal. Due to its strong spatial localization, the close resemblance to valence excitations in ionic crystals is stated.

The influence of the atomic rearrangement on the x-ray absorption process in solids has hardly been investigated until now. It is usually ignored, because in the framework of the two-step (*absorption-followed-by-emission*) model, this effect does not appear. But it does

appear if the absorption and recombination are regarded as interconnected processes, i.e. the XA π S cannot be satisfactorily described with the help of one time-independent potential. The quasi-atomic approach [23, 24] is suitable for obtaining a description of inner-shell-vacancy decay in solids via resonances in x-ray absorption. As a starting point, we use the atomic model [31]: the inner-shell resonance is approximated by a superposition of one-electron transitions $nl \rightarrow n'l'$ in the potentials (v_γ) corresponding to the various atomic configurations (γ) weighted with w_γ . Since the γ -configurations refer to different radiative and Auger decays of nl^{-1} -vacancies, w_γ is the ratio of the total (Γ) and partial (Γ_γ) inverse lifetimes [31]. Then, passing on to polyatomics, we have to add the summation over various channels of atomic relaxation (i.e., over different atomic configurations, α):

$$f_{nl}^{\text{atom-in-comp}}(\omega, E^{\text{res}}, \Gamma) \approx \sum_{\gamma\alpha} w_{\gamma\alpha} f_{nl\gamma\alpha}(\omega) \quad (1)$$

where $f_{nl\gamma\alpha} = f_0/[(\omega_{\gamma\alpha} - \omega)^2 + 4\Gamma_{\gamma\alpha}^2\omega^2]^{-1/2}$, the $w_{\gamma\alpha}$ -coefficient determines the probability that the electronic nl^{-1} -vacancy decay occurs inside an α -configuration, ω is the photon frequency of the x-ray, $\omega_{\gamma\alpha} - I(n_0l_0) = E_{\gamma\alpha}^{\text{res}}$ and $I(n_0l_0)$ is the threshold energy. Equation (1) provides an opportunity to determine the profile of a resonance in x-ray absorption with respect to post-collision effects on atomic and electronic structures and the probability of exciting various metastable configurations in molecules and solids due to the promotion of a core-level electron into unoccupied molecular orbitals (MO).

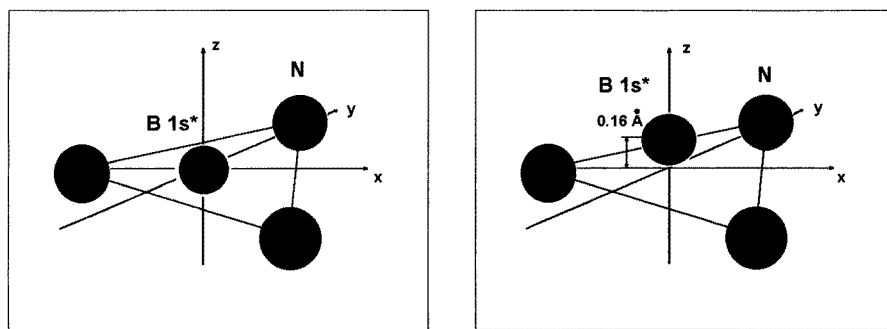


Figure 4. The planar (left-hand panel) and the pyramidal (right-hand panel) $[BN_3]$ configurations corresponding to the excited states at 191.8 eV and 193.1 eV, respectively.

Then, the π -resonance in h-BN can be presented as a sum over the $B 1s^{-1}2p$ π -excitations localized in the planar and pyramidal $[B^*N_3]$ configurations induced by the relaxation near the core-excited atom. The lifetime of the $[B 1s^{-1}]$ vacancy can be regarded as approximately independent of the configurations:

$$\Gamma_{\gamma,\text{plan}} \approx \Gamma_{\gamma,\text{pyramid}}. \quad (2)$$

But the dependence of the resonance frequencies $\omega_{\gamma\alpha}$ on α is essential for our analysis. Indeed, for the pyramidal C_{3v} configuration the antibonding character of the $\pi^*(a_1)$ MO increases as the potential of the surroundings is more repulsive than for the planar one in which the $W_{a_2''}$ -potential is very weak and the relevant ($\pi(a_2'')$) MO is nonbonding:

$$E_{\gamma,\text{plan}}^{\text{res}} < E_{\gamma,\text{pyramid}}^{\text{res}}. \quad (3)$$

For the C_{3v} configuration, the a_1 MO becomes antibonding (π^*) owing to the strong interaction of the $B 2p_z$ with the $N 2p_z$ and $3s$ functions and, therefore, an upward shift

($\epsilon_{\pi\pi^*}$) of the π^* -resonance energy relative to the π -resonance energy is expected. So, the local atomic deformation accompanying the π -excitation results in a noticeable change of the B–N bonding and leads to the appearance of the high-energy sideband of the main transition and its doublet (π and π^*) shape. Hence, the doublet peaks A and A' in the B K-shell absorption spectra of h-BN, BCl₃ (figures 1 and 2) and BBr₃ [21] can be assigned as superpositions of the planar (D_{3h}) and pyramidal (C_{3v}) configurations of the core-excited [BX₃] fragment, respectively. The two [BN₃] configurations are shown in figure 4.

The separation between the π - and π^* -peaks ($\epsilon_{\pi\pi^*} \sim 1.3$ eV) is a rather typical energy for the π -excitation shift observed in the x-ray absorption spectra of many compounds [32]. The $\epsilon_{\pi\pi^*}$ -value agrees with the observation [16] of very highly excited harmonic-oscillator states, +2 eV above the bottom of the potential well [16]. By calculating (using the same approximations as are used in reference [20]) the energy of the B 1s⁻¹2p(a₁) excitation in the pyramidal [BN₃] configuration as a function of the out-of-plane displacement, we found that the above-mentioned separation corresponds to the displacement of ~ 0.16 Å assuming that the nitrogen atoms are fixed at their regular positions (figure 4). Then, the shoulder A' could be assigned to transitions into other C_{3v} configurations with smaller angular deformations. However, there is another possibility: that of assigning it to the interlayer electronic states discussed in references [33, 34]. The observed energy differences between the A, 1, 2 and 3 peaks in figure 2 which are noticeably larger than expected for a single stretching mode for h-BN are an additional reason for the complex molecular-like motion of atoms inside the excited region. This complexity of the vibrational excitations in the absorption profile was noted recently in the work described in [35] (where high-energy resolution measurements of the 1s⁻¹(π) lines for the CO₂ molecule were carried out. In the framework of the quasi-atomic model, the peak s in figure 2 can be assigned as a B 1s⁻¹↑ → 2p(π)↑ transition with the conversion of the spin quantum number. Its energy is lower than that of the main transition A due to the exchange interaction of the partially filled B 1s and π -orbitals.

The measurement performed provides the intensity ratio of peaks A and A', $I_A:I_{A'} = f_{B\ 1s-2p\pi^*}:f_{B\ 1s-2p\pi} \approx 20$, which can be understood as the probability (p_d) of creating a defect atomic site in a h-BN lattice due to the out-of-plane displacement of a π -core-excited B atom. This offers an alternative way of checking this interpretation by measuring the concentration of boron defects in the crystal induced by the B K-shell excitation at 191.8 eV. However, the ratio found overestimates the probability p_d because (i) we cannot exclude the existence of some density of defects present initially in the sample investigated and (ii) the defects are accumulated in the sample during the measurement. For the latter reason, the kinetics of the process has to be taken into consideration. The increase of the intensities of the shoulder A' and the line A'', for i-BN (i ≡ incoherent phase), observed in reference [7], supports the proposed mechanism, as one can assume a noticeable density of the defect boron sites in a thin film of the metastable incoherent phase BN responsible for the higher intensity of these features relative to the main transition. In fact, Wada and Yamashita have shown that small variations in substrate temperature, laser fluence, ion fluence and gas pressure will produce BN thin films of hexagonal or incoherent structure [36]. The high sensitivity of the XA π S to short-range order effects was recently demonstrated by Jimenez *et al* [37] in a study of changes in the local bonding in h-BN induced by ion sputtering and ion implantation. In accordance with our results, the XA π S analysed in reference [37] has given a clear 'fingerprint' for recognizing [BN_x] defect sites.

By comparing the K-shell excitations in BN and carbon allotropes, similar structural changes in the graphite lattice accompanying the low-lying C 1s⁻¹2p(π) excitation are expected. But for graphite, there are difficulties with respect to the registration of the effect on the C K-shell XA π S due to strong π - π interaction within a basal plane because the

relevant π -MO is more delocalized in a basal plane [20]. We underline the weak van der Waals interaction between the neighbouring layers in h-BN and the fact that the graphite layers are favoured as regards experiencing this mechanism.

The essential x-ray emission intensity from the B $1s^{-1}2p(\pi)$ excitation makes it possible to assign it as a quasi-stationary defect centre which demonstrates the close resemblance to donor highly localized centres, labelled DX centres, for which the dominance of the lattice distortions is established [38].

4. Conclusions

Experimental and theoretical analysis of the excitations at 191.5–193.5 eV in h-BN crystal with respect to the main trends in B K-shell absorption in a long row of chemical compounds containing both free BHal₃ molecules and amorphous B₂O₃ has demonstrated their quasi-molecular origin and encouraged us to propose that an important contribution to the XA π S arises from the local deformation of the crystal lattice near the core-excited atom. The molecular modelling is applied not only to describing the promotion of a B 1s electron to unoccupied states in the crystal, but also in an effort to understand the changes in the atomic dynamics due to this transition.

According to our analysis, this excitation is strongly localized within the [BN₃] fragment, the ground-state symmetry of which can be broken due to the out-of-plane displacement of the core-excited atom resulting in defect boron sites in the crystal. As a result, a set of satellite peaks above the main transition is observed in the XA π S.

Applying the quasi-atomic model to the description of x-ray absorption structure taking into consideration the core-hole relaxation (electronic decay and atomic rearrangement), we have assigned the absorption peak A'' at 193.1 eV as a transition into the π^* -MO of the metastable pyramidally (C_{3v}) deformed [B*N₃] configuration.

Acknowledgments

The authors gratefully acknowledge the Deutsche Forschungsgemeinschaft, Germany, for financial support within the Sonderforschungsbereich 408, and the RFFI, Russian Federation, under contract number 96-03-33138.

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