# Quantitative band mapping of crystals from resonant inelastic X-ray scattering

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## Abstract

Using measurements of resonant inelastic X-ray scattering (RIXS) spectra and $k$-momentum conservation, quantitative site and symmetry projected band mapping is realized for broad sp-band materials Si and BP. It is shown that agreement between experimental and calculated band dispersion for Si and BP is observed only if Si 3d and P 3d states are taken into account in the band structure calculations.
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## 1. Introduction

The progress in resonant inelastic X-ray scattering (RIXS) made over recent years allows use of this method, as an alternative technique to angle-resolved ultraviolet photoemission (ARPES), to perform quantitative band mapping of crystals [1]. RIXS is applicable to many materials, such as insulators and polycrystalline materials, that are difficult or impossible to study by ARPES. Due to the different excitation and relaxation processes and their corresponding selection rules, RIXS also provides information that is complementary to the well-established ARPES technique. A disadvantage of RIXS is the fact that $\vec{k}$-selectivity is given rather indirectly, and depends on the dispersion of the unoccupied bands. Only at special points, such as band edges and high symmetry points, $\vec{k}$ can be determined unambiguously using an inelastic scattering experiment.

It has been shown that carbon Kα X-ray emission spectra (XES) of diamond strongly depend on the excitation energy [2]. Based on these measurements, it was concluded that the absorption and emission should be treated as a single inelastic scattering process with well-defined crystal momentum conservation for photoelectron and valence band hole. In other words, upon excitation of a core electron to the conduction band (with a certain crystal momentum, based on the incident photon energy), emission from the valence band at the same point in the Brillouin zone (same $\vec{k}$-vector) will take place. The calculation of X-ray emission spectra of diamond for different excitation energies using $k$-momentum conservation has shown a good agreement with experiment [2,3]. Similar calculations performed for graphite [4,5], Si [6], cubic and hexagonal BN [3] also have shown a reasonable accordance between calculated and experimental spectra. The capability of RIXS measurements for quantitative band mapping was demonstrated at first for SiC [7], and then for diamond, graphite and MgB$_2$ [8], where the experimental dispersion curves for occupied electron states were constructed. In the present paper the further development of this technique applied to broad sp-band materials, such as crystalline Si (c-Si) and BP is discussed. It is shown that for agreement of experimental and calculated $E(k)$-curves of c-Si and BP the 3d-like electrons are crucial.

## 2. Calculation and experimental details

Electronic structure of Si and BP was calculated using a self-consistent linearized muffin-tin orbital (LMTO) method within the local density approximation (LDA) with help of TBLMTO-47 computer code [9]. Two sets of LDA
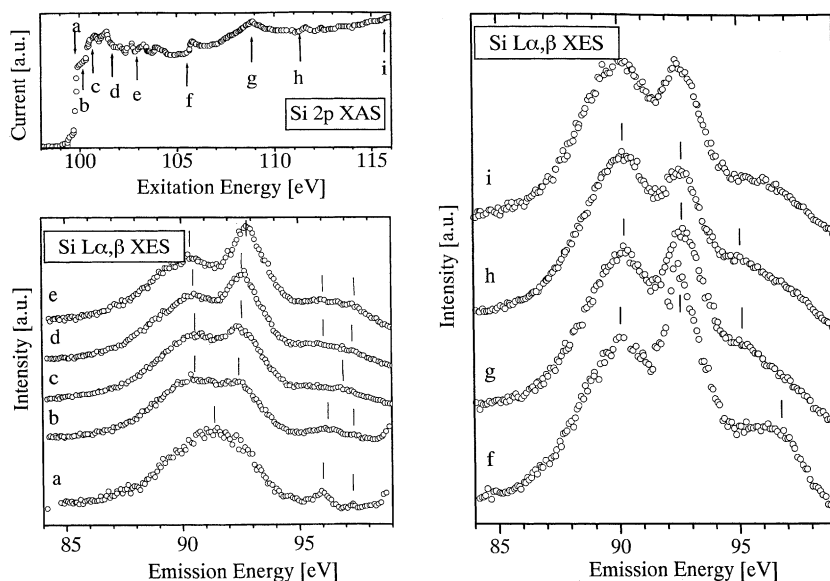
Fig. 1. RIXS spectra of c-Si measured in the vicinity of Si 2p XAS [10].

calculations were performed for c-Si and BP which neglect and take into account Si 3d and P 3d states.

For data treatment already published high-resolution RIXS spectra [10,11] of Si and BP which were measured in the vicinity of Si 2p, B 1s and P 2p edges at the beamline BL-3B at the Photon Factory (KEK) have been used. The general procedure for RIXS experiments starts by measuring the X-ray absorption spectrum (XAS) in total electron yield (TEY) mode. The X-ray emission spectra (XES) are then recorded at selected excitation energies. Boron Kα (2p → 1s transition), Silicon and Phosphorus Lα,β (3s3d → 2p transition) were measured with energy resolution 0.3–0.4 eV.

## 3. Results and discussion

According to the RIXS band mapping procedure [1], excitation energies for the emission spectra are selected at spectral features in the absorption spectrum, which correspond to points of high symmetry in the Brillouin zone. Then X-ray emission spectra are recorded at those selected excitation energies. Under resonant excitation, the emission spectra show features that are changing with excitation energy, and can characterize the different types of dispersive features.

The procedure of plotting the experimental points on the dispersion curves is described in detail in [7,8]. The top of the valence band in band structure calculations is related to the X-ray photon energy scale ($E_0$) using XPS binding energies of core levels [7] or by alignment of peaks in calculated density of states (DOS) with spectral features in XES curves [8]. We have found that in general the second way is more correct because binding energies of core levels in some cases can be influenced by core hole effects and we used this method in present paper for alignment of experimental

and calculated spectra. Then the dotted horizontal lines, corresponding to the selected excitation energies, are built up crossing the dispersion curves for unoccupied states. The intersection points determine the possible values of $\vec{k}$ that will induce X-ray emission transitions. Using $\vec{k}$-momentum conservation, the vertical lines from intersection points are drawn down to dispersion curves for occupied states. Then the energy of selected spectral features are determined on
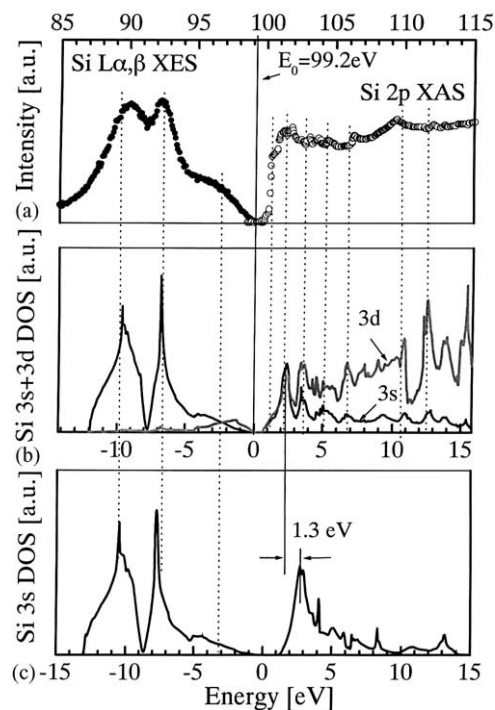


Fig. 2. Silicon L X-ray emission and absorption spectra (a) compared with band structure calculations (b–c) of c-Si. Si $L_{2,3}$ XES is measured with $E_{exc} = 145$ eV [10].
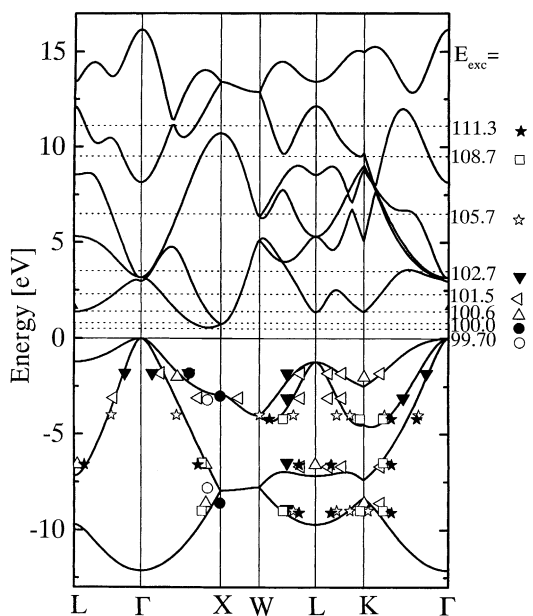
Fig. 3. Comparison of experimental and calculated dispersion curves of c-Si. Each symbol corresponds to selected excitation energy for Si L$_{2,3}$ XES.

XES curves and new horizontal lines are drawn through calculated dispersion curves for occupied states (not shown in Figs. 3 and 6). Finally, the intersection points of horizontal and vertical dotted lines give the experimental points on dispersion curves for occupied states. If band structure calculation is correct, each experimental point will be situated near the calculated dispersion curve for at least one possible $\vec{k}$ value.
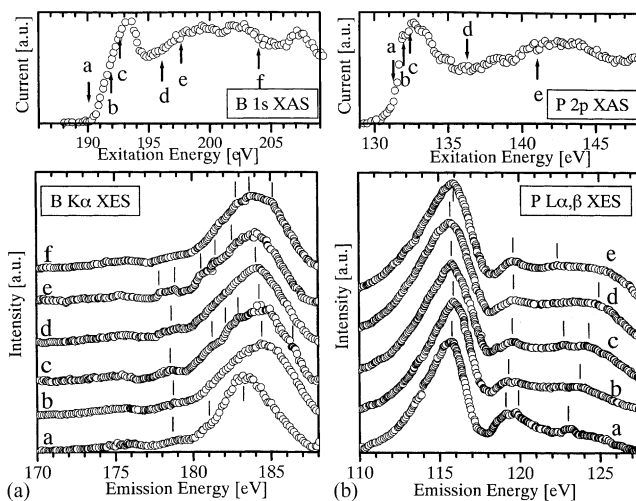


Fig. 4. RIXS spectra of BP measured in the vicinity of B 1s (a) and P 2p (b) XAS [11].

In Fig. 1, the RIXS spectra of c-Si measured in the vicinity of the Si 2p-absorption edge at various excitation energies [10] are presented. Fig. 2 shows the comparison of Si Lα,β X-ray emission and absorption spectra (panel (a)) and band structure calculations of crystalline Si (c-Si) including Si *3s* (panel (c)) and Si 3s + 3d states (panel (b)). One can see that the main spectral features of the X-ray emission and absorption spectra are consistent with the density of states (DOS) calculations. Basing on this comparison one can conclude that the inclusion of Si 3d states are very important for the electronic structure calculation of c-Si. The occupied states are found to be rather insensitive to the inclusion
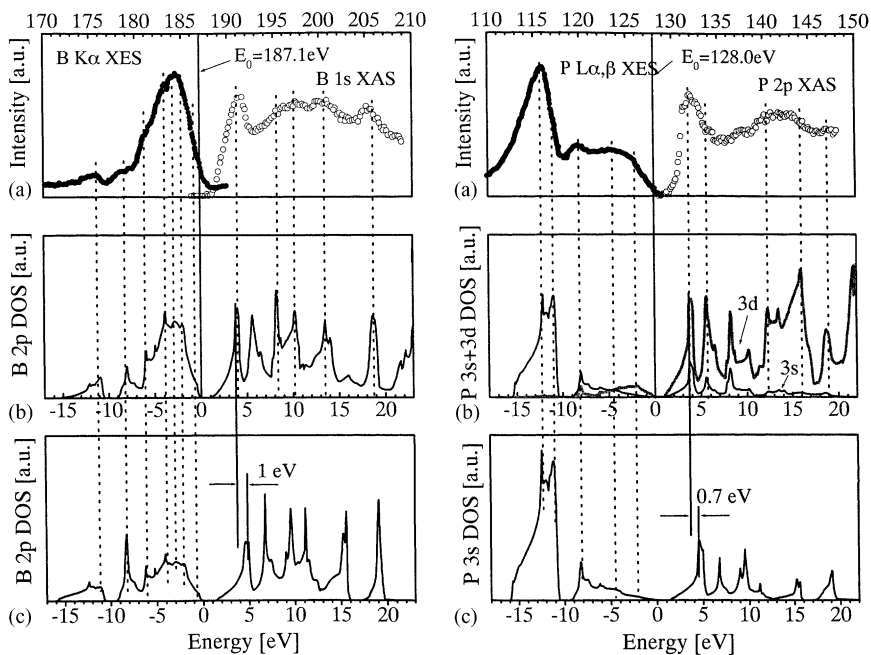


Fig. 5. Phosphorus L (left panel) and boron K (right panel) X-ray emission and absorption spectra (a) compared with band structure calculations (b–c) of BP. B K and P L$_{2,3}$ XES are measured with $E_{exc} = 210$ and $165\,eV$, respectively [11].
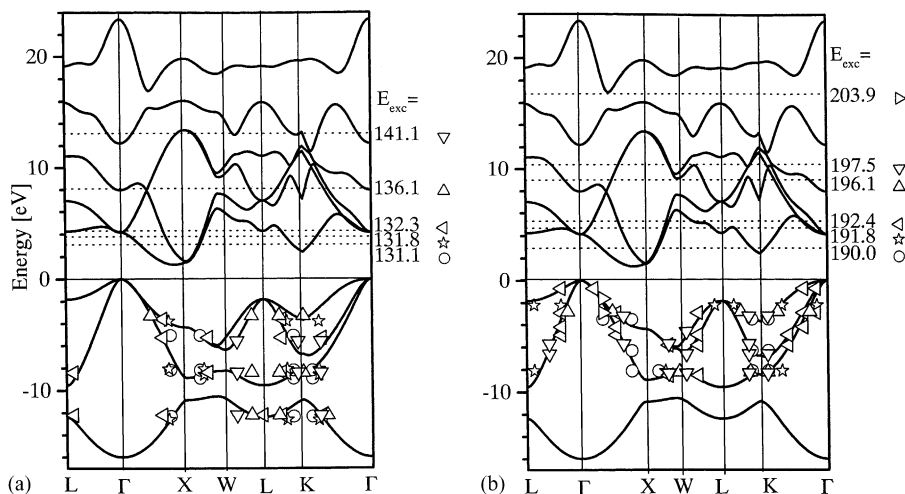
Fig. 6. Comparison of experimental and calculated dispersion curves of BP for phosphorus (a) and boron (b) sites. Each symbol corresponds to selected excitation energy for boron K and phosphorus L emission spectra.

of Si 3d states to the calculation basis, whereas the bottom of the conduction band is shifted by ∼1.3 eV, thus giving a better agreement with experimental Si 2p X-ray absorption spectra. Using the $E_0$ value, determined from Fig. 1, and RIXS spectra of c-Si excited at $L_{2,3}$-threshold [10] we have constructed experimental dispersion bands and compared them with calculated ones which take into account Si 3s + 3d states (Fig. 3). The comparison of experimental results and theoretical band structure calculation shows a general good agreement which demonstrates the importance of Si 3d states for the formation of chemical bonding and electronic structure of crystalline Si.

In Fig. 4, high-resolution RIXS spectra of BP measured at B K and P L edges [11] are presented. We have compared K and L emission and absorption spectra of constituents of BP with results of band structure calculations in Fig. 5 which allows to determine the $E_0$ of the X-ray photon energy scale. As in the case of c-Si, we can conclude that band structure calculations of BP, which take into account P 3d states, give a more close agreement with experimental spectra and can be used for comparison with experimental dispersion bands. Using the same procedure, as described for c-Si, and experimental RIXS spectra [11] shown in Fig. 4, the site and symmetry-projected experimental dispersion curves were constructed which are found in a good accordance with calculated ones for BP when P 3d states are taken into account (Fig. 6).

In conclusion, we need to point out that the role of 3d states in chemical bonding of sp-band materials was already discussed applying to Si [6], $SiO_2$ [12,13], MgO, $Al_2O_3$ and $AlPO_4$ [14] and it is found that the contribution of 3d states is essential to the interpretation of their X-ray emission and absorption spectra. On the other hand, it is supposed that contribution of d states is not sufficient to explain RIXS spectra quantitatively and correlation effects and core hole potential in the intermediate state must be taken into account [6]. Our results definitely show that LDA single electron

band structure which takes into account 3d states is consistent with RIXS quantitative band mapping for c-Si and BP.

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