Connection between spectral features of B K edge XANES of minerals and the local structure

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1. Introduction

Knowing the structure of borates glasses is crucial for a deeper understanding of their physical properties. This work concentrates on studying the local neighborhood around B atoms. Boron atoms participate in creating the B–O network which can be seen as a basic matrix onto which the whole complex structure of binary and ternary glasses is hooked. In a B₂O₃ glass, a B atom is coordinated by three O atoms. In binary and ternary glasses, boron atoms occur both in BO₃ and BO₄ structural units. Nuclear magnetic resonance (NMR) spectra of ¹⁰B proved to be very useful in determining the ratio of B atoms occurring in BO₃ and BO₄ environments. It would be useful, nevertheless, to have an independent method of measuring this quantity. Moreover, NMR cannot be used in situations where the content of boron is very small, such as in thin films or in materials where boron is the dopant. Therefore, there is a need for alternative ways of determining the ratio of threefold and four-fold coordinated B atoms. Also, it would be very useful to have a technique which might be able to probe not only the short range order but the medium range order as well, informing thus about participation of B atoms in superstructural units such as boroxol rings.

X-ray absorption spectroscopy has established itself as a method for studying structure of materials which often cannot be investigated by other means. It offers a view on the local geometry around a chemically specific atom. The extended x-ray absorption fine structure (EXAFS) spectrum can usually be analysed quantitatively and information about nearest-neighbour distances and about coordination numbers can be obtained in a more or less straightforward way. However, measuring EXAFS oscillations is often not possible in amorphous systems, due to their strong disorder-related damping. X-ray absorption near edge structure (XANES) signal can be measured under much broader circumstances. Unfortunately, it is not possible to extract structural information from XANES in a straightforward way. Typically, one relies on comparing XANES of a compound with unknown structure with spectra of compounds where the structure is known. Employing this technique bears several dangers because the correspondence between the shape of XANES spectrum and the local structure is not unique. Therefore, a thorough theoretical investigation of how relevant spectral features arise should be done wherever possible.

Recently, B K edge XANES spectra of several glasses were measured. In order to use these data

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efficiently, one needs to understand the mechanism by which the XANES peaks are generated in such compounds. This can be achieved by studying theoretically XANES spectra of boron containing minerals. The local neighborhood of B atoms in these systems is, namely, similar as in borate glasses; they are coordinated by three or four O atoms. Various features in a K edge XANES spectra of these minerals were identified as markers of presence of either $\text{BO}_3$ or $\text{BO}_4$ units and even were employed in studying the structure of borosilicate glasses in the past.$^{(9,11)}$ However, these assignments were done mostly on a semi-empirical basis. Theoretical investigations were limited only to small model clusters of four or five atoms.$^{(10)}$ No calculations of XANES involving full geometric structure of boron containing minerals have been performed so far.

The purpose of this work is thus to explore theoretically XANES spectra of boron containing minerals, to find out what structural elements give rise to characteristic spectral features, to compare the roles of short, medium and long range order in generating the XANES spectra and to assess the applicability of the XANES technique in studying the structure of borate glasses.

2. Theoretical method

XANES was calculated $ab$ initio via a real space full multiple scattering technique,$^{(12,13)}$ which means that infinite crystals were substituted by finite clusters centred on the photoabsorbing B atom. Spectra presented in this work were obtained for clusters containing around 120 atoms, unless explicitly stated otherwise. We checked that this cluster size is fully sufficient – adding more atoms does not change the resulting spectra in a considerable way.

A non-self-consistent muffin tin potential constructed according to the Mattheiss prescription was mostly used. The 1s core hole was taken into account by relying on the final state rule (‘relaxed and screened’ approximation).$^{(12,13)}$ For several compounds we obtained also selfconsistent scattering potentials by performing SCF-Xα molecular calculations for clusters of about 20 atoms embedded in a crystal.$^{(14,15)}$ We found out that the general shape of theoretical XANES spectra does not change if selfconsistent instead of non-selfconsistent potentials are used.

3. Minerals containing only $\text{BO}_3$ or only $\text{BO}_4$ units

3.1. Comparison between theory and experiment

In order to verify the applicability of our theoretical scheme, we start by comparing theoretical and experimental XANES for minerals containing only one type of B atoms. In that way, possible ambiguity connected with superposing spectra arising from nonequivalent sites can be avoided. Figure 1 summarises our results for minerals containing boron in a $\text{BO}_3$ coordination (calciborite, ludwigite, vonsenite) and in a $\text{BO}_4$ coordination (danburite, datolite, sinhalite). The experimental spectra were taken from

Figure 1. Theoretical (full lines) and experimental spectra (dashed lines) for minerals containing only $\text{BO}_3$ or only $\text{BO}_4$ units. The experiment is taken from Fleet et al.$^{(16,17)}$
earlier fluorescence yield measurements of Fleet and coworkers.\textsuperscript{(16,17)} The alignment between theoretical and experimental spectra of the same compound was done so that the best agreement between them is achieved; spectra of different compounds were aligned so that corresponding experimental peak positions match. The origin of the energy scale is arbitrary.

The first thing to notice in Figure 1 is that the spectra split into two groups, according to whether the compound contains boron in BO\textsubscript{3} or in BO\textsubscript{4} units. This distinction appears both in experimental and in theoretical spectra. Spectra of minerals with BO\textsubscript{4} units are characterised by an intensive prepeak just before the onset of continuum states (around 5 eV in the scale of Figure 1) and by a main peak around 15 eV. Minerals with BO\textsubscript{3} units give rise to spectra with one single main peak at -9 eV. We denote these peaks as A, B, and C (see Figure 1). Spectrum of sinhalite does not quite fit into this scheme; this can be attributed to the fact that coordination of boron in sinhalite is ‘three plus one’ rather than four (three B–O distances are 1.46 Å while the fourth distance is 1.58 Å). The intensity of the theoretical pre peak in BO\textsubscript{4}-containing compounds is significantly smaller than the experimental prepeak. This difference probably stems from our static treatment of the core hole. We found, namely, that the calculated intensity of this prepeak and even its very occurrence depend quite a lot on the scheme used for accounting of the core-hole (see Šipr et al.\textsuperscript{(14)} and Brydson et al.\textsuperscript{(18)} for more technical details). This indicates that the prepeak is closely related to the way in which other electrons react to the presence of the core hole and its accurate description is thus not possible within a static scheme.\textsuperscript{(12,13)}

Experimental spectra of BO\textsubscript{4}-containing minerals also exhibit a small prepeak. However, it is much less intensive than in the case of BO\textsubscript{3}-containing materials and it does not occur in theoretical spectra. This prepeak probably arises due to the presence of a small amount of threefold coordinated B atoms, which appear in these compounds as a result of radiation damage.\textsuperscript{(16,17)} Note also that the samples used in the experiments were natural minerals, so they could have contained a significant amount of impurities even before that start of the measurements.

The shoulders at the high energy side of the main peak in danburite and in datolite (around -13 eV) are not reproduced by our theory very accurately; we checked that employing selfconsistent potentials does not improve this situation. Spectra calculated for fourfold coordinated boron sites in minerals containing both BO\textsubscript{3} and BO\textsubscript{4} units do not display such features either (see below). This suggests that the highenergy shoulder observed in experimental XANES of BO\textsubscript{4}-containing minerals could also contain a significant contribution arising from structural defects, similarly as it is the case with the pre-edge in these compounds. Deficiencies of our theoretical scheme, such as muffin tin approximation to the potential and/or one electron treatment of electron excitations, could be another source of the disagreement between theory and experiment. These effects are usually not important but their precise quantification is very difficult.\textsuperscript{(13)}

3.2. Cluster size effect

Knowing the size of the region of the crystal within which the observed spectral structure is generated is essential for any physical interpretation of XANES. Therefore, spectra of all minerals displayed in Figure 1 were calculated for several cluster sizes. Representative results for datolite and for ludwigite are shown in Figure 2. One can see immediately that the basic features of XANES spectra, i.e. the single peak B for a BO\textsubscript{4}-containing mineral datolite and the prepeak A and the main peak C for a BO\textsubscript{3}-containing mineral ludwigite, are reproduced even for the smallest clusters employed. The fine structure between the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Spectra of datolite and ludwigite calculated for clusters of different sizes. Number of atoms in the cluster is indicated for each line type in the plot.}
\end{figure}
peaks A and C in XANES of ludwigite is reproduced if around 30 or more atoms are taken into account. Because a similar behaviour with respect to cluster size can be observed for spectra of the other minerals as well, one can draw a general conclusion that the characteristic shape of XANES of minerals is generated within the basic BO$_3$ or BO$_4$ units. The spectrum is thus dominated by short range order effects. The largest influence of medium range order can be observed in the fine structure between the peaks A and C in spectra of BO$_3$-containing minerals.

3.3. XANES of BPO$_4$

Boron phosphate BPO$_4$ has a simple crystal structure, with boron coordinated by four oxygens. Therefore it was frequently used as a model system for studying spectra of compounds with four-fold coordinated boron.\(^{(16,17)}\) In order to gain a better intuitive understanding of XANES of BPO$_4$, we calculated the B K edge XANES of BPO$_4$, and observed how it changes if the cluster size is varied. The results are summarised in Figure 3.

One can see that, unlike in the case of boron-containing minerals, XANES of BPO$_4$ is governed by long range order – even 17 atoms are not enough to reproduce the basic shape of experimental spectrum. The reason behind different behaviour of BPO$_4$ and of minerals may rest in the different symmetry of their crystal structures. The BPO$_4$ crystal is highly symmetrical and well defined coordination shells around boron can be resolved even at large distances. The scattering of excited photoelectron by more distant shells can thus contribute to the formation of XANES structure. On the other hand, the symmetry of boron-containing minerals is very low and the distribution of more distant atoms around boron thus resembles rather a continuum than individual coordination shells. The phases of photoelectrons scattered by these more distant atoms are consequently nearly random and the corresponding contributions cancel each other.

Another interesting aspect is that the theoretical spectrum of the 5 atom cluster in BPO$_4$ looks similar to spectrum calculated for the BO$_3$ unit in datolite (Figure 2). That suggests that, on the short range, spectra of BPO$_4$ and of BO$_3$-containing minerals are similar. The difference between them stems from the long range order effects. The dominance of long range order over the short range order in generating spectrum of BPO$_4$ implies that BPO$_4$ is not a good model example for studying XANES of glasses.

4. Minerals containing both BO$_3$ and BO$_4$ units

X-ray absorption spectrum of any material is a superposition of spectra generated at edges of all the inequivalent photoabsorbing sites. It is quite difficult to disentangle these individual contributions from experimental XANES. In a theoretical study, however, one calculates the spectra for each of the sites separately, making it thus possible to search for features characteristic for each individual coordination.

Our study is aimed at obtaining knowledge which could be useful in studying structure of borate glasses, so a significant statistical disorder has to be anticipated. Therefore we focus not on a detailed analysis of XANES of a single compound but rather on observing spectral features which would be common to all boron sites with threefold or fourfold coordinations. That requires an analysis of a large number of spectra. Figure 4 displays theoretical spectra of ten minerals, listed in Table 1. The spectra are shown for each boron site, meaning that we have 13 curves corresponding to threefold coordinated boron and 26 curves corresponding to fourfold coordinated boron. As an aid to an eye, spectra averaged over all sites in BO$_3$ units and in BO$_4$ units are shown via thick lines. The horizontal alignment of spectra generated at different sites of the same compound was provided by the theory itself, spectra of different compounds were aligned so that positions of the peak B at ~9 eV approximately coincide. Similarly, the vertical scale for spectra calculated at different sites of the same mineral is fixed by the theory, while mutual alignment of spectra of different compounds was done so that their intensities at high energies (E≥20 eV) would coincide.

Two basic patterns can be distinguished in the spectra shown in Figure 4, according to the coordination of the photoabsorbing site (similarly as in Figure 1). Characteristic shapes of spectra generated at BO$_3$ and BO$_4$ sites are thus well separated. This clearly indicates that the gross shape of B K edge XANES of

![Figure 3. Spectra of BPO$_4$ crystal calculated for different cluster sizes (as indicated for each line type in the plot). The experiment is taken from Rocca et al.\(^{(19)}\)](image)
The medium and long range order, which differs from compound to compound and from site to site, affects the ‘fine structure’ of peaks A, B, and C but has little influence on their very existence.

It follows, therefore, that peaks B and C could be involved in studying the short range order in borate compounds. For a quantitative treatment, assessing peak areas seems to be a natural choice. We evaluated areas of peaks B and C by subtracting from the spectra the high energy background and integrating the intensities over a 10 eV energy range. It turns out that all spectra connected with a particular boron coordination, either BO$_3$ or BO$_4$ coordination, yield very similar areas of the peaks: for each of the peaks B and C, individual areas deviate from the respective average by less then 5%. However, the peak area depends on whether the spectrum relates to boron in BO$_3$ or BO$_4$ coordination. The average area of the peak C in spectra at threefold coordinated boron sites constitute only ~75% of the average area of the peak B in spectra at fourfold coordinated boron sites. We checked that this conclusion remains valid even if various ‘technical parameters’ are varied (such as the scattering potential or the energy range over which the peak area is integrated).

It appears therefore that the ratio of areas of peaks C and B could serve as a criterion for estimating the ratio of BO$_3$ and BO$_4$ units in borate minerals and in borate glasses. However, before this criterion is applied, one would have to account for the effect of structural changes due to radiation damage and due to surface treatment. There is a strong evidence that these effects may ‘artificially’ increase the portion of threefold coordinated boron.$^{(16,17)}$

Contrary to the case of peaks B and C, the core-hole-related prepeak A depends quite a lot on the electronic structure of the material. One can expect that its intensity and area will be affected by complex many body processes, meaning that the direct influence of the local geometry will be obscured. Therefore, although the prepeak A could serve as a marker of presence of BO$_3$ units, its usability in quantifying the ratio of threefold and fourfold coordinated B atoms seems to be limited.

### 5. Peak width and distortion of BO$_4$ tetrahedra

It follows from the intuitive picture of generating x-ray absorption spectra that positions of XANES peaks depend on bond lengths.$^{(12)}$ Hence, presence of several slightly different B–O distances ought to give rise to broader ‘smeared’ peaks in comparison with situation when all the B–O distances are equal. Fleet & Liu$^{(17)}$ suggested that the width of the peak B could serve as an indicator of the spread of the B–O distances in BO$_4$ tetrahedra. We can test this conjecture against our theoretical spectra. Figure 5 shows the dependence of the width of the peak B on the spread of B–O distances for all the spectra at fourfold coordinated boron sites displayed in Figures 1 and 4 and, additionally, for spectrum of axinite (which contains BO$_4$ units only). The width of the peaks was evaluated at the height which corresponds to 40% of the maximum peak height (after subtracting the background), the spread of the B–O distances is defined simply as the difference between the longest and the shortest bond in the BO$_4$ tetrahedron as obtained from the crystallographic data. One can see that sites with larger spread of B–O distances generally give rise to broader peaks. However, this correlation is not very strong. For most typical spreads of B–O distances, the widths of peak B appear to be distributed quite uniformly between 3 and 5 eV. It seems, therefore, that in most situations the main peak width is not a

![Figure 4. Spectra calculated at all boron sites in minerals listed in Table 1. Thin lines represent spectra at individual sites, thick lines show averages over all spectra at sites with BO$_3$ or with BO$_4$ coordination.](image)

**Table 1.** Minerals involved in this study that contain both three-fold and four-fold coordinated B atoms. For each compound, numbers of boron sites in BO$_3$ and in BO$_4$ coordinations are shown in the second and in the third columns. Theoretical XANES spectra of these minerals are displayed in Figure 4.

<table>
<thead>
<tr>
<th>Name</th>
<th>BO$_3$</th>
<th>BO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>boracite</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>borax</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>colemanite</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>howlite</td>
<td>4</td>
<td>1</td>
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<tr>
<td>kernite</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>kurnakovite</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>meyerhoffenite</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>probertite</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>ticalcomite</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ulexite</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>
reliable indicator of the distortion of the BO$_4$ tetrahedron. Rather, one could assume that exceptionally large distortions get revealed through exceptionally broad peaks.

Because of the irregular shape of the B peak, the height in which the peak width is measured may affect the outcome. The overall picture offered by Figure 5 remains essentially unchanged as long as the peak width is evaluated between 30–45% of the maximum peak height. Beyond these limits, the correlation between the peak width and the spread of the B–O distances gradually fades away.

A similar analysis was done also for the widths of the main peak C in spectra generated at the BO$_3$ sites (Figure 6). In that case, however, no manifest relation between the peak widths and the spread of B–O distances in the BO$_3$ units can be found.

### 6. Discussion

Our main conclusion, namely, that the B K edge XANES in minerals is dominated by short range order effects, was obtained under broad circumstances. It remains valid even in case that the disagreement between our calculations and the experiment at the high energy side of the peak B in XANES of danburite and datolite is caused by deficiencies of the theory (see Figure 1 and accompanying text). Namely, factors not described by our scheme, such as non-muffin tin effects or multielectron excitations, would influence the calculated spectra always in the same way, independently on the size of the cluster involved in the calculation. Therefore, it is fair to assume that the trends in cluster size effect, evident from Figure 2, would not change if a more accurate theory was used.

Our study involves boron in many crystallographic positions, in various compounds. Because of this variety of nearest boron neighborhoods, our results can be transferred from crystals to glasses. An argument in support of a local character of XANES spectra of a B$_2$O$_3$ glass was recently presented by Preobrajenski et al, who analysed resonant Auger spectra with photon energies covering the B K absorption edge.

In our theoretical study, we did not address the problem of isolating the peaks B and C from the experimental spectrum of a compound with boron atoms in BO$_3$ as well as in BO$_4$ units. Such an effort will have to cope with the fact that the high energy shoulder of peak B partially overlaps with peak C. At least part of this shoulder comes from radiation damage – a process too complicated to be described by ab initio approaches. Therefore, in order to identify peaks B and C in experimental data, one should also rely on comparisons with experimental spectra of materials with different BO$_3$ and BO$_4$ content, recorded under similar circumstances.

Relation between the width of the peak B and the spread of B–O distances was also investigated by Fleet & Muthupari. Their results based on analysing experimental spectra seem to suggest that a stronger correlation exists between these two quantities than what was found in our study (Figure 9b of Fleet & Muthupari exhibits less scatter of data points than our Figure 5). However, the widths of peak B in the experimental spectra were estimated from fitting these spectra by several gaussians, which involves some ambiguity. Such a procedure was obviously not needed in our theoretical study. Apart from that, our Figure 5 includes nearly twice as many data points as the corresponding plot of Fleet & Muthupari. Therefore, it seems that our study describes the relation between the width of the peak...
B and the spread of B–O distances more reliably than the earlier work.

7. Conclusions

B K edge XANES spectra of minerals arising from sites in BO$_3$ units differ considerably from spectra arising from sites in BO$_4$ units; the characteristic shape of these spectra is governed by short range order. The prepeak appearing in spectra of three-fold coordinated boron is essentially affected by the core hole. Areas of main XANES peaks depend only on whether the photoabsorbing atom is in a BO$_3$ or in a BO$_4$ unit and can thus be used for studying structure of materials. The width of the main peak of spectra at four-fold coordinated boron sites generally increases with the spread of the B–O distances but deviations from this correlation may be substantial. In contrast to spectra of minerals, XANES of a BPO$_4$ crystal is governed by long-range order and is thus not a suitable model for studying XANES of borate glasses.

Acknowledgement

This work was supported by the project 202/04/1440 of the Grant Agency of the Czech Republic and by the CNR-AV CR Common Research Project 'Interplay between structural and electronic properties in nanostructures'. The research in the Institute of Physics AS CR was supported by the project AV0Z-10100521 of AS CR.

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