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X-ray absorption fine-structure investigation of the ionic compounds NaBr, KBr and RbCl: full multiple-scattering analysis

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Abstract. The x-ray absorption near-edge structures (XANES) of the Br K edge in NaBr and KBr and the Rb K edge in RbCl have been analysed. In spite of the fact that these compounds have the same type of crystal lattice (NaCl type) the published experimental spectra show different structures. We have used a full multiple-scattering method to investigate the conduction band structures of NaBr, KBr and RbCl. The partial densities of Br and Rb p states in the conduction bands were obtained over a large energy interval for both the ground and the excited states. The latter were used to analyse the experimental data. In contrast with our recent study of AgBr, the Br K XANES in NaBr and KBr and the Rb K XANES in RbCl are found to be determined by the multiple scattering of photoelectrons in a large cluster (30 or more atoms). We also show that, for the energy interval up to 80 eV above the main edge, the single-scattering approximation in the present study seems to be less satisfactory.

1. Introduction

The investigation of the electronic energy bands and local crystal structures of the ionic compounds is at present of great interest. X-ray fine-structure analysis has become a powerful tool for such studies [1]. X-ray absorption spectroscopy has been applied to the study of the dynamics of the local structure in some ionic conductors (mostly containing Ag) [2–5].

Recently a multiple-scattering analysis of the AgBr x-ray absorption near-edge structure (XANES) has shown [6] that in this system, in spite of the existence of atoms in a collinear geometrical arrangement, the single-scattering term in the expansion of the absorption coefficient determines the main features of the experimental XANES [7] within 80 eV above the absorption threshold. Moreover, it was found that the main contribution to the Br XANES in AgBr was given by the second shell of surrounding atoms, showing the minor role of the first coordination shell. In the present study we analyse the electronic structures of KBr, NaBr and RbCl ionic materials by means of an XANES multiple-scattering analysis to determine whether the rules found for AgBr [6] are common to all $A^I B^{VII}$ -type ionic compounds. Comparison is made with the experimental results [8].

2. Calculation

The full multiple-scattering calculation scheme used here has been discussed previously [9]. We performed the calculations with the help of the computer code G4XANES, an improved

version of the multiple-scattering computer programs described elsewhere [10]. We assumed the NaCl structure, with lattice constants equal to 6.600 Å for KBr, 5.973 24 Å for NaBr and 6.5810 Å for RbCl [11]. For the calculation, we used clusters of up to three shells (the addition of the fourth and fifth shells essentially did not affect the spectrum structure). The procedure for constructing the muffin-tin (MT) potential and choosing MT radii has been described elsewhere [12]. The values of the MT sphere radii and MT constants (i.e. constant value of MT potential in the region between MT spheres in relation to vacuum energy level) for the unrelaxed (see later) case are reported in table 1. In the calculation we included phase shifts with orbital momentum $l \leq 3$. For an energy interval up to 50 eV there are no changes if the restriction $l \leq 2$ is used. The changes in spectra observed in the energy interval above 50 eV with increasing maximum l became almost negligible when one took into account all the main factors that caused the broadening of the spectra (i.e. the final lifetime of the core hole, the limitations of the mean free path of the photoelectron and also the experimental resolution). All these factors would contribute to the imaginary part of the complex potential used (see [12] for details). However, in order to obtain more visible XANES fine features, we did not specifically include all these factors for the calculations of the spectra that we show. Instead, we used a constant imaginary part of the potential, equal to -0.1 eV.

Table 1. The muffin-tin radii R_{MT} and muffin-tin energies V_i according to the unrelaxed calculation.

| NaBr | | | KBr | | | RbCl | | |
|------|------------|---------------|------|------------|---------------|------|------------|---------------|
| Atom | R (Å) | V_i (eV) | Atom | R (Å) | V_i (eV) | Atom | R (Å) | V_i (eV) |
| Br | 1.5934 | -9.826 | Br | 1.7071 | -9.1582 | Rb | 1.4125 | -9.634 |
| Na | 1.3914 | -10.364 | K | 1.5647 | -9.5186 | Cl | 1.6713 | -9.762 |

3. Discussion

In figure 1 we show the experimental data [8] for the compounds investigated. In spite of the same surroundings of absorbing Br atoms in NaBr and KBr, and similar properties of Na and K atoms, in XANES there are no simple energy shifts of maxima with the change in lattice parameter according to the $1/R^2$ rule [1] described in the single-scattering approximation, but changes in relative intensity and the appearance of new maxima (figure 1, curves B and C). The K XANES of a metal (Rb in RbCl) atom in the same type of crystal structure (figure 1, curve A) shows a very similar structure in comparison with the halogen atom spectrum in NaBr. One can suppose that the significant broadening of the first maximum in the RbCl spectra in comparison with NaBr arises because it is not resolved after taking into account all the broadening factors (see section 2) of the multiplet. Therefore, we decided to perform also a multiple-scattering calculation of Rb XANES in order to separate the effects of atomic scattering and structural properties in the formation of the XANES. So, we believe it is especially interesting to analyse these XANES data with the help of a full multiple-scattering method.

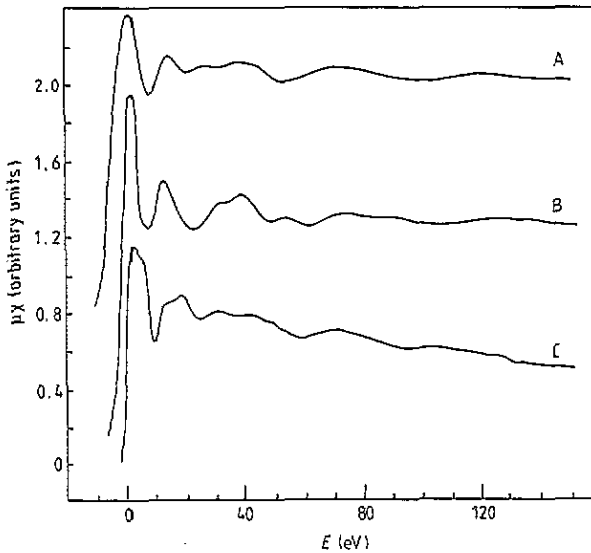


Figure 1. Experimental Rb XANES in RbCl (curve A) and Br XANES in NaBr (curve B) and KBr (curve C).

3.1. NaBr

The first step in the theoretical multiple-scattering XANES analysis is the choice of the minimum size of the cluster, i.e. determination of the set of surrounding atoms which primarily determines the electronic density of states in the conduction band of the compound. As one can see from figure 2, the main structure of the Br XANES in NaBr has already appeared for a cluster of two shells having a sufficiently small radius (4.2 Å). However, some fine details arise because of the next few shells. It should be noted that the results shown in figures 2 and 3 (except for the curve labelled 'relax.')

correspond to the ground-state potential and therefore reflect the projected density of Br p states. So, one can conclude that a cluster of three shells containing 27 atoms and with a radius of about 5 Å has such solid state properties as a density of states. In order to compare with the experimental data, it would be more correct to perform a calculation for the excited state, which takes into account the relaxation effects. We have made such a calculation in the so-called $Z + 1$ approximation [1]. However, as one can see in figure 2 there are almost no visible differences between the theoretical XANES of the two approaches; only the relative intensities of the first two maxima change and become closer to the experimental data. This result is not surprising because the well delocalized p bands are not expected to be affected strongly by the relaxation potential, in contrast with the $L_{2,3}$ edge XANES where relaxation effects are very strong [13].

In order to study the adequacy of the single-scattering approximation for the description of the Br XANES in NaBr, we compare in figure 2 the results of the single- and multiple-scattering calculations for the three-shell cluster. As one can see, in the case of NaBr, the single-scattering term makes it possible to obtain the general structure of the Br XANES but not the fine structure (the feature at 55 eV) and details in the energy interval from 25 to 35 eV.

3.2. KBr

The structure of the Br XANES in KBr differs from that of NaBr (figure 1). The full multiple-scattering results allow one to describe all the details of the experimental spectra using a

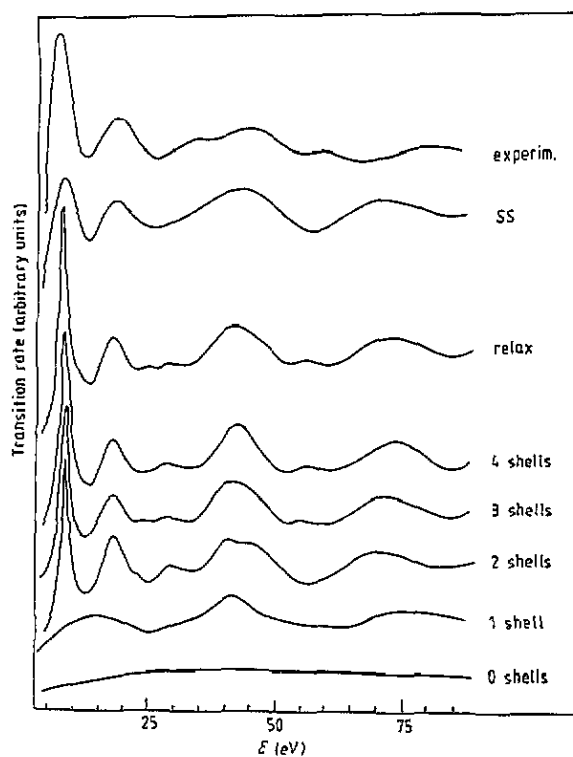


Figure 2. X-ray absorption coefficient above the Br K edge in NaBr calculated for clusters of different sizes, compared with that calculated by taking into account only single-scattering (SS) photoelectron pathways and in fully relaxed approximation (relax.), together with the experimental data (experim.).

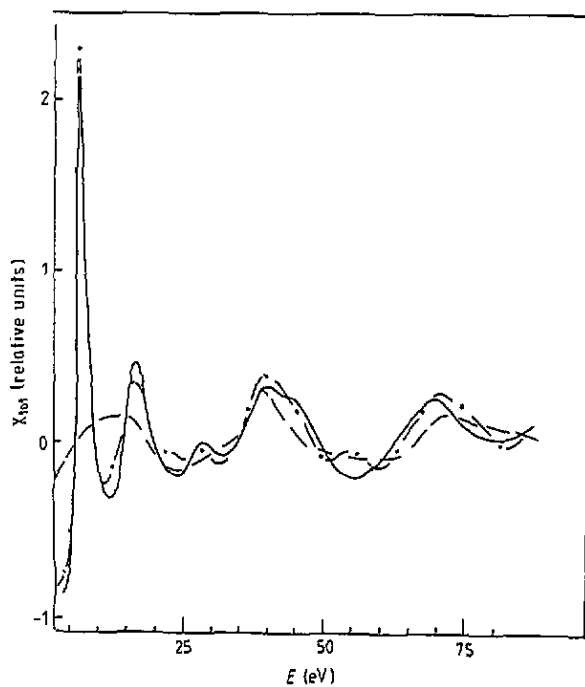


Figure 3. Total multiple-scattering term $X_{tot}(E)$ for clusters of one shell (---), two shells (—), and three shells (— · —) for the Br XANES in NaBr.

cluster of three shells (or even two shells) as shown in figure 4. The inclusion of the core hole relaxation effects does not change the spectrum much, but the relative intensities of the

first two maxima change and become closer to those of the experiment in the same manner as for NaBr.

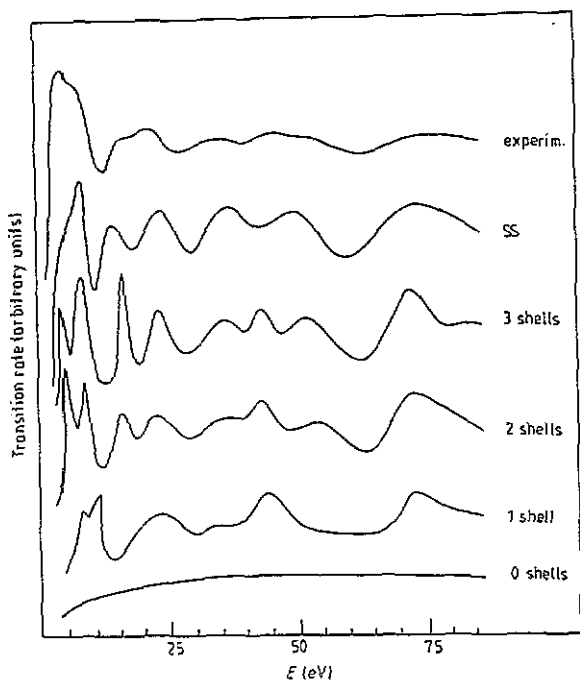


Figure 4. X-ray absorption coefficient above the Br K edge in KBr calculated for clusters of different sizes, compared with that calculated by taking into account only single-scattering (SS) photoelectron pathways, together with the experimental data.

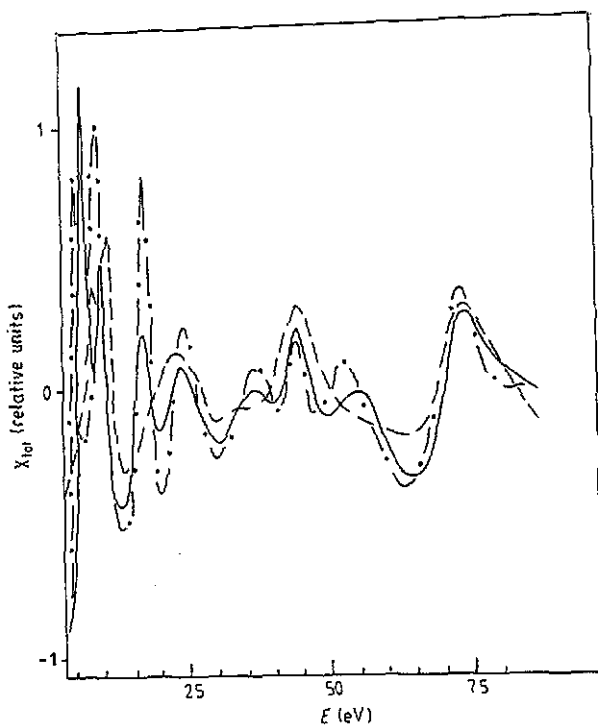


Figure 5. Total multiple-scattering term $X_{tot}(E)$ for clusters of one shell (---), two shells (—), and three shells (— · —) for the Br XANES in KBr.

The total multiple-scattering term changes with the cluster size, showing the importance of the second and even the third shell (figure 5). When one takes into account only single-scattering pathways of photoelectrons, there is only the possibility of describing the general features of the Br K XANES in KBr. The fine structure in the energy region from 30 to 60 eV above the edge and the lowest-energy part of the spectrum is not well reproduced (see figure 4).

3.3. RbCl

In the case of RbCl we investigate the cation (Rb) XANES in contrast with the cases of NaBr and KBr. For the NaCl-type crystal structure the arrangements of both kinds of atom are the same. The lattice constant for RbCl is nearly equal to that of KBr. However, in spite of these similarities the experimental XANES are quite different, especially in the near-edge energy region (see figure 1).

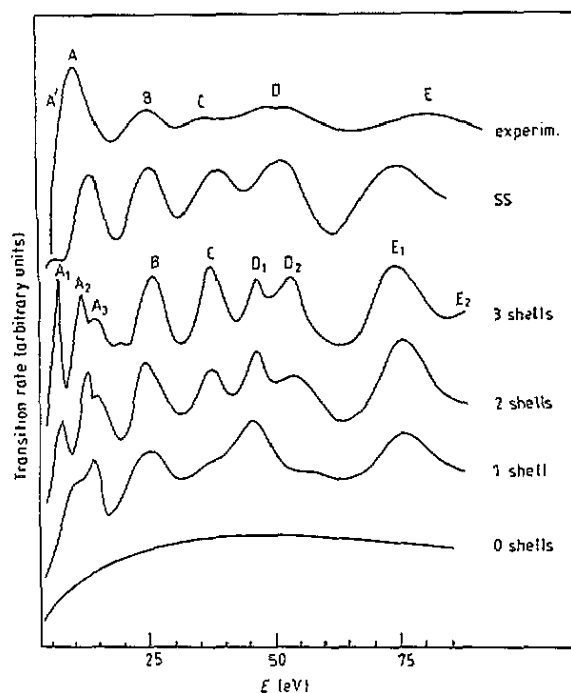


Figure 6. X-ray absorption coefficient above the Rb K edge in RbCl calculated for clusters of different sizes, compared with that calculated by taking into account only single-scattering (SS) photoelectron pathways, together with the experimental data.

As one can see from figure 6, the results of the full multiple-scattering calculation of the XANES, within an atomic cluster of three shells, describe all the features of the experimental data. When we do not take into account the broadening factors, our theoretical curves have sharp details that make it possible to analyse the origin of even small features in the experimental XANES. In figure 6 we show the results of calculations using the ground-state potential, i.e. corresponding to the density of Rb p states in the conduction bands. Here, as well as in the cases of the Br K XANES in NaBr and KBr, the spectra calculated for the ground state and the relaxed state differ negligibly.

From figure 6, one can conclude that in the lowest part of the RbCl conduction band there are two (or perhaps three) Rb p subbands and the low-energy shoulder A' on the

Rb XANES is due to the first of them. The two subbands A_1 and A_2 result in one maximum, A, in the experimental data because of the large value of the broadening factors that increase with increasing energy. As a result, two subbands that are theoretically well resolved (D_1 and D_2 , as well as E_1 and E_2) result in singlet peaks, D and E, in the experimental XANES.

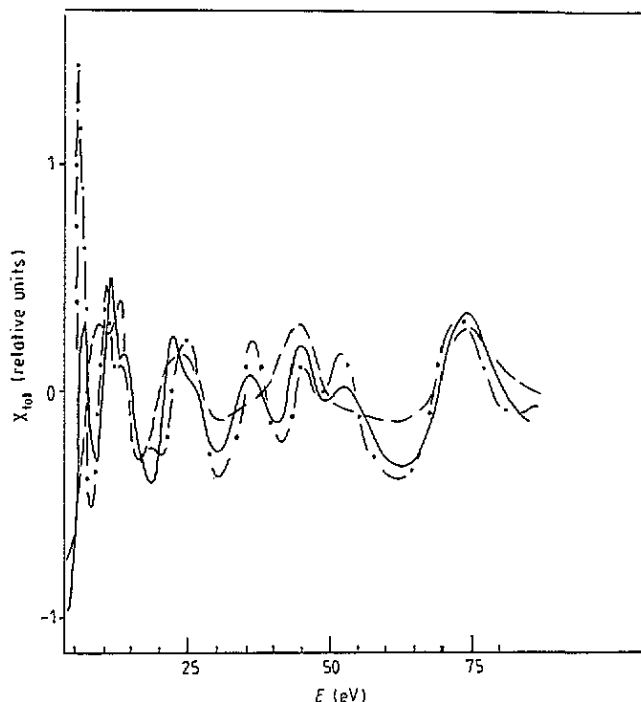


Figure 7. Total multiple-scattering term $\chi_{\text{tot}}(E)$ for clusters of one shell (---), two shells (—) and three shells (— · —) for the Rb XANES in RbCl.

In figure 7 we plot $\chi_{\text{tot}} = (\alpha - \alpha_0)/\alpha_0$, which is commonly used in EXAFS analysis. Here, α is the absorption coefficient for the cluster of atoms, and α_0 is the atomic absorption coefficient (which here is that calculated for the cluster containing no shells of surrounding atoms). The analysis of the total multiple-scattering term χ_{tot} versus the number of shells for the Rb K XANES in RbCl makes it clear that, in contrast with the Br XANES in AgBr [6] for RbCl, the contribution of the third shell to the Rb XANES is important. The single-scattering term in the case of RbCl allows one to describe generally the experimental XANES, but the position of the low-energy maximum A is not correct and there is no splitting of peak B at an energy of about 50 eV (see figure 6).

4. Conclusions

(1) Full multiple-scattering calculation results show a very good correspondence to the experimental XANESs of the ionic compounds NaBr, KBr and RbCl.

(2) The relaxation effects in the presence of the core hole during x-ray absorption do not strongly influence the K-edge XANESs of NaBr, KBr and RbCl. So, it is possible to derive information on the projected p density of states in the conduction bands of the investigated compounds directly from experimental XANESs.

(3) In contrast with AgBr, the Br K XANES in NaBr and KBr and Rb K XANES in RbCl are determined by the multiple scattering of photoelectrons in a large cluster containing about 30 atoms and having a radius of about 5 Å. Thus one can estimate the minimum size of a crystal fragment having the character of a solid for the compounds investigated.

(4) For an energy interval up to 80 eV above the main edge the single-scattering approximation describes the XANES data only in general and does not seem to be good enough for the Br K XANES in NaBr and KBr and the Rb K XANES in RbCl.

Acknowledgments

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