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Electronic structure of RbBr during the phase transition: x-ray absorption near-edge structure analysis

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Abstract. The x-ray absorption near-edge structure (XANES) at the Br and Rb K edges in the low-pressure (B1) and the high-pressure phase (B2) of RbBr has been analysed. We have used a full multiple-scattering method to investigate the structure of the RbBr conduction band. Theoretical K-edge absorption spectra obtained over a large energy interval were used to analyse the experimental data. The XANES is found to be determined by the multiple scattering of the photoelectron in a large cluster (30 or more atoms). For an energy interval up to 50 eV above the main edge, the single-scattering approximation is found to be less satisfactory. Comparative analysis of the XANES of the two different crystal phases makes it possible to examine the role of local symmetry and the characteristics of neighbouring atoms around the absorbing site as well as the conduction band of RbBr.

1. Introduction

Recently, x-ray absorption spectroscopy has become a powerful tool for the study of electronic energy bands and local crystal structures of ionic compounds [1]. Previous analyses of the x-ray absorption near-edge structures (XANESs) in NaCl-type alkali halides have been performed [2–5], but the most interesting results have been obtained while studying the phase transition in ionic compounds associated with both XANES [6–8] and EXAFS [9] regions. Recently, in a series of studies, the analysis of AgBr, KBr, NaBr and RbCl electronic structures using joint experimental and theoretical XANES studies have been made [10–13]. We have found that for RbCl and KBr the single-scattering model gives one the opportunity of describing only the main features of the absorption spectra within the 50 eV above the K edge. However, beyond that interval a single-scattering approach is quite adequate for the study of local structure changes during pressure-induced phase transitions in NaBr, KBr and RbCl. The joint analysis of the XANES data of the different crystallographic phases lets us determine the local symmetry around the absorbing atom and also investigate the conduction band structure and its changes during phase transitions. In the study we consider the electronic structure of RbBr in both the low-pressure (B1) and high-pressure phase (B2), in terms of an XANES multiple-scattering analysis of the experimental data.

2. Experiment and analysis

Experimental x-ray absorption spectra above both Rb and Br K-edges in the low-pressure phase (B1) and high-pressure phase (B2) were measured at the Stanford Synchrotron

Radiation Laboratory. We used zero pressure for the B1 phase and 0.8 GPa for the B2 phase. The experimental set-up for the high-pressure XAFS measurements has been described earlier [8].

The algorithm of the full multiple-scattering method used in this study has been described earlier [14–16]. For the calculation we used the NaCl-type crystal structure, with a lattice constant of 6.85 Å, for the low-pressure phase [17], and the CsCl-type structure, with a lattice constant of 4.05 Å, for the high-pressure phase [18]. The cluster of neighbour atoms around the central atom is divided into shells as reported in table 1. For the calculation of the phase shifts we used a crystal muffin-tin potential with touching spheres. The muffin-tin parameters that we obtained according to our procedure are reported in table 2. We used the muffin-tin approximation according to Mattheiss' [19] prescription with an exchange parameter equal to 1.0. Atomic charge densities were obtained with the help of the self-consistent Dirac–Slater method. In our calculation we included phase shifts with orbital momentum up to three for all types of atom. To compare the theoretical spectra obtained from projected density of states and dipole transition matrix element with experimental XANES, one must take into account the Fermi distribution function and all main factors that cause the broadening of the spectra: experimental resolution (0.5 eV), width of the K core hole level (2.52 eV for Br and 2.99 eV for Rb [20]) and final mean free path of the photoelectron [21]. The last factor is an energy-dependent function, specific for each compound and, according to our knowledge, not yet published for RbBr. We treated only the first two factors contributing to the imaginary part of the complex potential used for the calculation of the spectra to be compared with the experimental data in figures 2 and 3. The absence of the mean free path broadening term results in a sharper theoretical XANES than in the corresponding experimental data.

Table 1. Structure of the clusters around Rb site.

Shell number	B1 phase			B2 phase		
	Atom	Number of atoms	Radii sphere (Å)	Atom	Number of atoms	Radii sphere (Å)
1	Br	6	3.4270	Br	8	3.5074
2	Rb	12	4.8465	Rb	6	4.0500
3	Br	8	5.9351	Rb	12	5.7276
4	Rb	6	6.8540	Br	24	6.7162
5	Br	24	7.663	Rb	8	7.0148
6	Rb	24	8.3944	Rb	6	8.1000
7	Rb	12	9.6930	Br	24	8.8267
8	Br	30	10.2810	Rb	24	9.0560
9	Rb	24	10.8371	Br	24	9.9204

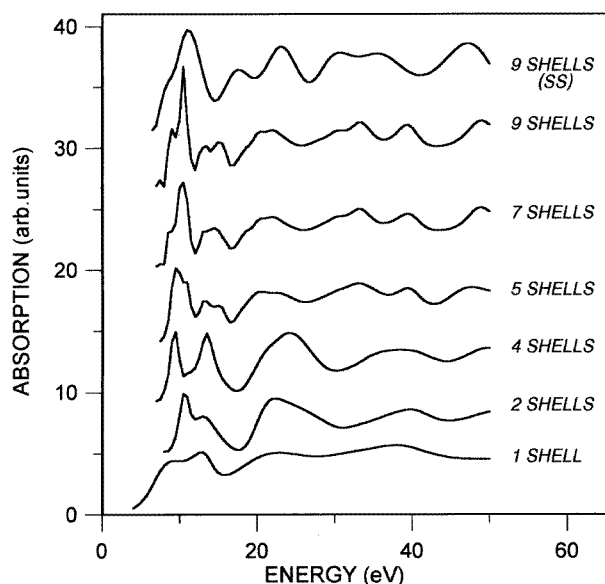
3. Discussion

The first step in the multiple-scattering analysis of the XANES data is the determination of the minimum size of the cluster of neighbour atoms around the absorbing atom, within which the scattering of the photoelectron can reproduce all the fine structure of the XANES (and of course the corresponding density of unoccupied states).

In figure 1 we report the results of the Rb K-edge XANES calculation for RbBr in the low-pressure phase by considering clusters of different sizes. In figure 1 we do not take

Table 2. The muffin-tin radii R_{mt} of the atoms included and the muffin-tin constants V_0 (if the origin of energy scale is at vacuum level).

Atom	B1 phase		B2 phase	
	R_{mt} (Å)	V_{mt} (eV)	R_{mt} (Å)	V_{mt} (eV)
Rb	1.6199	-9.8382	1.7675	-9.3486
Br	1.9916	-10.1932	1.7565	-9.2517

**Figure 1.** X-ray absorption coefficient above the Rb K edge in the B1 phase of RbBr calculated within clusters of different sizes. All spectra except those labelled SS are calculated in the full multiple-scattering approach. The single-scattering result (curve SS) has been obtained for a nine-shell cluster. All curves are presented without any broadening factors (see text).

into account any factors that cause the broadening of the spectra to see the changes which take place with the increasing cluster size. For the case of a cluster of one shell, where only six bromine atoms surround the central rubidium atom, the shape of the XANES is quite different from the experimental data. However, when adding the next shells of neighbour atoms the features of the spectrum become closer to the experimental features. On the other hand, we find the single-scattering approach that is widely used for x-ray absorption analysis to be unsatisfactory in the case of Rb K-edge XANES in the B1 phase of RbBr even for a large cluster of 147 atoms (see curve labelled as SS in figure 1). The same analysis of the theoretical data for all cases (both B1 and B2 phases and both Rb and Br K edges) causes one to conclude that within the single-scattering approximation it is not possible to describe the XANES data above both the Rb K edge and the Br K edge of RbBr in the energy interval up to 50 eV above the main edge. Large values of the mean free path of the low-energy photoelectron and high symmetry of crystal lattice seem to be the main reasons for the breakdown of the single-scattering approach here.

The analysis of the results presented in figure 1 let us conclude that the Rb K-edge XANES in RbBr is a result of a multiple scattering of the excited photoelectron within a sufficiently large cluster. Such a cluster includes both types of atom and the photoelectron on its pathways is scattered on both types of atom. In quantum chemistry language, one can say that the wavefunction of the electron in the conduction band of RbBr includes some degree of covalency. In other words, there exists a small hybridization of Rb p and Br p states. Indeed, in the B1 phase of RbBr the first two sharp low-energy peaks of the Rb XANES correspond in energy to the first two low-energy shoulders of the Br XANES (table 3). This is another piece of evidence for such hybridization. Because of the large value of the core hole lifetime broadening for Rb (2.99 eV) and Br (2.52 eV) there is a lack of obvious structure in the experimental Rb K XANES and Br K XANES in the B1 phase. So we cannot find the precise position of the low-energy shoulder (about 8 eV) for the Rb K XANES (table 3). One can see the analogy in the B2 phase XANES. The first Rb peak for the B2 phase (theory, 10 eV; experiment, 9.5 eV) corresponds to the shoulder on the left-hand part of the Br XANES (theory, 10 eV; experiment, 9.5 eV). This is assumed to be evidence for the hybridization of Rb p and Br p states in the B2 phase.

Table 3. The energy positions of the first two shoulders.

N of shoulder	Energy (eV)			
	Rb		Br	
	Theory	Experiment	Theory	Experiment
1	10	8	10	9
2	11	10.5	12	11.5

The Br and Rb K edges XANES in RbBr reflect the distribution of unoccupied p states in the conduction band of RbBr. According to the present results, these XANESs are determined by the multiple scattering of the photoelectron in the cluster of a large size (containing 57 atoms and having a radius of about 8 Å). Thus one can estimate the minimum size of a crystal fragment having all the main characteristics of the solid RbBr energy band structure.

In figure 2 we reported the theoretical XANES together with experimental data for the Rb K edge in both the B1 and B2 phases of RbBr. The energy scale of the experimental data has been aligned with the theoretical scale by matching the energy position of the first (main) maximum. All spectra are normalized (i.e. the absorption coefficient is in the relative units of atomic absorption, α_0 at high energy—about 40 eV above the edge). Thus, if one needs to obtain absolute values of the absorption coefficient, it is possible to do so by multiplying these normalized data by the corresponding value of the atomic absorption.

There are large changes in the XANES on going from the B1 to the B2 phase. This demonstrates the very high sensitivity of XANES to the changes in the electronic structure of the conduction band of RbBr during the phase transition. As one can see, we succeed in obtaining a qualitative agreement in the changes in XANES shapes of the theoretical full multiple-scattering results and in the experimental data during the phase transition. We plot the theoretical and experimental spectra separately to present qualitative changes which take place during the phase transition. The same comparison for the data above the Br K-edge XANES in both the B1 and the B2 phases of RbBr (see figure 3) also

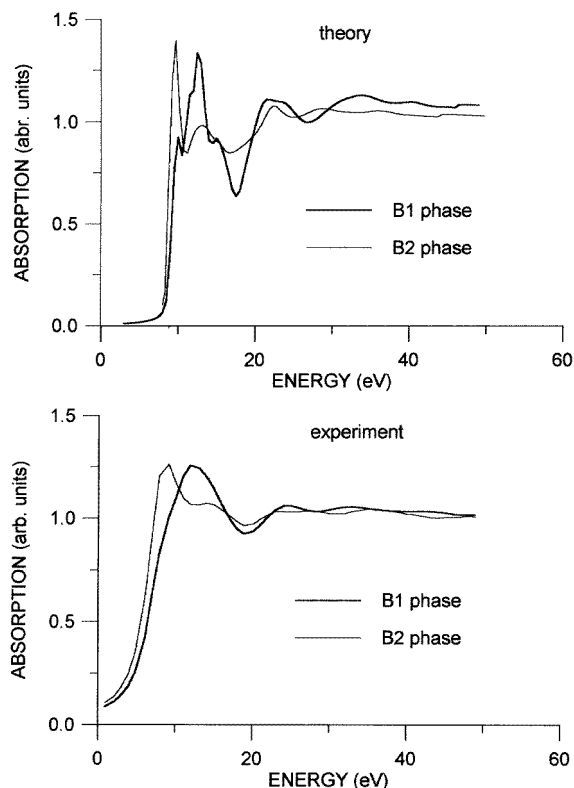


Figure 2. Comparison of the theoretical XANES and experimental data for the Rb K edge in both the B1 and the B2 phases of RbBr. All spectra are normalized to the value of absorption at high energy (about 40 eV above the edge). The energy scale of the experimental data has been aligned to the theoretical data by matching the positions of the first (main) maximum.

shows agreement. We note that an alternative (intermediate between full multiple-scattering and single-scattering) approach used in [7], exploring only the main multiple-scattering pathways of the photoelectron [22], results in worse agreement with experiment. For example, it does not reproduce correctly the XANES shape in the first 10 eV above the edge.

4. Conclusions

We have shown the Rb and Br K-edge XANESs to be very sensitive to the fine details in the electron density of unoccupied states. Thus XANES is a useful tool for the study of changes in the electronic structure of solids which undergo phase transitions. The full multiple-scattering approach is found to be successful in analysing experimental Br and Rb K-edge XANESs in RbBr, while the single-scattering approximation is not valid in this case. We suggest unoccupied bromine and rubidium p states to be slightly hybridized in the conduction band of RbBr.

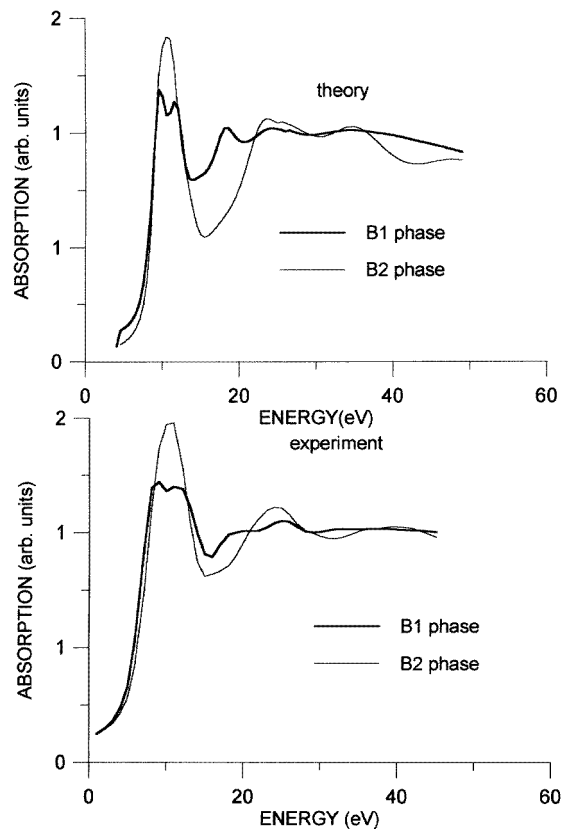


Figure 3. Comparison of the theoretical XANES and experimental data for the Br K edge in both the B1 and the B2 phases of RbBr. All spectra are normalized to the value of absorption at high energy (about 40 eV above the edge). The energy scale of the experimental data has been aligned to the theoretical data by matching the positions of the first (main) maximum.

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