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Conduction bands and invariant energy gaps in alkali bromides

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Abstract. Electronic structure calculations of the alkali bromides LiBr, NaBr, KBr, RbBr and CsBr are reported. It is shown that the conduction band has primarily bromine character. The size of the band gaps of bromides and alkali halides in general is reinterpreted.

PACS. 71.20.Nr Semiconductor compounds

Alkali halides are model systems in the sense that they belong to the most simple ionic two-element compounds. They have the structural formula RX where R denotes an alkali Li, Na, K, Rb or Cs and X an halogen F, Cl, Br or I. In general the alkali halides have the NaCl structure though cesium halides, except CsF, have the simple cubic CsCl structure [1].

In compound formation the s-electron of the alkali is transferred to the halogen atom, where it fills the p-shell. From a bandstructure point of view this results in a completely filled valence band of halogen p-character with a gap between these states and the unoccupied conduction band. All alkali halides are insulators with gaps ranging from about 6 eV for iodides up to 10-14 eV for fluorides [2].

This article focuses on the character of the lowest conduction band. The common picture, found in almost any textbook, is that the wave functions of the conduction band are primarily composed of cation states, although the earliest work, back in 1936, emphasizes the possible importance of anion states [3]. In this article the electronic structure of some alkali halides is studied and it will be shown that the conduction band has primarily anionic character.

The electronic structure of the prototype compounds LiBr, NaBr, KBr, RbBr and CsBr (structural data from Ref. [1]) is calculated. The results and conclusions of this article are valid for all alkali halides. The reason we concentrate on the bromides is to avoid unnecessary repetition.

The calculations were performed with the LSW method [4] and with the full potential LAPW method [5]. Both methods make use of the Local Density Approximation (LDA). It is known that the spurious self-interaction, inherent to LDA, tends to shift occupied states to higher energies, leading to band gaps which are usually too small compared with experimental values. Also the exchange and correlation potential in LDA lacks the required discontinuity at the Fermi energy. The first order effect is a rigid shift of the conduction band with respect to the
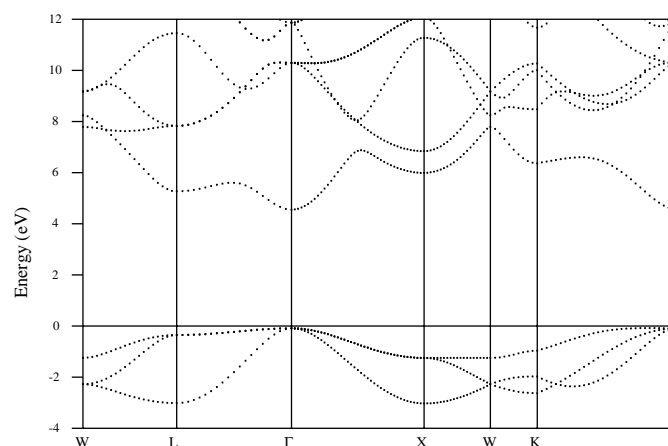

Fig. 1. The bandstructure of LiBr, calculated with the full potential LAPW method.

valence band, while changes in the topology of the conduction band are much less pronounced [6,7]. Therefore an analysis of these bands based on LDA calculations is justified.

First we will discuss the electronic structure of LiBr, calculated with the full potential LAPW method. This method is more reliable because no approximations to the shape of the potential are made. Approximately 300 plane waves were used, to obtain numerical convergence of the basis set. To describe the semi-core Li-$1s$, Br-$3p$, Br-$4s$ and Br-$3d$ states as accurately as possible the basis set was extended with local orbitals. The Brillouin zone integration was performed using the modified tetrahedron method with a special mesh of 104 k-points in the IBZ. The sphere radii of Li and Br were 1.5 respectively 2.5 atomic units.

The bandstructure of LiBr is shown in Figure 1. The zero of energy is defined to be the top of the valence band. The three bands just below zero energy are the Br-$4p$ bands. The Br-$4s$ band, not shown in the Figure, lies at 13 eV below zero energy. The gap between the top of
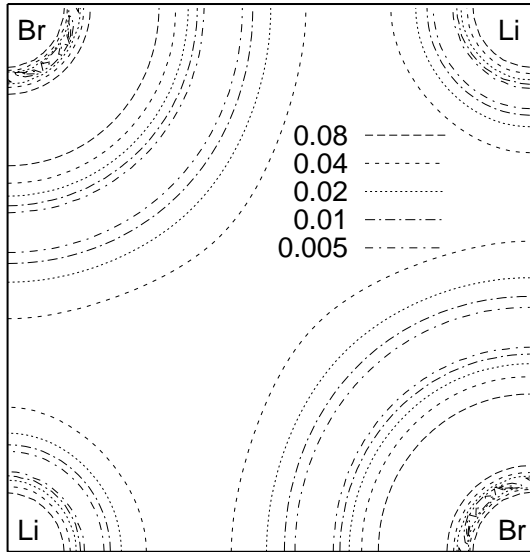
Fig. 2. Contour plot of the charge density (in atomic units) of the lowest conduction band at the Γ-point in the (001)-plane of LiBr.

Fig. 3. LSW bandstructure of LiBr. Br-5s Hankel functions were included in the basis set.

Fig. 4. LSW bandstructure of LiBr. Br-5s Hankel functions were not included in the basis set.

the valence band and the bottom of the conduction band, which both lie at the Γ-point, is 4.6 eV. Above the lowest conduction band lies a complex of bands which is threefold degenerated at the Γ-point at 10.4 eV. The bandstructure is in agreement with previous calculations [8].

Usually the lowest conduction band of alkali halides is described as being derived from cation s states. The charge density related to this band is however not localized at the cations. According to Figure 2, which shows a contour plot of the charge density of the lowest conduction band at the Γ-point, the charge is even predominantly centered at the anions. It is therefore not justified to attribute this band to the cations.

The analysis on the basis of the charge density is somewhat disturbed by the delocalized character of the conduction band. In order to facilitate an analysis in terms of atomic-like basis functions and to allow a study of their influence on the conduction band we repeat the calculations with the LSW method. It is important to select these basis functions with care. The Br-4s electrons have an energy quite far below the zero of energy and are almost completely localized at the Br sites, while corrections to the LDA approach will tend to localize them even further. The Br-5s states are unoccupied but it is not known *a priori* how far they lie above the valence bands. Since the subject of this study is the conduction band, it is important to allow enough variational degrees of freedom in this energy range. For these reasons the Br-4s electrons were treated as core states, while the Br-5s states were explicitly included as valence states.

The LSW bandstructure of LiBr (see Fig. 3) is similar to the LAPW bandstructure in Figure 1. The band gap is again 4.6 eV and also the valence band width is the same. Small deviations for higher unoccupied states are visible but the global structure is unaffected. This assures the reliability of the atomic sphere approximation and justifies
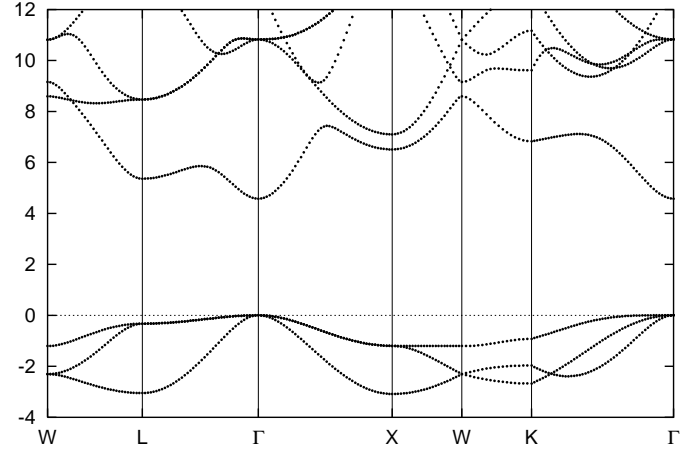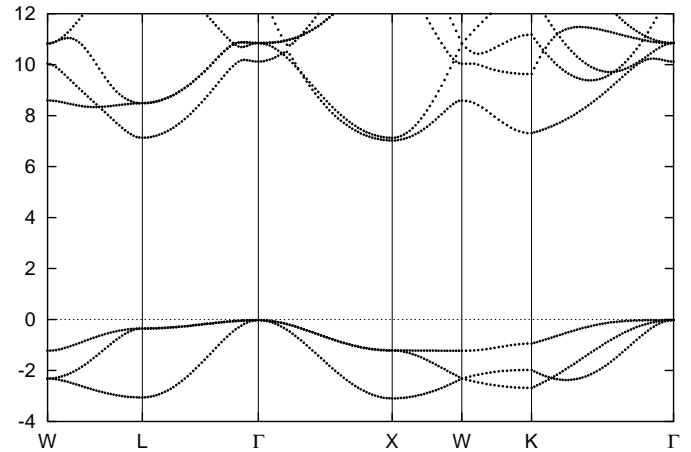
the assumption that the error in the treatment of the 4s electrons as core states is negligible.

To stress the importance of including Br-5s Hankel functions in the basis set, we also calculated the bandstructure of LiBr omitting the 5s states (see Fig. 4). The difference with the bandstructures in Figures 1 and 3 is large. The valence band is correctly reproduced but the shape of the conduction band is fundamentally different. The band gap is indirect now and has increased to 7.2 eV, the direct gap at Γ even being 10.1 eV. The fact that the exclusion of Br-5s Hankel functions leads to an incorrect bandstructure is evidence that the 5s states are very important in the description of the conduction band.

Another illustration that the lowest conduction band is the Br-5s band is the bandstructure of a fcc lattice of Br$^-$ ions. This can be viewed as LiBr with the Li$^+$ ions taken out altogether. The bandstructure (Fig. 5) shows a striking resemblance to the LAPW bandstructure. The width of the lowest conduction band is larger, the valence band width is a little bit larger and the band gap is smaller than for LiBr. However, the topology of the lowest conduction band is essentially the same. In fact even the bands directly above this band, mainly formed by Br-4d (t_{2g})
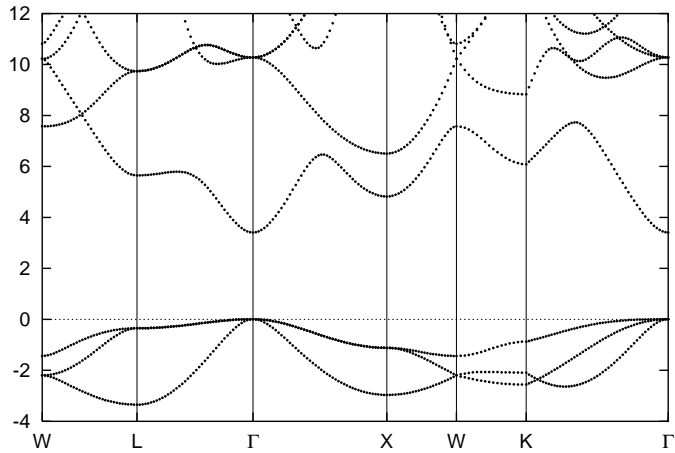
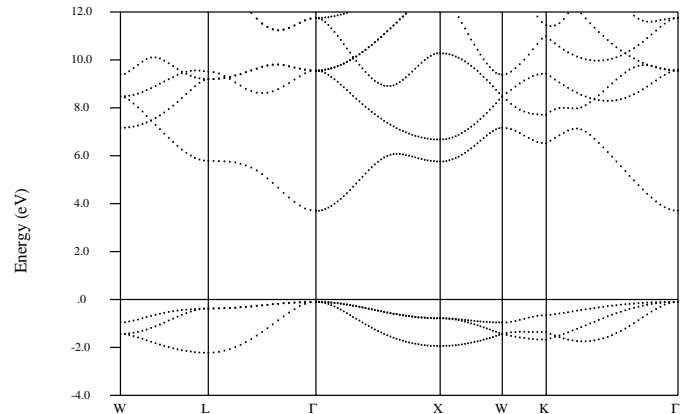**Fig. 5.** The bandstructure of a fcc lattice of Br$^-$ ions with the same lattice parameter as LiBr.
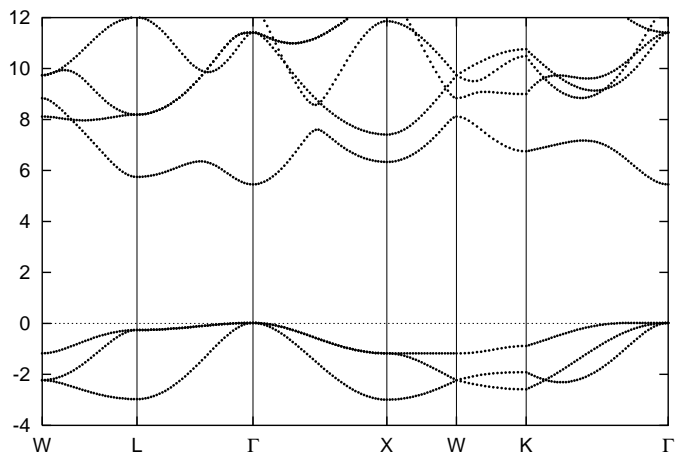
Fig. 6. LSW bandstructure of LiBr. The basis set excluded Br-5s Hankel functions, but was extended with Hankel functions centered at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ and $\frac{3}{4}\frac{1}{4}\frac{1}{4}$.

Fig. 7. The bandstructure of NaBr.

Fig. 8. The bandstructure of KBr.

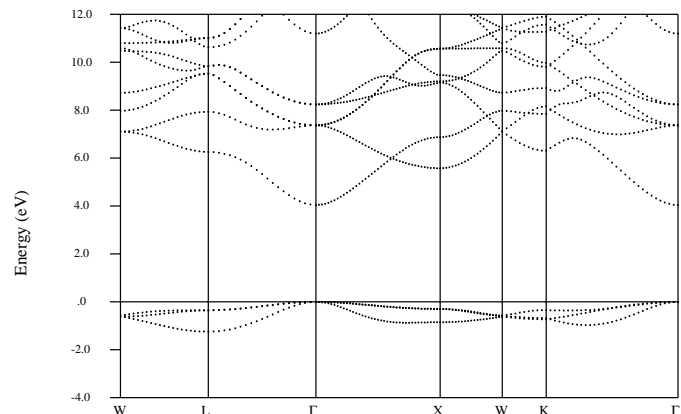**Fig. 9.** The bandstructure of RbBr.

states, look very similar. This leads to the conclusion that all the bands shown in Figure 1 are primarily derived from Br states, *i.e.* going from low to high energies successively Br-4p, Br-5s and Br-4d states. The Li-2s band in LiBr lies in fact above 15 eV. The role of the cation is therefore merely to stabilize the bromide in its existing crystal structure.

Adding empty spheres introduces extra variational degrees of freedom, which could qualitatively enhance the bandstructure. Figure 6 shows the bandstructure of LiBr, calculated with a basis set excluding Br-5s Hankel functions but including 1s, 2p Hankel functions centered at Wyckoff position 2c. It shows again some resemblance to the LAPW bandstructure, though the band gap of 5.4 eV is almost 20% larger. The reason that the Br-5s band can be qualitatively well described by basis functions at other sites is because the 5s states are very delocalized.
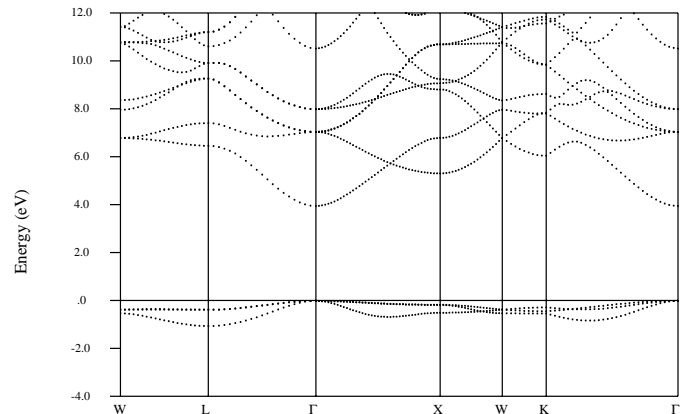
For completeness the bandstructures of NaBr, KBr, RbBr and CsBr are also calculated (see Figs. 7–10). The conclusions for LiBr also hold for NaBr, *i.e.* the lowest conduction bands are essentially formed by Br-5s and Br-4d states. The similarity between the bandstructures of LiBr and NaBr is due to the fact that they both correspond to a fcc Br$^-$ bandstructure, the main difference being the different lattice parameter.

The lowest conduction band of KBr shows some minor differences with those of LiBr and NaBr, as is most pronounced in the direction ΓX. The reason is that K-3d states now play a role in the conduction band. The d-bands at 7-10 eV above zero cannot be assigned to Br alone but are formed by hybridization of Br-4d and K-3d
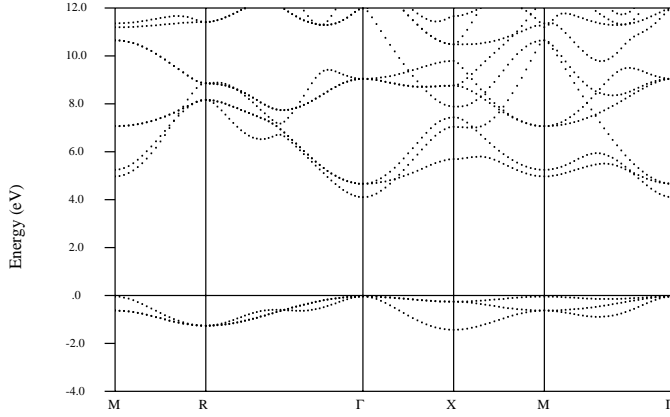
Fig. 10. The bandstructure of CsBr.

Table 1. Calculated and experimental band gaps and valence band widths in eV.

	E_g (calc.)	E_g (exp.) [9]	E_w (calc.)	E_w (exp.) [2]
LiBr	4.6	7.6	2.9	3.0
NaBr	3.8	7.1	2.1	2.0
KBr	4.0	7.4	1.2	1.4
RbBr	4.0	7.2	1.1	1.6
CsBr	4.1	7.3	1.4	1.6

states. However, the lowest conduction band has still its origin in the Br-5s state. The bandstructure of RbBr is resemblant to KBr, where the differences again are mainly caused by the different lattice parameters.

CsBr forms in the CsCl crystal structure and shows therefore a different bandstructure. However, also in this case the lowest conduction bands are the Br-5s band and hybridized d-bands, the lowest unoccupied state at Γ having mainly Br-5s character.

Since both the valence band and the conduction band are formed by Br states, the band gap of the alkali bromides is expected to be independent of the metal. Table 1 shows calculated and experimental band gaps and band widths of the alkali bromides. The experimental values were determined by photoemission and inverse photoemission measurements. We use these data for comparison in order to avoid complications due to excitons. The experimental band gaps are larger than the calculated ones of course, but the expected independence of the band gap on the metal is observed in both calculated and experimental values indeed. The small dependence of the band gap results from 1) the influence of the cation on the lattice parameter and 2) the influence of the hybridization of the conduction band states with cation s- and d-states.

The valence band width is almost completely determined by the anion-anion interaction, as is shown by the fictitious fcc Br$^-$ bandstructure. The differences of the valence band widths of the alkali bromides are therefore mainly due to the differences in lattice parameters. The larger the lattice parameter, the smaller is the overlap between wave functions centered at different atoms, and the smaller the band width.

Finally, we note that the anion character of the conduction band described here should not be confused with covalency. Covalency, in *e.g.* III-V semiconductors, leads to an anion character of the conduction band *on the expense of the anion character of the valence band*. The alkali halides are fundamentally different in the sense that the lowest unoccupied unhybridized states are of anion character, unlike the III-V semiconductors. Consequently,

III-V semiconductors *do* show a strong dependence of the size of the band gap on the metal (*e.g.* AlAs: 3.099 eV, GaAs: 1.519 eV, InAs: 0.416 eV [10]).

In conclusion, we showed that the conduction bands of alkali bromides are primarily derived from atomic Br-states. As a first consequence, calculations on halides, based upon methods employing atomic-like basis functions like LSW, ASW and LCAO, should take unoccupied halogen s- and d-states into account for a proper description of the conduction band. Secondly, interpretations of experiments which consider excitations of electrons from the valence band to the conduction band should be based upon the fact that the top of the valence band and the bottom of the conduction band both have primarily anionic character.

References

1. R.W.G. Wyckoff, *Crystal Structures* (New York, London, Sydney: John Wiley & Sons, 1963).
2. R.T. Poole, J. Liesegang, R.C.G. Leckey, J.G. Jenkin, Phys. Rev. B **11**, 5190 (1975).
3. J.C. Slater, W. Shockley, Phys. Rev. **50**, 705 (1936).
4. H. Van Leuken, A. Lodder, M.T. Czyżyk, F. Springelkamp, R.A. De Groot, Phys. Rev. B **41**, 5613 (1990).
5. P. Blaha, K. Schwarz, P. Dufek, R. Augustyn, *WIEN95, Technical University of Vienna 1995* (Improved and updated Unix version of the original copy-righted WIEN-code, which was published by P. Blaha, K. Schwarz, P. Sorantin, S.B. Trickey, Comput. Phys. Commun. **59**, 399 (1990)).
6. R. Hott, Phys. Rev. B **44**, 1057 (1991).
7. M. Rohlfing, P. Krüger, J. Pollmann, Phys. Rev. B **48**, 17791 (1993).
8. W.Y. Ching, F. Gan, M.-Z. Huang, Phys. Rev. B **52**, 1596 (1995), and references therein.
9. F.C. Brown, C. Gähwiller, H. Fujita, A.B. Kunz, W. Scheifley, N. Carrera, Phys. Rev. B **2**, 2126 (1970).
10. D.J. Arent, Phys. Rev. B **41**, 9843 (1990).