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# Conduction Band of the Photographic Compound AgCl

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Electronic structure calculations on the photographic compound AgCl are reported. It is shown that the conduction band has a large Cl-4s character, contrary to the common picture of the conduction band being derived from Ag-5s states. Possible consequences for the photographic process are discussed.

## I. Introduction

The photographic process has been studied for more than a century now but is still a subject of active research. The process takes place in two steps. When a photographic film is exposed to light, a latent image is formed. The latent image can be converted into a visible image by a photographic developer.

The main component of a photographic film is a silver halide crystal. Silver halide crystals usually have many defects like vacancies, impurities, and interstitial ions, especially in small crystallites. A photon with an energy exceeding the band gap can promote an electron to the conduction band of the halide. The electron is able to recombine with an interstitial $Ag^+$ ion to produce a Ag atom. When more photons are absorbed at the same spot, a small cluster of silver metal is formed. A photographic film contains many small crystallites. Crystallites which have absorbed enough photons can be further reduced to silver metal by a developer. The small silver clusters catalyse the reduction process. A thorough review on the photographic process is given by Hamilton.[1]

Because of the microscopic level at which the formation of the latent image and the development to a visible image takes place, the process is still not completely understood. One of the questions is why there is a minimum size requirement to silver clusters to be able to catalyze further reduction to silver metal. A single interstitial Ag atom is not stable and will dissociate shortly after the photoformation. $Ag_2$ clusters are stable but are not developable. Only clusters containing at least three or four Ag atoms can act as catalysts.

An important property of the silver halide crystals is the electronic structure. AgCl and AgBr, the most important halides in photography, are insulators with experimentally determined band gaps of 3.2 and 2.7 eV, respectively. Several electronic structure calculations on AgCl and AgBr have been reported.[2,3] They showed that the valence band consists of strongly hybridized Ag-4d and Cl-3p or Br-4p wave functions with an energy maximum at the symmetry point $L$ in the Brillouin zone (BZ). The conduction band minimum is at the Γ-point, leading to an indirect band gap. The conduction band is commonly seen to be derived from Ag-5s states.[1]

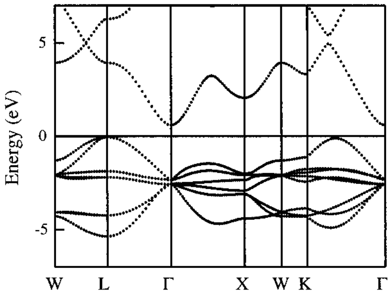

**Figure 1.** Band structure of AgCl along some high-symmetry lines in the Brillouin zone, calculated with the LAPW method.

The latter appears not to be true. We calculated the electronic structure of AgCl and we will show that the conduction band has in fact a large anion character. We will discuss the possible consequences of this finding for the understanding of the photographic process.

## II. Calculational Method

Calculations were performed with the full potential linearized augmented plane wave (LAPW) method.[4] In this method no approximations are made to the shape of the potential. The LAPW method is based upon density functional theory with the exchange−correlation energy treated within the local density approximation (LDA). Experimental equilibrium unit cell parameters are used.[5] The basis set contained approximately 450 plane waves and was improved by including local orbitals for good description of the semicore Ag-4p and Cl-3s states. Sphere radii of 2.0 and 2.5 au were used for Ag and Cl, respectively. The BZ integration was performed using the modified tetrahedron method on a special mesh of 47 k-points in the irreducible part of the BZ.

In order to facilitate an analysis of the conduction band in terms of atomic states, the calculations were repeated with the localized spherical wave (LSW) method.[6] This method is based upon LDA as well. The basis set was formed by spherical Hankel functions, augmented in atom-centered spheres. Sphere radii of 2.505 and 3.757 au for Ag and Cl, respectively, were used. The spheres were space filling, and the crystal potential was represented by a Spherical Hankel functions with $nl$ = 5s, 4d, 5p for Ag and 4s, 3d, 3p for Cl were taken into account.

## III. Results

The band structure of AgCl, calculated with the LAPW method, is shown in Figure 1. The zero of energy is taken to be the top of the valence band. The lower three bands can be identified as the Cl-3p bands while the remaining five valence

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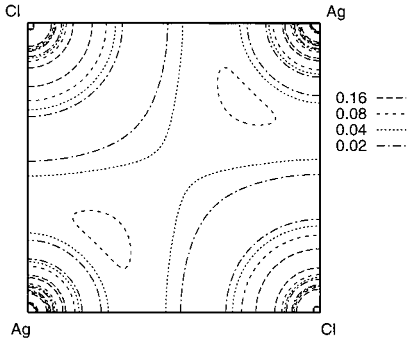

**Figure 2.** Contour plot of the charge density (in atomic units) in the (001)-plane of AgCl of the wave function at the bottom of the conduction band.

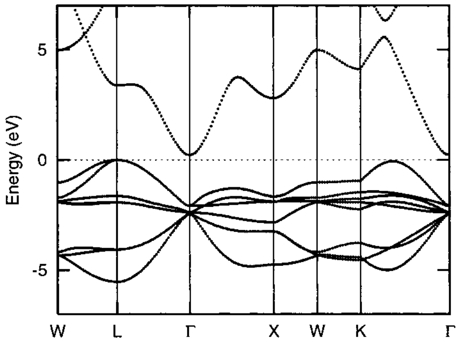

**Figure 3.** Band structure of AgCl, calculated with the LSW method.

bands between −2.5 and 0 eV are primarily derived from Ag-4d states. The Ag-4d and Cl-3p states are, however, strongly hybridized. The Cl-3s band, not shown in the figure, lies at −15 eV. The indirect gap between the top of the valence band and the bottom of the conduction band is 0.56 eV.

The lowest conduction band is wide, approximately 5 eV, and is commonly associated with Ag-5s states.[1] The states in this band are however very delocalized. Figure 2 shows a contour plot of the charge density in the (001)-plane of AgCl of the wave function at the bottom of the conduction band. The integrated charges within the atomic spheres are 0.15 electrons in each Ag sphere and 0.18 electrons in the Cl spheres. The remaining charge per unit cell of this state (0.67 electrons) is distributed in the interstitial space. It should be mentioned that these charges depend in some extent on the sphere radii chosen in the calculation. It is, however, clear that the wave function is not confined to the Ag atom.

In order to analyze which atomic states are the origin of this band, the calculation is repeated with the LSW method (see Figure 3). Besides minor details in both the valence band and conduction band, almost no differences with the band structure in Figure 1 are visible. The band gap is 0.23 eV, but the difference between this value and the LAPW gap is of the same order as differences with gaps calculated by other methods.[2] It is known that within the ASA approximation the band structure of semiconductors is sensitive to the choice of the sphere radii. The band structures of Figures 1 and 3 are, however, very similar. This assures the reliability of the ASA approximation and justifies a further analysis of the conduction band based on the LSW method.

The importance of Cl-4s states for the conduction band is illustrated by Figure 4, which shows the band structure of AgCl, calculated with the LSW method, but with the Cl-4s states omitted. The valence bands, with primarily Ag-4d and Cl-3p character, are nearly the same as those in Figure 3. The topology of the conduction band is however completely destroyed and the size of the gap has increased enormously.

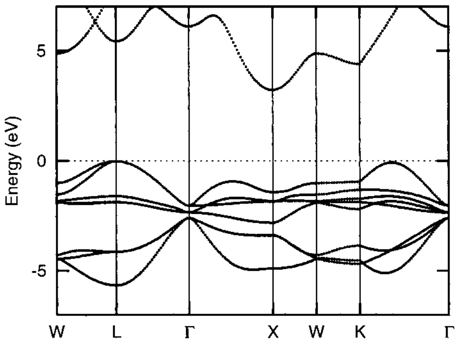

**Figure 4.** Band structure of AgCl, without Cl-4s states.

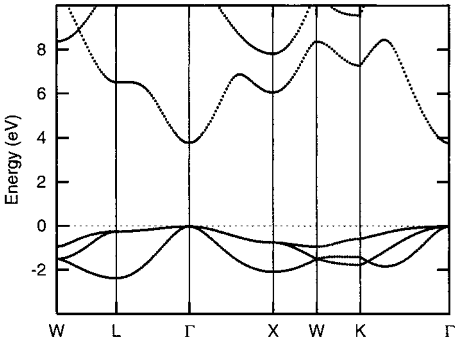

**Figure 5.** Band structure of hypothetical fcc Cl$^-$.

Another illustration of the importance of Cl-4s states for the conduction band is the band structure of hypothetical fcc Cl$^-$, i.e., AgCl with the Ag$^+$ ions removed altogether (see Figure 5). The three Cl-3p valence bands are fully occupied. The topology of these bands is very similar to the lower three valence bands in Figure 3. The conduction band, derived from Cl-4s states, shows a striking resemblance to the conduction band of AgCl. The band gap is 3.8 eV, somewhat larger than the gap of 2.7 eV between the Cl-3p band at the Γ-point and the bottom of the conduction band in AgCl. The difference is primarily caused by the larger widths of the Cl-3p bands and the conduction band in AgCl, due to the hybridization with Ag states.

For completeness, we also calculated the band structure of hypothetical Ag$^+$, i.e., AgCl with the Cl$^-$ ions omitted. The topology of the Ag-5s band shows much less resemblance to the conduction band of AgCl in fcc Ag$^+$ than the Cl-4s band in fcc Cl$^-$.

## IV. Discussion

The results of the calculations with respect to the valence band and the size of the band gap should be considered with care, because of LDA. The exchange−correlation energy in LDA lacks the required discontinuity at the Fermi energy and LDA suffers from the spurious self-interaction. The main effect of the self-interaction is a positioning of the valence bands at higher energies. This effect is quantitatively different for the Ag-4d states respectively the Cl-3p states. Therefore, binding energies are not well predicted by LDA.[2,7] Furthermore, since the valence band energies are too high, the calculated size of the band gap is much smaller than the experimental value, a common artifact of the LDA approximation.

The application of LDA, however, does not have important consequences for the conduction band. This band is unoccupied and therefore does not suffer from the self-interaction. It has been shown that in other semiconductors the topology and the wave function character of the conduction band is not much altered by improvements on LDA.[8] Recently it has been shown that the application of self-interaction in ab initio electronic structure calculations on AgCl leads to a lowering of the Ag-4d-Cl-3p valence band states and to a band gap which agrees well with the experimental value, while the conduction band remains unaffected.[3]

A more fundamental improvement on LDA is possible in the application of the GW methods, which generally gives the correct bandgap. In a recent paper it was shown that the electron of the electron−hole pair of the lowest energy exciton in the alkali halide LiF is primarily confined to the fluorine ions.[10] The lowest energy exciton is generally composed of conduction band states. LDA calculations on the alkali halides showed a conduction band with predominant anion character.[11] Hence, in the case of the alkali halides, the LDA approximation and the GW approximation completely agree with respect to the character of the conduction band. The most important difference between silver halides and alkali halides is the valence band, due to the presence of Ag-4d states in the silver halides. The conduction band of the silver halides however is very similar to the conduction band of the alkali halides.[12] It is, therefore, expected that the GW approximation, or any other improvement on LDA, will lead to the same conclusions on the conduction band of AgCl.

Taking these considerations into account, an analysis of the conduction band on the basis of LDA calculations is justified. It is clear from the results of the calculations, presented in the previous section, that the conduction band has a large Cl-4s character. It is therefore not justified, to say the least, to see the conduction band as being derived from Ag-5s states. In fact, since this band has a very delocalized, free electron-like character, it is not appropriate to associate this band with atomic states. However, if one insists on doing so, on the basis of charge density at the bottom of the conduction band and the bandstructure of hypothetical $Cl^-$, the conduction band should rather be associated with Cl-4s states.

Bennebroek et al. have reported experimental evidence of the chlorine character of the conduction band.[9] They determined, by ENDOR measurements, the wave function character of the intrinsic shallow electron center. A shallowly trapped electron strongly resembles a conduction electron, and it was found that it has indeed a large Cl character.

The origin of the conduction band in silver halides could have consequences for the understanding of the photographic process. The common picture is that the conduction band of the silver halides is derived from Ag-5s states and that the 5s level of an interstitial Ag ion lies below the bottom of the conduction band because of the smaller Madelung potential at interstitial positions. The highest occupied states of clusters of Ag atoms have even lower energies, while the Fermi energy of bulk silver metal lies 1.2−1.5 eV below the conduction band of the halides. It cannot be excluded that, because of the anion character of the conduction band, the 5s level of a single interstitial ion lies in fact above the bottom of the conduction band and that only clusters of more than one Ag atom have an highest occupied level below the conduction band. This would serve a possible explanation why single interstitial Ag atoms are not stable and why the minimum size of a silver metal cluster to be stable and developable is three or four atoms.

To our knowledge, two electronic structure calculations on interstitial $Ag^+$ ions in AgCl, based on the CNDO (complete neglect of differential overlap) method[13] and the DV-Xα method,[14] respectively, have been reported: in both references it is claimed that the 5s level of interstitial $Ag^+$ ions lies below the conduction band. However, in both calculations the Cl-4s states were neglected.

It is rather difficult to test the hypothesis that the 5s level of an interstitial $Ag^+$ ion lies above the bottom of the conduction band with calculations based on LDA, because of the underestimation of the band gap. Elaborate electronic structure calculations, going beyond LDA and taking Cl 4s states into account, are therefore highly desirable. It is suggested that the conduction band of AgCl, as calculated with self-interaction corrections to LDA included,[3] are thoroughly analyzed. Further, GW calculations, along the line of ref 10, could give conclusive theoretical evidence of the chlorine character of the conduction band.

Experimentally, the chlorine character of the conduction band could be directly measured by Cl *L* edge (2*p*) X-ray absorption spectroscopy, complementing the ENDOR measurements.

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