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Electronic structure of AgF, AgCl, and AgBr

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Self-consistent Hartree-Fock calculations have been performed for AgF, AgCl, and AgBr in the fcc phase. Correlation and relaxation corrections have been included and are essential to permit band-gap predictions. Qualitatively these results agree well with other calculations for these systems. There are found to be some quantitative differences which may be significant. Experiments to probe these differences are suggested. Although relativistic corrections are absent in these calculations, the effect of such corrections on the nonrelativistic bands is discussed within the confines of a simple model. Extensive comparisons are made to recent photoemission determination of the occupied valence bands for AgCl and AgBr.

I. INTRODUCTION

The silver halides have a fair number of properties in common with the alkali halides. They are, therefore, often considered in the category of I-VII compounds. The trio considered here—AgF, AgCl, and AgBr—form in the fcc (rocksalt) NaCl structure, a form that they have in common with the majority of the alkali halides. From the standpoint of electronic structure, the chief distinction of the silver halides is the presence of the cation (Ag^+) 4*d* level in the valence region. The potential importance of this distinction was first recognized by Krumhansl.[1] The presence of the *d* level was thought to hybridize with the outer valence *p* level of the anion ($X^- = F^-, Cl^-, Br^-$), producing the indirect absorption edge postulated by Seitz.[2] The fourth silver halide, AgI, does not normally form in the NaCl structure and is ignored in this paper.

In general, the silver halides are far more important technologically. They serve as superionic conductors and as a basis for the photographic industry. It is, therefore, surprising that a vast number of band calculations exist for the alkali halides and very few for the Ag*X* systems. The existing calculations are: AgCl, non-self-consistent linear combination of atomic orbitals (LCAO) valence only of Bassani *et al.*[3]; AgCl, AgBr, non-self-consistent augmented plane wave (APW) using a muffin-tin potential by Scop[4]; AgCl, an empirical pseudopotential study by Wang *et al.*[5]; AgF, a non-self-consistent LCAO study by Butcher *et al.*[6] for valence levels alone, and AgF, AgCl, and AgBr, a non-self-consistent mixed-basis study at points of high symmetry by Fowler.[7] All these calculations except the empirical one employ the local density approximation for exchange correlation. In general, there seems to be a high degree of agreement among these studies. There are, however, some points of disagreement.

In a typical alkali-halide system, the valence-band structure is essentially formed from the outer occupied *p* subshell of the halogen ion. In the case of a silver halide, one finds a difference. For the free halogen atom and the free silver atom, the orbital energy of the outer occupied halogen *p* subshell and the occupied silver 4*d* subshell is about the same. Upon forming a negative halogen ion, the outer *p* energy is raised by some 6 or 8 eV, whereas the outer *d* energy for Ag going to Ag^+ is lowered by a similar amount. When, however, the ions are combined to form the Ag*X* crystal, the long-range ionic potentials combine to form a Madelung potential. The effect of this Madelung potential is to restore the Ag^+ 4*d* energy and the X^- *np* energy to about the atomic value. Thus one has degeneracy or near degeneracy between the halogen *np* and the Ag 4*d* levels. It is found that for AgCl and AgBr the X^- *np* level lies somewhat above the Ag^+ 4*d* level,[4,5,7] whereas in the case of AgF, the Ag^+ 4*d* level is found to lie higher than the F^- 2*p* level.[6] This change in order is sufficient to permit a simple resolution of the question as to why the band gap in AgF is intermediate between those of AgCl and AgBr.[8] This result is, of course, in contrast to all known alkali-halide systems, where for a given alkali the band gap for the fluoride exceeds that of the chloride, exceeds that of the bromide, exceeds that of the iodide.

The silver ion sits in a site of cubic point symmetry (O_H) and thus neglecting spin-orbital effects, the silver 4*d* level will split into a threefold degenerate state ($\Gamma_{25'}$) and a twofold state (Γ_{12}). Normally for systems of such symmetry, crystal-field theory predicts that the $\Gamma_{25'}$ level will lie below the Γ_{12} level.[9] There may be exceptions to this rule and it is possible that the Ag*X* systems may be among them. Consider the calculations for AgCl. The result of Scop finds the Γ_{12} level to lie above the $\Gamma_{25'}$ level (the expected order[4]), whereas the calculations of Bassani *et al.*[3] and Wang *et al.*[5] find the $\Gamma_{25'}$ substantially above the Γ_{12} level (an inversion of what one expects by 0.5 – 1.5 eV, depending upon which calculation). This discrepancy does not seem to have been previously discussed. It is, therefore, useful to probe this point since if an inversion occurs, its origin could be significant, and in any event it seems that one set of bands at least is in serious error. In this paper, the author reports a new self-consistent series of calculations using correlated Hartree-Fock techniques for AgF, AgCl, and AgBr. In Sec. II, a brief discussion of the methods are presented. In Sec. III, the results are described and contrasted to other theory and to experiment. Finally in Sec. IV, arguments are presented to justify the crystal-field splitting found in this study and conclusions are drawn.

II. METHOD OF CALCULATION

The methods used here represent substantial updates of the self-consistent Hartree-Fock plus correlation methods employed by the author for a series of studies on the alkali halides and rare-gas solids a decade ago. The updates and improvements are detailed in a recent paper and will only be briefly alluded to here.[10]

Self-consistency is achieved by using the proper multicenter localized orbitals technique which eliminates exactly all four-center integrals for both localization and band calculations within the LCAO framework.[11] The basis set developed for these systems by Mickish and Kunz[12] augmented to allow greater freedom for the Ag^+ ion is used for the local orbitals calculation. The bands are then obtained in the Hartree-Fock limit using the recent highly efficient update[10] of the mixed-basis method.[13] Correlation corrections (both relaxation and polarization) are then included using the technique of Pantelides *et al.*[14] Finally, the occupied density of states is integrated using techniques developed earlier by Mickish *et al.*[15]

As discussed in Ref. 10, a basis set consisting of *all* occupied local orbitals, including the outer *p* on the halogen and the Ag 4*d* level augmented by 27 plane waves, was used here. Convergence to 0.1 eV is achieved here. The experimental lattice constant was employed. The values used are 4.936 Å for AgF,[16] 5.550 Å for AgCl,[17] and 5.775 Å for AgBr.[17] Self-consistency in terms of charge density of one part in a million is achieved.

III. DISCUSSION OF RESULTS

Self-consistent Hartree-Fock and correlated energy bands have been obtained for the three fcc silver halides. The energy bands are seen in Fig. 1 for AgF, Fig. 3 for AgCl, and Fig. 5 for AgBr. The valence density of states is seen in Fig. 2 for AgF, Fig. 4 for AgCl, and Fig. 6 for AgBr. In the subsections which follow, each compound will be considered separately.

A. AgF

The first reliable optical measurements of AgF were performed by Marchetti and Bottger.[8] These studies revealed that AgF was an indirect band-gap material with an indirect edge at about 2.8 eV, a direct transition of an excitonic nature at 4.63 ± 0.02 eV, and a speculative direct transition at the *L* point in the Brillouin zone of about 6.34 ± 0.15 eV. The direct band gap has not been established by reliable techniques; however, a rise in optical density at about 5 eV or about 0.4 eV above the direct exciton may well be the optical direct band gap. The present calculations yield a value of 14.3 eV in the Hartree-Fock Koopmans limit and of 5.7 eV in the correlated case. The band gap at *L* is computed to be 16.44 eV in the Hartree-Fock Koopmans limit and 7.8 eV in the correlated case. Given the error in the direct band gap, this value is consistent with the assignment of the 6.34-eV transition to the *L* point, particularly if the observed transition were excitonic, which would push the band edge to a greater value than 6.34 eV.

The bands for AgF are shown in Fig. 1 and the valence density of states in Fig. 2. The essential band structure for AgF is in agreement with the results of Birtcher *et al.*[6] and of Fowler,[7] and further comment on this is not needed. There is a point of potential error here. This is in the width of the indirect edge. The indirect edge is from $L_3^1(v)$ to $\Gamma_1(c)$ and has a width of only 0.5 eV.

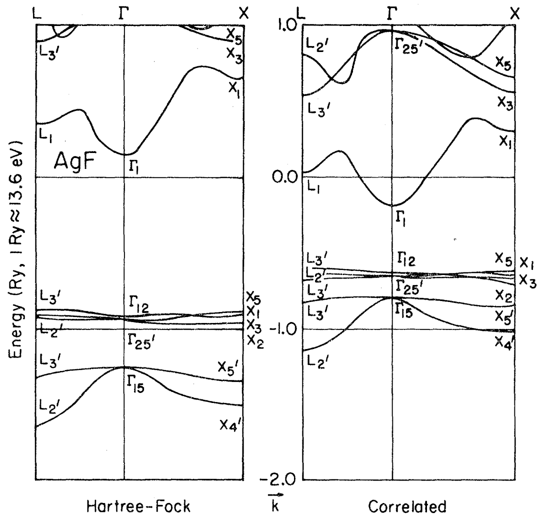

FIG. 1. Self-consistent Hartree-Fock band structure for AgF is shown, along with the correlated band structure.

Experimental evidence indicates that this edge could be as broad at 1.8 eV.[8] The author believes the current calculation underestimates the width of the indirect edge. The reason is as follows: Bands are computed in the Hartree-Fock limit first, and correlation corrections are added perturbatively. The electron-polaron model used for polarization corrections properly includes $\vec{k}$-dependent corrections. The cluster-relaxation model does not have $\vec{k}$ dependence. This is proper provided either one has an isolated band such as the outer *p* band in an alkali halide or for interacting bands if each band member has about the same relaxation energy as is true for Ag 4*d* and Cl 3*p* or Br 4*p*. This is not true for AgF. The F 2*p* relaxation is about 2 eV greater than the Ag 4*d* relaxation. Thus the correlated 2*p* band lies much closer to the Ag 4*d* band than in the Hartree-Fock limit. This will substantially enhance the interaction between the F 2*p* L_3^1 level and the Ag 4*d* L_3^1 levels and broaden the indirect edge. Projecting bands after correlation rather than before is a formidable task and one which the author is presently unable to perform. It is hoped that the next few years will allow us to compute the bands after correlation. Finally, as is clear from Fig. 1, the Ag 4*d* band does indeed lie above the F 2*p* band.

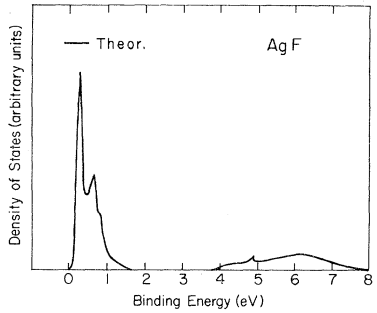

FIG. 2. Density of valence states is seen for AgF, measured with respect to the top of the valence band. Hartree-Fock results are seen here.

B. AgCl

The energy bands for AgCl are seen in Fig. 3, and the valence density of states is seen in Fig. 4. The essential results are that the Cl^- 3*p* level at Γ_{15} is the top of the valence band. The Ag 4*d* levels lie below with the Γ_{12} level lying above the Γ_{25}^1 level. Thus this ordering is in accord with that due to Scop[4] and in disagreement with that of Bassani *et al.*[3] and of Wang *et al.*[5] The present result is in accord with simple crystal-field ideas, and at the end of this section the author speculates on the reasonableness of this result. The valence maximum is at the *L* point and has symmetry L_3^1. The origin here for symmetry analysis is the halogen ion. This feature has been verified by piezo-optical measurements due to Ascarelli[18] and by cyclotron resonance data of Tamura and Masumi.[19] Valence-band photoemission data has been obtained by Bauer, Spicer, and White[20] and by Tejeda *et al.*[21] The later data were obtained for a wide variety of initial photon energy, allowing a rough

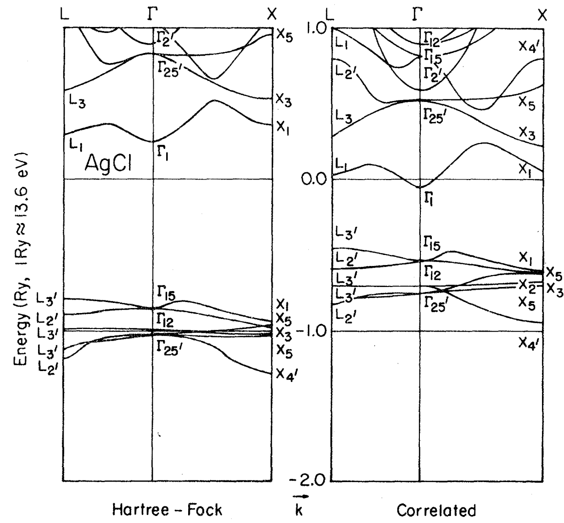

FIG. 3. Self-consistent Hartree-Fock band structure for AgCl is shown along with the correlated results.

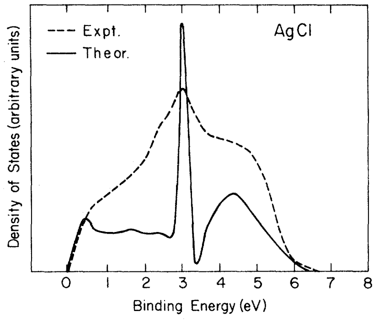

FIG. 4. Density of valence states is seen for AgCl. The experimental results are from Tejeda *et al.* (Ref. 21) and the theory is for the current calculation. Zero of energy is the absolute top of the valence band. Thus neither result has been adjusted to promote a best fit.

determination of density of states. This is seen in Fig. 4. The energy zero is the top of the valence bands as determined by theory for the theoretical result and experiment for the experimental case. If one allows for temperature and resolution broadening of the experimental result, one must admit the agreement of theory and experiment is excellent.

In the case of optical measurements, one finds an onset of indirect absorption at 3.25 eV followed by an excitonic direct absorption at 5.1 eV.[22] A higher absorption speculatively assigned to the L point is found at 6.25 eV. Thus an indirect edge of about 1.75 eV width is found. The direct band gap lies at about 5.6 eV.[3] In the present calculation, a width of 1.2 eV is found for the indirect edge and a direct band gap of 14.9 eV in the Hartree-Fock limit, or of 6.6 eV in the correlated limit. The L transition is found to lie at 6.7 eV in the correlated limit. This lowness of the L transition is in part due to neglect of relativity as discussed after the discussion of AgBr. It is also possible that the observed peak is an excitonic one at the X point. The present correlated calculation has a direct X transition $(X_5^1 - X_1)$ at 9.81 eV. Even allowing for a 1-eV error in gap and a 0.5-eV exciton binding, this would only reduce the X transition to 8.26 eV, a value rather too high to be viable. It may not be ruled out that the 6.25-eV transition is simply a pile-up in state density due to nearly parallel upper valence and lower conduction levels, particularly along the midpoint of the Γ-L direction as seen in Fig. 3.

C. AgBr

The energy bands for AgBr are seen in Fig. 5, and the valence density of states is seen in Fig. 6.

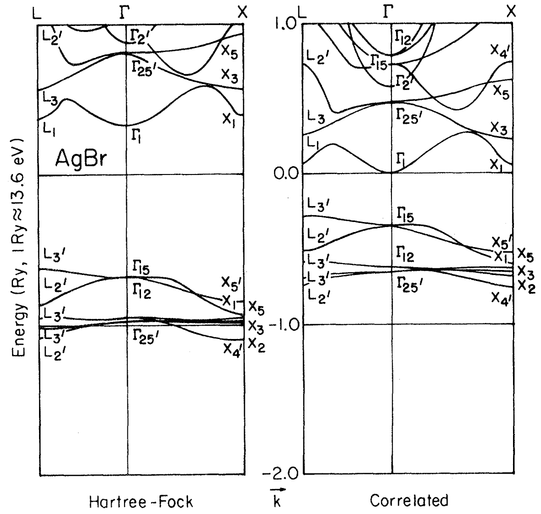

FIG. 5. Self-consistent Hartree-Fock band structure for AgBr is seen along with the correlated results.

Here, as for AgCl, the halogen outer p band ($4p$ Br^- here) is the top valence band at the Γ point (Γ_{15}). The silver $4d$ bands lie lower and the Γ_{12} level lies atop the $\Gamma_{25'}$ level. This order agrees with Scop.[4] The valence maximum is at L (L_3^1 symmetry) and the direct band gap is found to be both at L and Γ. There is an indirect band gap $L_3^1(v)$ to $\Gamma_1(c)$ as well. Experimentally the onset of indirect absorption is at 2.68 eV, with a direct excitonic absorption at 4.25 eV and a speculative L absorption at 6.1 eV.[21] The band gap (direct gap) probably lies at about 4.8 eV.[3] The present calculation finds the indirect band width to be 0.9 eV, compared to a possible 1.6 eV from experiment, a direct band gap (both L and Γ) of 14.0 eV in the Hartree-Fock limit or 5.5 eV in the correlated limit. Again relativistic corrections as discussed below

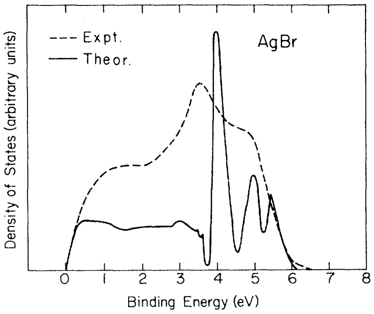

FIG. 6. Density of valence states is seen for AgBr. The experimental result is due to Tejeda *et al.* (Ref. 21), and the theory is from the current calculation. Energy zero is the absolute top of the valence band and neither curve is shifted to enhance agreement.

will move the L transition to higher energy. Nonetheless, it is possible that the speculative L transition is just a joint density-of-states phenomenon along the line Γ-L as in AgCl. The valence density of states has been measured by Bauer *et al.*[20] and Tejeda *et al.*[21] The results of the latter measurement along with the results of the present calculation are seen in Fig. 6. The experimental zero is used for experiment and the theoretical valence maximum defines the zero for the theoretical. Despite this lack of adjustment, the agreement is very good. The overall width is just about perfect, and the peak placement is in disagreement by only 0.3 eV or so.

D. General considerations

Silver has an atomic number of 47 and Br of 35. Prior studies on LiI and NaI, for example, have found significant corrections are needed due to relativity.[13] Iodine has an atomic number of 53. Therefore, we expect the AgX system to behave similarly, although with a slightly smaller effect. There are three particular areas in which these corrections will manifest themselves. These manifestations are due to spin-orbit interaction, the mass-velocity term, and the Darwin shift. In the present case, spin orbit will split the halogen p level and also further split the Ag d level. These splittings are relatively small for the valence band (0.5 eV) or the conduction levels (0.1 eV) and are neglected here as in other calculations. The Darwin term is essentially a contact term and is thus greater for s states than p or d states. This can cause some modification in the band shapes if *spd* hybridization occurs as in the conduction bands. The cited studies for LiI and NaI have found such effects. The author speculates that the AgX conduction bands, which are very similar to those of NaI, will behave similarly. For NaI, one finds that the $\Gamma_1(c)$ state falls with respect to $L_1(c)$ by about 0.5 eV or so. This is in the desired direction as seen in Secs. III B and III C. The band gap is unmodified by any significant amount. Clearly then one may wish to include relativity in future studies on AgX systems as well as improve the fundamental correlation approach.

The second point of speculation concerns the crystal-field splitting of the Ag 4d levels. The threefold $\Gamma_{25'}$ orbitals are xy-, xz-, and yz-like, and the twofold Γ_{12} orbitals are x^2-y^2 and $3z^2$-r^2—like. In normal crystal-field theory, for an O_H symmetry one has the $\Gamma_{25'}$ orbitals pointing directly at the nearest like neighbors, while the Γ_{12} orbitals point between the nearest like neighbors. Assuming the potential due to the neighbor to be attractive, one predicts the $\Gamma_{25'}$ level to lie at lower energy than the Γ_{12} levels. This need not be so for AgX since the halogen lies between the nearest Ag neighbors and hence the Γ_{12} orbitals point at the halogen. Therefore, an inverted crystal-field splitting is possible. Nonetheless, the author believes the current assignment, in agreement with Scop,[4] is correct. The reason is as follows: First, the atomic number of Ag is greater than that of F, Cl, or Br, and hence the Ag potential is stronger. Second, Ag exists as Ag^+ in the crystal and hence the Ag potential is strongly attractive for all distance, whereas the X^- potential is repulsive, not attractive, away from the nucleus. Therefore, it seems reasonable for normal crystal-field splittings to occur, although the inverse is certainly possible.

IV. CONCLUSIONS

The author finds all three silver halides studied to be indirect-gap systems. The indirect edge width is in great error for AgF and slight error for AgCl or AgBr. This was discussed thoroughly in the text in Sec. III A. The band gaps are found to be 5.7 eV for AgF, 6.6 eV for AgCl, and 5.5 eV for AgBr. By comparison, the experimental results are 5, 5.6, and 4.8 eV or so experimentally. Therefore, the current results are in error by 1 eV or so but nonetheless preserve the correct trend and find the AgF gap intermediate between the AgCl and AgBr gaps. This result is not expected since in the alkali halides the gap increases monotonically as halogen atomic number decreases. This apparent anomaly is quickly resolved by noting the outer valence band in AgF is Ag 4d—like, not halogen p-like as for AgCl, AgBr, and the alkali halides.

The present work, in agreement with Scop, finds the usual crystal-field splitting of the silver 4d level (Γ_{12} above $\Gamma_{25'}$). This is a point in need of verification. It would be useful to perform angle-resolved photoemission studies on these systems to either verify or reject the present assignment. It was seen that the present valence results for AgCl and AgBr agree well with current gross photoemission features. It would also be useful to map the conduction levels the same way. This is particularly true since relatively little detailed agreement on the conduction bands is obtained in the available calculations.

There is much room for future theory. Self-consistent calculations incorporating relativity and relaxation corrections are needed to finalize the quantitative features of both valence bands (AgF, in particular) and the conduction bands (AgCl and AgBr, chiefly).

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