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Ab initio electronic structure of silver halides calculated with self-interaction and relaxation-corrected pseudopotentials

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We present results of first-principles atomic and electronic structure calculations for a number of silver halides. For a most accurate treatment of the halides we employ our self-interaction and relaxation-corrected pseudopotentials together with Gaussian-orbital basis sets. Our results for the rocksalt-structure crystals AgCl and AgBr, as well as for the wurtzite and zinc-blende modifications of AgI are in very gratifying agreement with a host of experimental data yielding a consistent description of structural and electronic properties of this class of technologically important semiconductor compounds. [S0163-1829(98)03031-8]

Silver halides are of paramount importance as photographic materials,[1] as solid electrolytes,[2] and as liquid semiconductors.[3] The promotion of electrons, e.g., from the valence to the conduction bands in these halides by light capture plays a major role in the photographic process.[1] In spite of the importance of silver halides for applications, their electronic structure has been studied self-consistently, to the best of our knowledge, only by three first-principles investigations, to date.[4–6] In the first of these,[4] AgCl was addressed within the linear combination of muffin-tin orbitals–atomic sphere approximation. Kirchhoff *et al.*[5] have studied AgCl employing the local density approximation of density functional theory using standard pseudopotentials. Victora[6] has investigated five common silver halide crystals employing a full-potential linear augmented Slater-type-orbital implementation of the local-density approximation. (For earlier theoretical studies, see, e.g., Refs. 7–12.) The *ab initio* calculations[4–6] did not take spin-orbit interaction into account. For AgI, however, spin-orbit coupling has an appreciable influence on the band structure.

Now it is well known that LDA calculations for wide-band-gap semiconductor compounds using standard pseudopotentials fail to correctly describe energy gaps and semicore d bands originating from highly localized states. These shortcomings occur as well for the silver halides. We find LDA band-gap underestimates ranging from 73% for AgI over 81% for AgCl up to 96% for AgBr.

In this communication, we report the results of recent applications of new pseudopotentials[13,14] to silver halides that allow to partially overcome the problems identified above. All calculations have been carried out fully relativistically in the sense that the mass-velocity and Darwin terms, as well as spin-orbit interaction, have been taken into account explicitly. The employed pseudopotentials incorporate self-interaction corrections (SIC's), as well as self-interaction and relaxation corrections (SIRC's) in an approximate, physically well-founded, mathematically well-defined and very efficient way. The corrections sensitively depend on the localization of the involved states so that they are significantly different for s, p, and d states, respectively. The properties of the constituent atoms of the silver halides are built into these pseudopotentials as accurately as possible from the start by taking *atomic* SIC contributions and electronic relaxation *in the atoms* fully into account. The resulting SIC and SIRC pseudopotentials are then transferred to the solids in a well-defined way yielding effective one-particle Hamiltonians that can readily be employed in any LDA code. The construction of this type of pseudopotentials has been discussed in depth in Ref. 14 and they were shown, so far, to be extremely useful for a most quantitative description of II-VI compounds[13,14] and group-III nitrides.[15]

The usefulness of our SIC and SIRC pseudopotentials for the current studies derives from the fact that silver halides are strongly ionic wide-band-gap compound semiconductors very much like II-VI compounds or group-III nitrides. In Table I we have summarized some atomic parameters that characterize these halides. They are strongly ionic since the electronegativity of the Cl, Br, and I anions is much larger than that of the Ag cation. In addition, they are characterized by highly localized orbitals (Cl 3s, Cl 3p, and Ag 4d) that generate the strongly ionic bonds giving rise to the relatively large band gaps. Furthermore, they are distinguished by a certain disparity of their covalent and an extreme disparity of their ionic radii (see Table I). Their main characteristics, namely, the dominance of strongly localized orbitals and their large ionicities, are precisely of the same nature as the obstacles that have hampered accurate band-structure calculations for II-VI compounds and group-III nitrides for a long time.

AgCl and AgBr crystallize in the rocksalt (RS) structure

TABLE I. Atomic parameters characterizing the constituent atoms of the silver halides. Listed are the electronic configuration, the number of valence electrons (Z_v), the electronegativity (χ) and the covalent (r_c), as well as, the ionic (r_{ion}) radii of the singly charged ions.

	Configuration	Z_v	χ	r_c	r_{ion}
Cl	[Ne]$3s^2 3p^5$	7	2.8	0.93	1.81
Br	[Ar]$3d^{10} 4s^2 4p^5$	7	2.7	1.05	1.96
I	[Kr]$4d^{10} 5s^2 5p^5$	7	2.2	1.23	2.20
Ag	[Kr]$4d^{10} 5s^1$	1	1.4	1.34	0.67

TABLE II. Calculated lattice constants a, c, and internal parameter u (in Å) of the studied silver halides in comparison with experimental data (see Ref. 23).

		PP	SIC-PP	Expt.
AgCl	a	5.39	5.53	5.55
AgBr	a	5.58	5.71	5.78
$\mathrm{AgI}^{\mathrm{ZB}}$	a	6.30	6.37	6.47
$\mathrm{AgI}^{\mathrm{W}}$	a	4.45	4.50	4.58
	c	7.28	7.35	7.49
	u	0.376	0.376	0.375

TABLE III. Measured energy gaps E_g, halogen s-band positions E_{ns} and upper valence-band widths W (in eV) of silver halides in comparison with theoretical literature data from Refs. 4–6 and our PP and SIRC-PP results.

		Ref. 4	Ref. 5	Ref. 6	PP	SIRC-PP	Expt.
AgCl	E_g^{ind}	0.5	1.3	1.3	0.6	2.3	3.2[a]
	E_g^{dir}	2.7	3.6	3.5	2.8	4.5	5.2[a]
	E_{3s}		−14.8		−14.7	−15.0	−14.3±0.6[b]
	W		5.3	5.5	5.5	5.4	~6.0[b]
AgBr	E_g^{ind}			1.3	0.1	1.6	2.7[a]
	E_g^{dir}			3.0	1.9	3.1	4.3[a]
	E_{4s}			−14.7	−14.7	−15.3	−14.8±0.6[b]
	W			5.1	5.4	5.7	~6.0[b]
$\mathrm{AgI}^{\mathrm{W}}$	E_g^{dir}			1.5	0.8	1.5	3.0[a]
	E_{5s}			−12.7	−12.8	−13.4	
	W			4.5	4.7	6.1	
$\mathrm{AgI}^{\mathrm{ZB}}$	E_g^{dir}			1.4	0.8	1.4	
	E_{5s}			−12.7	−12.8	−13.4	
	W			4.6	4.7	6.1	

[a] Reference 23.

[b] Reference 12.

and thus differ considerably from AgI, which crystallizes under normal conditions in the wurtzite (W) structure and can be grown in the zinc-blende (ZB) structure, as well. The main difference between AgCl and AgBr and their tetrahedral counterpart AgI is due to the inversion symmetry of the rocksalt lattice. All these silver halides are characterized by the presence of Ag 4d orbitals in the energy region of the top of the valence bands in near degeneracy with the p-valence orbitals of the halogens. The Ag 4d orbitals are intimately mixed with the p-valence functions of the halogens. The degeneracy of these states leads to a very strong p-d hybridization and a considerable complexity in the valence-band structure. For example, in AgCl and AgBr, this hybridization and the respective orbital mixing has pronounced effects, causing these materials, e.g., to have indirect band gaps and large valence-band widths.[8–12] The tetrahedrally coordinated AgI, in contrast, is a direct gap semiconductor. AgCl is the most ionic compound of the three. AgBr is somewhere in between and AgI is the least ionic or the most covalent, respectively, of these halides. Therefore, AgCl and AgBr crystallize in the RS structure while AgI crystallizes in the W or ZB structure, respectively. We find the W structure of AgI to be lower in total-energy by 0.112 eV in our standard PP and by 0.114 eV in our SIRC-PP calculations. These values are close to the respective total energy difference of 0.08 eV as found by Victora.[6] Our SIRC pseudopotential approach is very well suited to treating these wide-band-gap semiconductors appropriately.

In our PP reference calculations, we employ the nonlocal, norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter[16] for Cl, Br, I, and Ag. These PP's enter, as well, the construction of the necessary SIC and SIRC-PP's (see Refs. 13–15). All pseudopotentials are transformed into the separable Kleinman-Bylander form[17] and we use the Ceperley-Alder[18] exchange-correlation potential as parametrized by Perdew and Zunger.[19] As basis sets we employ 80 Gaussian orbitals per unit cell for the RS and ZB and 160 Gaussian orbitals per unit cell for the W compounds, respectively, with appropriately determined decay constants.[20] These basis sets yield well-converged results.

The structural parameters obtained from our SIC-PP calculations are compiled in Table II. As ground-state properties they are not subject to relaxation corrections (cf. the discussion in Ref. 14). We observe that the lattice constants resulting from our SIC-PP calculations are 1–2 % larger than those resulting from our standard PP calculations and they agree with experiment roughly within 1% in most cases. Thus we arrive at a very good description of the atomic structure of the silver halides by our SIC-PP approach.

Let us now discuss the results of our electronic structure calculations employing the SIRC pseudopotentials. To allow for a more meaningful comparison with experiment and with theoretical literature data,[4–6] they have been carried out at the experimental lattice constants.[21] Using standard pseudopotentials, we obtain good general agreement with the *ab initio* literature data for the valence bands.[4–6] As far as the respective band gaps are concerned our results are in close agreement with the results of Ves *et al.*[4] (see Table III). The deviations between our results and those of Refs. 5 and 6 seem to be due to differences in the methodology used in the calculations.

We first address the bulk band structure of AgCl. The left panel of Fig. 1 shows our standard PP result. The band structure is characterized by a Cl 3s band near −15 eV, eight strongly mixed upper valence bands in the energy region from 0 eV to about -5.5 eV (originating from five Ag 4d and three Cl 3p bands) and the lowest conduction band, which is derived mainly from Ag 5s states. The gap is indirect with the top of the valence bands occurring at the L point and the bottom of the conduction bands at Γ. The strong hybridization of the Ag 4d and Cl 3p valence states gives rise to a strong repulsion between the 4d- and 3p-derived upper valence bands. This causes the upward bending of the topmost valence band yielding its maximum at the L point and rendering AgCl and AgBr indirect semiconductors, as was pointed out already by Mason[9] and by Tejeda *et al.*[11]

Our PP band structure of AgCl (see the left panel of Fig. 1) clearly reveals the above-mentioned LDA shortcomings.

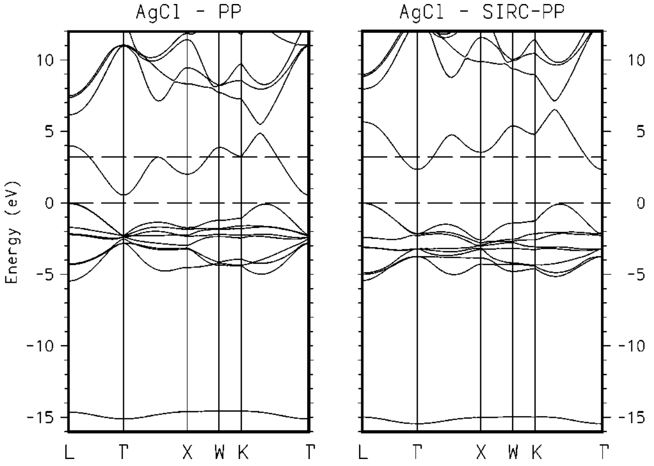

FIG. 1. LDA bulk band structure of AgCl as calculated using standard PP's (left panel) and SIRC-PP's (right panel) including spin-orbit coupling. The horizontal dotted lines indicate the measured gap.

The band-gap energy results as 0.6 eV and thus underestimates the experimental value by about 80%. This is due to the fact that the energy position of the highly localized Ag 4*d* states relative to the Ag 5*s* and Cl 3*p* states is not appropriately described by the standard PP. In addition, this inappropriate treatment of the Ag 4*d* states gives rise to an incorrect description of their hybridization with the Cl 3*p* states. The SIRC-PP band structure in the right panel of Fig. 1, on the contrary, yields a gap energy of 2.3 eV in much better agreement with experiment. In addition, the *p*-*d* hybridization is more correctly described. The Cl 3*p* valence bands are no longer pushed up in energy in an unphysical way so that the calculated gap opens up drastically now being in much better accord with the measured gap. The improvements are even more pronounced for AgBr and also for AgI we find a better gap energy than within the standard PP approach (see Table III).

In Fig. 2 we show the band structures of RS AgBr, ZB AgI and W AgI as resulting from our calculations employing SIRC-PP's in direct comparison. The reference values of the gap energies, the *s*-band positions, and the upper valence band widths, as resulting from our standard PP calculations are compiled in Table III together with the respective results of our SIRC-PP calculations. The most significant differences between the band structures of AgCl and AgBr, as compared to ZB and W AgI are as follows: (1) The former are *indirect* semiconductors with the top of the valence bands at the *L* point and the bottom of the conduction bands at the Γ point. The calculated halogen *s* band, in both cases, resides close to −15 eV in very good accord with experiment;[8–12] (2) AgI in both the ZB and the W structure is

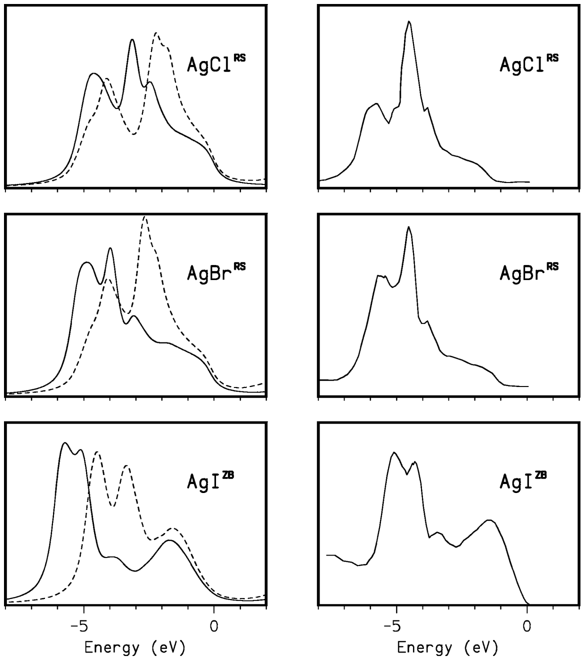

FIG. 3. Bulk density of states of RS AgCl and AgBr, as well as of ZB AgI (left panels) in the upper valence-band region, as calculated using our SIRC-PP's (full lines) and standard PP's (short-dashed lines). Experimental spectra of Refs. 9 and 22 are given for comparison in the right panels. To ease the comparison with the experimental data, the DOS has been Lorentzian broadened by 0.3 eV.

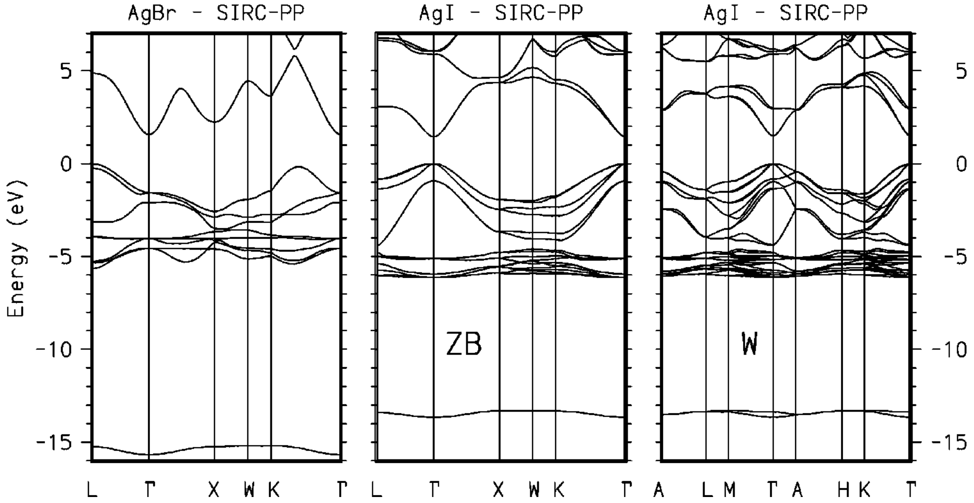

FIG. 2. LDA bulk band structure of RS AgBr, as well as of ZB and W AgI as calculated using our SIRC-PP's including spin-orbit coupling.

TABLE IV. Measured peak positions in the valence bands (in eV) of silver halides in comparison with our PP and SIRC-PP results. Experimental and theoretical data for AgCl and AgBr were obtained for RS crystals while the DOS for AgI was calculated for the ZB crystal. The measured values for AgI were obtained by Mason (a) for the W and by Goldmann *et al.* (c) for the ZB crystal. To ease the direct comparison between theory and experiment, we have shifted the measured band groups rigidly as discussed in the text.

		PP	SIRC-PP	Expt.[a]	Expt.
AgCl	Cl_{3p}	-1.0	-1.0	-1.4 ± 0.4	-0.6 ± 0.2[b]
	Cl_{3p}	-1.7	-2.5	-2.5 ± 0.2	-2.5 ± 0.2[b]
	Ag_{4d}	-2.2	-3.1	-3.2 ± 0.1	-3.2 ± 0.2[b]
	Ag_{4d}	-4.1	-4.6	-4.4 ± 0.2	-4.6 ± 0.2[b]
AgBr	Br_{4p}	-1.0	-1.9	-2.3 ± 0.4	-2.0 ± 0.2[b]
	Br_{4p}	-2.2	-3.1	-3.2 ± 0.1	-3.1 ± 0.2[b]
	Ag_{4d}	-2.7	-4.0	-3.9 ± 0.1	-3.9 ± 0.2[b]
	Ag_{4d}	-4.5	-4.9	-4.9 ± 0.1	-4.9 ± 0.2[b]
AgI	I_{5p}	-1.6	-1.7	-2.3 ± 0.2	-2.1 ± 0.1[c]
	I_{5p}		-3.9		-4.0 ± 0.1[c]
	Ag_{4d}	-3.4	-5.1	-5.0 ± 0.1	-4.9 ± 0.1[c]
	Ag_{4d}	-4.5	-5.7	-5.7 ± 0.1	-5.7 ± 0.1[c]

[a] Reference 9.
[b] Reference 12.
[c] Reference 22.

a *direct* semiconductor with the gap at the Γ point. The calculated I 5*s* band results noticeably higher in energy near −13.5 eV in these two crystals, which have their top of the valence bands at the Γ point.

The results in Figs. 1 and 2 and Tables II and III confirm the general trend that our approximate SIRC-PP approach is best suited for very ionic semiconductors, as has been discussed in detail in Ref. 14. Therefore, we arrive at the relatively best value for the band gap, as compared to experiment, for the most ionic of the considered halides, namely, AgCl, and the least appropriate description for the most covalent of the considered halides, namely, AgI.

Figure 3 shows the calculated densities of states of three cubic silver halides in the upper valence band region in comparison with photoemission data.[9,22] In contrast to the standard PP results, our SIRC-PP results show a very good qualitative and quantitative agreement with the data. In agreement with experiment, the SIRC-PP densities of states, most noticeably for AgI, exhibit four distinct structures within the upper valence-band region. We have compiled respective experimental and theoretical values in Table IV. The calculated energy separations between these peaks are in very gratifying agreement with experiment (see Table IV). To make the direct comparison easier, we have rigidly shifted the experimental peak positions for AgCl and AgBr as measured by Mason[9] by 1.3 eV and 0.6 eV, respectively. This brings the theoretical and the measured top of the valence bands in direct agreement. It is quite obvious from the right panels of Fig. 3, where we show the original nonshifted experimental data, that the measured top of the valence bands does not coincide with the zero of energy for AgCl and AgBr. For further direct comparison with the peak positions, as measured by Tejeda *et al.*,[11] we have included in Table IV their respective values, which were shifted rigidly for AgBr and AgI to agree with the calculated position of the lower Ag 4*d* peak. The resulting values show very good agreement both between the two experimental data sets, as well as with theory, disregarding the rigid shifts on an absolute energy scale. The latter could easily be due to differences in the extrinsic Fermi levels of the different samples used. The densities of states of the three silver halides clearly highlight the differences in basic physical properties of AgCl, AgBr, and AgI, as discussed above. Note that the density of states (DOS) of AgCl and AgBr is very similar while it is significantly different for AgI due to the different crystal structure of the latter.

TABLE V. Electron effective masses (in m_0) of some silver halides, as calculated using standard PP's and SIRC-PP's in comparison with measured values (from Ref. 23).

	PP	SIRC-PP	Expt.
AgCl	0.25	0.30	0.30
AgBr	0.16	0.20	0.22
AgI^{ZB}	0.12	0.16	

Finally, we have calculated electron effective masses for some silver halides. Those resulting from our SIRC-PP's are in much better agreement with experiment than those that we have obtained from our standard PP calculations (see Table V) proving once more the superiority of our SIRC-PP over the standard PP approach. The increase of the effective masses in our SIRC-PP results is caused by the opening of the gap. The bands are not only shifted rigidly by the effects of the SIRC-PP's. The increased gap energy leads to a weaker interaction between the upper valence and lower conduction bands. Thereby the dispersion of the respective bands is reduced and the electron effective masses increase accordingly. These results show that not only energy gaps, valence-band widths, halogen *s* valence-band positions, and densities of states but also the *dispersion* of the technologically most relevant bands is described more appropriately.

In summary, we have presented lattice parameters, bulk band structures, densities of states, and effective masses of common silver halides as calculated using standard PP's, SIC-PP's and SIRC-PP's. The SIC- and SIRC-PP results are in good agreement with available experimental data. We have thus arrived at a most quantitative description of structural and electronic properties of silver halides on the basis of effective one-particle Hamiltonians. Since our approach is not more involved than any standard LDA calculation it can readily be applied to the important problem of defects in silver halides.

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