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Interaction potentials for AgCl and AgBr

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We present interaction potentials for AgCl and AgBr derived from quantum-mechanical approximations and fitted to the experimental lattice constant and energy, elastic and dielectric constants, and special phonon frequencies. The expressions are simple enough for atomistic calculations of crystal defects and molecular dynamics while sufficiently representing the peculiar features of silver halides. The outstanding finding is the dominance of strong van der Waals interaction. Two-body van der Waals forces determine the observed small lattice constant, large lattice energy, and small elastic constant c_{44}, while three-body van der Waals forces contribute mostly to the violation of the Cauchy relation and the large bulk modulus. We could not find convincing indications of partial covalency in silver halides nor of an easy quadrupole deformability of the Ag^+ ion.

I. INTRODUCTION

Silver halides are interesting materials from both a theoretical and a practical point of view. They are considered as "essentially ionic" in their bonding.[1] The ionic aspect is largely suggested by the position of the component elements in the Periodic Table, corresponding to one and seven electrons in the outer shells of silver and halogen atoms, respectively. High ionicity of silver salts is furthermore indicated by the crystallization of AgCl and AgBr (hereafter AgX) in the rocksalt structure which is characteristic for most alkali halides, by their crystal color which arises from large band gaps, and by their electrical conductivity in solid and molten states. On the other hand, silver halides show special features which distinguish them clearly from alkali halides. Such features are unusually small lattice constants, large lattice energies, large dielectric constants, distinct peculiarities among their elastic constants and phonon spectra, extremely low solubility in water, predominance of Frenkel defects, and high mobilities of interstitial silver ions and of dislocations. The latter properties lead to technological application of silver halides in photography[2] and as fast-ion conductors.[3]

It appears that the ionic framework which successfully describes the properties of alkali halides is not sufficient to account for the peculiarities of the silver halides. Therefore, various explanations have been proposed which may be grouped into three main streams. The earliest one assumes that the chemical bond of AgX is mainly ionic, but also partly covalent. This idea is supported by the thermochemical and spectroscopic electronegativity scales of Pauling[4] and of Phillips and Van Vechten.[5,6] Problems of the ionicity-covalency scheme have recently been reviewed by Catlow and Stoneham.[7]

The second explanation is based on the assumption that the Ag^+ ion is likely to undergo quadrupole deformations in order to accommodate particular lattice distortions. Accounting for a quadrupolar deformalibility of the Ag^+ ion provided good agreement between experimental data and calculations of lattice dynamics[8–10] and ionc mobility[11] in AgX. In further investigations, the effect of quadrupolar deformation on the mobilty[12] of Ag^+ and off-center behavior[13] of impurity Ag^+ have been examined and quantum-mechanical origins of ionic deformation modes have been explored.[14]

The third approach emphasizes strong van der Waals interaction in silver halides. This concept was proposed by Mayer[15] and was confirmed in lattice-defect calculations.[16–18] It has also been supported by an analysis of ionic radii and orbital moments in AgX.[19]

The interaction potentials presented in this paper provide further insight into the nature of bonding in silver halides and allow an evaluation of all three proposed explanations. More important is their application in atomistic calculations of properties of crystal defects such as formation and migration energies of interstitial ions, vacancies, dislocations, and more complicated aggregates. Other important applications exist in molecular-dynamics calculations. Given reliable interaction potentials, it seems feasible that such calculations could furnish a valuable tool[20,21] for investigating mechanisms crucial to photographic processes or fast-ion conductance.

The first set of interaction potentials for AgX was proposed by Mayer.[15] He assumes long-range Coulomb interaction between point ions and short-range interactions depending on the distance between ion pairs (two-body central potentials). Parameters in the repulsive and van der Waals terms of the non-Coulombic interaction are fitted to experimental data of the lattice constant, lattice energy, bulk modulus, and optical-absorption spectrum. The use of only two-body central potentials leads to the Cauchy relation between theoretical values of the elastic constants, $c_{12}=c_{44}$. Experimental values of elastic constants are found to satisfy the Cauchy relation approximately in the case of alkali halide crystals. For AgX, however, c_{12} is about five times larger than c_{44}, i.e., the Cauchy relation is strongly violated by experimental data of the elastic constants. These circumstances limit considerably the use of Mayer's interaction potentials for AgX.

An improved set of interaction potentials for AgX has recently been proposed by Catlow, Corish, Jacobs, and Devlin[17,18,11] (CCJD). The authors incorporate the shell model to account for the dielectric properties of AgX. The corresponding shell parameters are fitted to the high-frequency and static dielectric constants. A quadrupolar deformation for migrating Ag^+ ions is simulated by effective interaction distances affecting the short-range terms. The deformation parameters are derived from experimental data of migration energies of lattice defects. Despite all improvements of the CCJD potentials they still contain only two-body central potentials. Consequently they cannot account for the strong violation of the Cauchy relation between the elastic constants of AgX. This deficiency gives rise to uncertainties in calculations of all those structural properties which depend sensitively on the elastic behavior of a crystal.

In this paper we propose new interaction potentials for AgX. Our objective is to present interaction terms which are simple enough for numerical handling in atomistic calculations, but which sufficiently represent those features which are characteristic for silver halides. To this end we have derived the formal structure, i.e., the distance and angular dependence of interaction terms from quantum-mechanical approximations. The actual strength of the various interactions, however, has been fitted to experimental data. Those data were the lattice constant and energy, the elastic and dielectric constants and special phonon frequencies. Quantum-mechanical approximations for the interaction potentials also revealed relations which were used to reduce the number of parameters to a small set. We expect that these values bear physical significance and provide better insight into the special nature of bonding in silver halides.

II. MODEL

A. Quantum-mechanical background

Let us briefly outline the quantum-mechanical approximations which lead to the terms chosen for our interaction potentials. The many-body problem of a crystal is separated in nuclear and electronic parts by the Born-Oppenheimer approximation. The electronic part can be decoupled into one-electron systems (orbitals) by the Hartree-Fock approximation. The deviation of the Hartree-Fock solution from the exact interaction is due to electron correlation.

The localized wave functions of ionic crystals can be constructed from wave functions of free ions according to the Löwdin approximation.[22,23] This leads to long-range Coulomb interaction between ionic point charges and short-range terms arising from orbital overlap, exchange interaction, and Coulomb correction. Since all the short-range interactions between two ions i and j decrease exponentially with the interionic distance r_{ij}, we can combine them to one simplified interaction potential $A_{ij}\exp(-r_{ij}/\rho_{ij})$. The strength coefficient A_{ij} and hardness parameter ρ_{ij} are characteristic for the particular kind of interacting ions i and j. In addition to the leading pair potentials the Löwdin theory gives rise also to three-body interaction terms such as $A_{ijk}\exp[-(r_{ij}+r_{jk})/\rho_{ijk}]$ between three ions i, j, and k.

The actual motion of interacting electrons about the (time-independent) probability density of their orbitals can be regarded as correlated fluctuating multipoles. The correlation interaction between different atoms or ions is known as dynamical or van der Waals (vdW) interaction.[24] The leading term $-C_{ij}/r_{ij}^6$ represents the interaction between mutually inducing dipoles located at ions i and j. The fact that mutual inductions between all dipole pairs in a crystal are not independent from one another is accounted for by correction terms depending on the position of three or more ions. The largest of these correction terms is the Axilrod-Teller potential introduced below.

B. Long-range Coulomb interaction

We assume the lattice particles of AgX crystals to be ions of charges $\pm Ze$ with $Z=1$ and the elementary charge e. The long-range Coulomb interaction energy between two ions i and j is then $Z_iZ_je^2/r_{ij}$. The Coulomb contribution to macroscopic properties of crystals is conveniently expressed with the help of corresponding lattice sums.

C. Short-range repulsion

Starting with unspecified expressions having exponential distance dependence, we arrived at the following interaction potentials for short-range repulsion:

$$U_{\text{rep}}(1,2)=b\exp\left[\frac{r_1+r_2}{\rho}\right]\exp\left[-\frac{r_{12}}{\rho}\right], \quad (1)$$

$$U_{\text{rep}}(1,1)=\beta b\exp\left[\frac{2r_1}{\rho_{11}}\right]\exp\left[-\frac{r_{11}}{\rho_{11}}\right], \quad (2)$$

$$U_{\text{rep}}(2,2)=b'\exp\left[\frac{2r_2}{\rho}\right]\exp\left[-\frac{r_{22}}{\rho}\right]. \quad (3)$$

The subscripts 1 and 2 denote cations and anions, respectively. The quantities b and b' are interaction strength coefficients. Basic ionic radii r_1 for Ag^+ and r_2 for Cl^- or Br^- appear in the first exponential term. The use of basic radii has proven to be successful for alkali halides, since the radii give nearly constant b values around 0.25 eV for the entire crystal family.[1] The quantities ρ and ρ_{11} are hardness parameters, and the r_{ij} denote interionic distances.

It is known from alkali halides that the contribution from the cation-anion repulsion, Eq. (1), dominates in most physical properties. Therefore, we used approximations in the short-range repulsion terms between like ions, Eqs. (2) and (3). For the hardness parameter ρ_{11} we used the corresponding quantity associated with the total orbital overlap between two free Ag^+ ions.[25] The hardness parameter ρ in cation-anion repulsion is mainly determined by the softer electron cloud of the anion. Therefore, we used the same ρ also in the anion-anion repulsion, Eq. (3).

Notice that the strength coefficient b for cation-anion repulsion, Eq. (1), appears also for cation-cation repulsion, Eq. (2), together with a correction factor β. We estimated the amount of β by assuming the same ratio between nearest-neighbor and cationic next-nearest-neighbor repulsion as between their corresponding overlap energies which establish the largest contribution to short-range repulsion.[22] The results showed β values near 1 as also found for alkali halides. Considering the approximations involved, we decided to use a fixed value of $\beta=1$.

As a result of the incorporated relations among repulsion parameters in Eqs. (1)—(3) we have only three parameters, namely, b, b', and ρ, left to be fitted to experimental crystal data. Concerning the actual interaction range of short-range repulsions, the contributions from nearest- and next-nearest-neighbor ions proved to be sufficient for all crystal properties of our interest.

D. van der Waals interaction

The leading dipole-dipole interaction potential between two ions i and j is given by the London formula[26]

$$U_{\mathrm{vdW}}(i,j) = -\frac{C(i,j)}{r^6} \; . \tag{4}$$

The fact that this interaction is attractive is expressed by the negative sign which leaves positive vdW strength coefficients $C(i,j)$. The next higher-order term which accounts for dynamical dipole-quadrupole interaction shows a distance dependence of inverse eighth power. It is known from Mayer's interaction potentials[15] for AgX that the contribution from dipole-quadrupole interaction to the lattice energy is $\sim 20\%$ of the contribution from dipole-dipole interaction. The powers $n=-6$ in Eq. (4) and $n=-8$ for dipole-quadrupole interaction actually represent the asymptotic form for large ion separations. For small ion distances, additional terms appear.[24] In view of the uncertainties in determining strength coefficients for all various vdW pair potentials, we decided to use only the term with power $n=-6$ of Eq. (4) to account for the leading dipole-dipole interaction and to approximate dipole-quadrupole and other effects of vdW pair interactions.

The largest three-body vdW term is given by the Axilrod-Teller formula,[27]

$$U_{\mathrm{vdW}}(i,j,k) = C(i,j,k)\frac{1+3\cos\phi_i\cos\phi_j\cos\phi_k}{r_{ij}^3 r_{jk}^3 r_{ki}^3} \; . \tag{5}$$

Here ϕ_j is the angle formed by the lines connecting ion j with ions i and k. From London's theory of vdW interaction,[26,24] it follows that vdW strength coefficients are approximately proportional to the polarizabilities α_i of the interacting ions. Therefore, we assume the following relation between vdW coefficients and polarizabilities:

$$\begin{aligned} h &= \alpha_1{:}\alpha_2 = C(1,1){:}C(1,2) = C(1,2){:}C(2,2) \\ &= C(1,1,1){:}C(1,1,2) = C(1,1,2){:}C(1,2,2) \\ &= C(1,2,2){:}C(2,2,2) \; . \end{aligned} \tag{6}$$

Knowledge of the ratio h together with the relation of Eq. (6) reduces the number of independent vdW parameters to only one two-body and one three-body strength coefficient, for example, $C(2,2)$ and $C(2,2,2)$.

The convergence behavior of our vdW lattice sums[28] shows that for crystal properties of our interest, two-body contributions due to Eq. (4) from nearest and next-nearest neighbors are sufficient. In regard to the three-body part of Eq. (5), we find satisfying convergence only if we include up to fourth-order neighbors. For the sake of an equal treatment of two- and three-body vdW interactions, we take into account contributions from both terms up to fourth-order neighbors.

E. Dipole mechanisms

We assume that two kinds of dipoles are present in AgX. The first kind is the electronic dipole $\hat{p}_i$ induced by the local electric field $E_{\mathrm{loc}}(i)$ at the position of ion i. The dipole strength is determined by the polarizability α_i as

$$\hat{p}_i = \alpha_i E_{\mathrm{loc}}(i) \; . \tag{7}$$

The second kind is the deformation dipole $\tilde{p}_i$ resulting from mechanisms closely related to short-range repulsion.[29–37] In lattice dynamics it is common to combine the effect of deformation dipoles and of displaced point charges to effective charges $Z_m^*(\vec{k},s)$ which depend on the mode m, wave vector $\vec{k}$, and polarization s of lattice waves. The effective charge associated with optical phonons of wave vector $\vec{k}=0$ (Γ point of the Brillouin zone) is known as the Szigeti charge[38] Z^*e.

The dominant deformation dipole $\tilde{p}_i$ at an ion i, caused by the presence of a nearest-neighbor ion j, is oriented toward j and has a magnitude of

$$\tilde{p}_i = e\tilde{r}_i A^* \exp\left[-\frac{r_{ij}}{\rho}\right] . \tag{8}$$

The quantity $\tilde{r}_i = S_{ij}^{-1}\langle \psi_i r_i \psi_j \rangle$ is the distance between the nucleus of ion i and the center of overlap of free-ion wave functions ψ_i and ψ_j with the overlap integral $S_{ij}=\langle \psi_i \psi_j \rangle$. The strength coefficient A^* is related to the Szigeti charge by

$$\begin{aligned} A^* &= (Z^*-Z)\exp\left[\frac{r_0}{\rho}\right] \\ &\quad \times \left[(\tilde{r}_1-\tilde{r}_2)\left[\frac{2}{\rho}-\frac{4}{r_0}\right]\right]^{-1} , \end{aligned} \tag{9}$$

where r_0 is the nearest-neighbor distance in the crystal.

Effective charges associated with other phonons, i.e., $\vec{k}\neq 0$, contain contributions from dipole deformations caused not only by nearest neighbors but also by next-nearest neighbors. Since the latter mechanisms are subject to large uncertainties, we did not attempt to determine corresponding deformation parameters.

F. Quadrupole deformation

Short-range three-body interaction terms with exponential distance dependence appear in the Löwdin formalism[22] and have been studied by many investigators.[29,39–48] Sarkar and Sengupta[49] (SS) propose a phenomenological three-body interaction potential,

$$U_{\mathrm{SS}}(i,j,k) = D_j \exp\left[-\frac{r_{ij}+r_{jk}}{\rho_3}\right] , \tag{10}$$

which accounts for monopole deformation of ions (breathing-shell model in lattice dynamics) and for the negative deviation from the Cauchy relation, i.e., $c_{12}-c_{44}<0$. The strength coefficient D_j is characteristic for the deformability of the central ion j which is deformed by its nearest-neighbor ions i and k. The hardness parameter ρ_3 is usually, and also in our case, assumed to be the same as ρ in the cation-anion repulsion, Eq. (1). We have shown[50,51] that Eq. (7) can be generalized to simulate quadrupolar deformations of ions and to account for the positive deviation from the Cauchy relation, $c_{12}-c_{44}>0$. To this end we discriminate strength coefficients $\hat{D}_j$ and $\bar{D}_j$ for angular respectively aligned configurations of ion triples ijk. With the assumption that only one ion species, Ag^+ for example, is quadrupolar deformable (E_g symmetry[8]) while the other ion species is rigid, we find a value of $q=\bar{D}/\hat{D}=-4$ for the ratio of Ag^+ deformation coefficients.[52]

In our interaction potentials for AgX we account for the possibility that the Ag^+ ion is deformable by a generalized Sarkar-Sengupta potential, Eq. (7), with a strength coefficient $\hat{D}$ and the ratio $q=\bar{D}/\hat{D}$ to be fitted to experimental crystal data. The deformation term of Eq. (7) is not strictly derived from quantum-mechanical approximations but merely represents an empirical expression. Nevertheless, its structure seems to be suited to simulate the kind of three-body short-range interactions which appear in the Löwdin formalism. In addition we can expect that the values of $\hat{D}$ and q provide some information about the quadrupole deformability of Ag^+.

III. EXPERIMENTAL DATA

Silver halides show considerably larger anharmonic effects than alkali halides.[9] In order to eliminate any thermal influence, we have fitted our interaction potentials to experimental crystal data at or near zero temperature, $T=0$, as listed in Table I. The elastic constants for AgCl in Table I are averages of the close values of the cited references. The elastic constants for AgBr were obtained by Fujii *et al.* from inelastic neutron scattering experiments. They differ appreciably from the data of Marklund *et al.*,[53] $c_{11}=65.94$, $c_{12}=34.95$, $c_{44}=10.03$, all in GPa, obtained from ultrasonic experiments. The latter elastic constants for AgBr are frequently referred to in the literature. When we used the data of Marklund *et al.* we found no interaction potentials within reasonable limits of interaction parameters. Therefore, we have more confidence in the data of Fujii *et al.*

One would expect that ultrasonic experiments are more sensitive than neutron-scattering methods in determining elastic constants. Considering the large discrepancies between the measurements of Marklund *et al.* and Fujii *et al.* it seems desirable to have new ultrasonic data for elastic constants of AgBr. Because of the emphasis on elastic constants in the fit of our interaction potentials, the results depend strongly on the experimental data. We noticed that both the interaction parameters of our potentials for AgBr and their contributions to crystal properties showed less systematic features than those for AgCl. Also applications of our AgBr potentials in crystal-defect calculations were less satisfactory than with AgCl potentials. We therefore consider the possibility that newly determined elastic constants of AgBr might help in deriving improved interaction parameters for AgBr.

TABLE I. Experimental crystal data at $T=0$. Symbols: r_0 is the nearest-neighbor distance; U_0 is the lattice energy; c_{11},c_{12},c_{44} are elastic constants; $\epsilon_\infty,\epsilon_0$ are high-frequency and static dielectric constants; f_{0t} is the frequency of the transverse optical-phonon mode at the Γ point. The last four frequencies correspond to longitudinal (l) and transverse (t) phonons at the L point of the Brillouin zone. In these modes only the cation or anion sublattice vibrates as denoted by subscripts 1 and 2, respectively, while the other sublattice is at rest.

	AgCl	AgBr
r_0 (Å)	2.755[a]	2.867[b]
U_0 (eV)	−9.46[c]	−9.33[c]
c_{11} (GPa)	74.91[a,d]	71.2[e]
c_{12} (GPa)	39.08[a,d]	35.5[e]
c_{44} (GPa)	6.908[a,d]	8.51[e]
ϵ_∞	3.97[f]	4.68[f]
ϵ_0	9.55[f]	10.64[f]
f_{0t} (THz)	3.63[f]	2.74[f]
f_{1l} (THz)	3.00[g]	2.90[e]
f_{1t} (THz)	1.91[g]	1.93[e]
f_{2l} (THz)	6.05[h]	4.00[e]
f_{2t} (THz)	2.30[h]	1.62[e]

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Concerning phonon data, we have not included the frequency of the longitudinal-optical—phonon mode at the Γ point since it provides no additional information to the data in Table I. This is because of the Lyddane-Sachs-Teller relation[54] which is in accordance with the dielectric theory underlying our interaction potentials.

IV. RESULTS

A. Fitting procedure

The fixed interaction parameters in Table II were either *a priori* determined or they turned out to be insignificant so that their variation was not worthwhile. Previously determined quantities were the basic radii r_i for short-range repulsion[19] and the overlap distances $\tilde{r}_i$ calculated by Bauer.[55] Our polarizabilities α_i (and their ratio h) were derived with the Clausius-Mossotti relation and additional assumptions of two mechanisms characteristic for AgX.[56] The Szigeti charge Z^* is obtained from dielectric data with the Szigeti relation.[38] The hardness parameter

TABLE II. Fixed interaction parameters.

	r_1 (Å)	r_2 (Å)	ρ_{11} (Å)	β	h	q	α_1 (Å^3)	α_2 (Å^3)	Z^*	$\tilde{r}_1$ (Å)	$\tilde{r}_2$ (Å)
AgCl	1.26	1.81	0.26	1	0.51	1	1.67	3.29	0.68	1.24	1.52
AgBr	1.26	1.95	0.26	1	0.37	1	1.67	4.55	0.66	1.24	1.63

ρ_{11} for cation-cation repulsion was adapted from overlap data,[25] and β was estimated as explained in Sec. II. Tests confirmed that variations of both ρ_{11} and β had very small effects in the potential fit. The ratio $q=\bar{D}/\hat{D}$ between strength coefficients of the Sarkar-Sengupta potential, Eq. (10), was varied from -10 to 10 in steps of 1. Favorable solutions for interaction potentials, according to the criteria stated below, were found with q values around 1. We did not obtain values around $q=-4$ which simulates a quadrupole deformation of Ag^+. Considering the phenomenological background of Eq. (10) and the finding that Sarkar-Sengupta contributions to lattice energy and elastic constants were, on the average, 1 order of magnitude smaller than contributions from three-body vdW interaction, Eq. (5), we decided to use a fixed parameter $q=1$.

As we will see below (Table V), short-range repulsion and vdW interaction between nearest neighbors provide very large counteracting contributions which considerably cancel one another. In order to obtain interaction parameters within reasonable limits, strong guidance is necessary. We decided to use the same ratio h between vdW coefficients, Eq. (6), as between the polarizabilities. This leaves six quantities, namely, the hardness parameter ρ and the strength coefficients b, b', $C(2,2)$, $C(2,2,2)$, and $\hat{D}$ to be fitted.

Important information about quadrupole deformability of Ag^+ ions can be expected from L-point phonons[8] provided all other contributions are sufficiently known. We found that the Coulomb contributions to frequencies of L-point phonons are comparable to those from (vdW and Sarkar-Sengupta) three-body interactions. The Coulomb terms involve effective charges at the L point. Since we have no reliable prior information about these effective charges, we decided not to fit to frequencies of L-point phonons. This leaves six crystal properties, namely, U_0, r_0, c_{11}, c_{12}, c_{44}, and f_{0t} to be fitted to. Notice that the crystal equilibrium condition at the observed nearest-neighbor distance r_0 can be formulated as vanishing hydrostatic pressure $c_1=0$ (first-order elastic constant[57]).

For a given value of ρ the five properties c_1, c_{11}, c_{12}, c_{44}, and f_{0t} establish linear equations with the five strength coefficients as unknowns. We varied ρ in steps of 0.001 Å and solved exactly for the strength coefficients in the equations for the five above properties. We finally adopted the set of parameters which showed the least deviation from the experimental U_0. The values are listed in Table III.

B. Comparison with other authors

Our polarizabilities in Table II are very close to Mayer's values.[15] They differ, however, by $\sim 15\%$ from the CCJD (Refs. 17 and 18) values (in Å^3) $\alpha_1=2.17$, $\alpha_2=3.03$ for AgCl and $\alpha_1=2.36$, $\alpha_2=4.27$ for AgBr. The CCJD polarizabilities are derived from a shell model with the assumption of polarization of independent ions. Problems of this concept have been discussed by Catlow *et al.*[58]

All parameters for short-range repulsion of the CCJD potentials were obtained using theoretical techniques based on the electron-gas method with conserved density approximation.[59,60] The CCJD repulsion terms show slightly "harder" distance dependences than ours. However, the contributions to U_0 from both methods agree closely although they were quite differently derived. The dominant cation-anion repulsion energies are about twice as large as Mayer's values.[15]

Large discrepancies exist among two-body vdW coefficients from the different authors shown in Table IV. Our values are about 5 times as large as Mayer's coefficients. It has been repeatedly noted that Mayer's vdW coefficients for alkali halides are too small and amount to roughly one-third of more recent values.[61–63] CCJD used as $C(2,2)$ for AgX averages of Mayer's vdW coefficients between anions in alkali halides.[64] This choice is based on the concept of independent anions, which works well for alkali halides but less satisfactory when halide quantities are transferred to AgX. The limitation of the concept of independent anions is indicated by differences around 15% when we compare Mayer's α_2 and $C(2,2)$ for alkali halides with those for AgX. For the vdW strength $C(1,1)$ between two Ag^+ ions, CCJD adapted 4 times Mayer's $C(1,2)$ (i.e., for cation-anion; compare Table IV) of AgCl. The authors justify this rather arbitrary choice with successful lattice-defect calculations and the finding that the ratio of calculated elastic constants c_{44}/c_{11} comes close to the ratio of experimental data.

Our strength coefficients $C(1,1)$ between two Ag^+ ions in AgCl or AgBr agree within 10%. Since this result was not anticipated, we regard it as a good indicator for the

TABLE III. Fitted interaction parameters.

	ρ (Å)	b (meV)	b' (meV)	$C(2,2)$ (eV Å^6)	$C(2,2,2)$ (eV Å^9)	$\hat{D}$ (eV)
AgCl	0.340	210.74	12.22	483.34	1913.1	79 498
AgBr	0.341	188.48	41.18	852.38	4415.3	40 604

TABLE IV. Comparison of van der Waals coefficients, all in eV Å^6.

	AgCl $C(1,1)$	AgCl $C(1,2)$	AgCl $C(2,2)$	AgBr $C(1,1)$	AgBr $C(1,2)$	AgBr $C(2,2)$
Mayer[a]		55.55	83.01		68.03	129.82
CCJD[b]	224.00	219.52	75.00	224.00	228.39	124.70
This work	125.72	246.50	483.34	116.69	315.38	852.38

[a] Reference 15.

[b] References 17 and 18.

quality of our interaction potentials. Our $C(1,1)$ are ~ 3.6 times as large as Mahan's recent vdW coefficients between two free Ag^+ ions obtained from quantum-mechanical calculations.[65]

The quantity $C(1,2)$ is (besides shell parameters for Ag^+) the only fitted strength coefficient of the CCJD potentials. The values are $\sim 10\%$ and $\sim 30\%$ smaller than our $C(1,2)$ coefficients for AgCl and AgBr, respectively. The ratios between the CCJD strength coefficients are in striking contrast to the ratios between polarizabilities of ions, Eq. (6). Nevertheless, in spite of some disturbing features among the individual vdW coefficients, the CCJD potentials certainly give support to the notion of strong vdW interaction in AgX.

Concluding our comparison with other authors we want to point out that our interaction potentials reproduce accurately the bulk crystal properties U_0, r_0, and f_{0t}, elastic and dielectric constants (exact fit). No experimental data from lattice defects have been used in their derivation. This is in contrast to the CCJD potentials which provide calculated formation and migration energies of point defects in AgX (Refs. 11, 17, and 18), in good agreement with experiment. The CCJD potentials, however, are less successful in reproducing the simpler bulk-crystal data. The elastic constant c_{11} for AgCl calculated by CCJD is $\sim 10\%$ larger than experiment; c_{44} is $\sim 40\%$ higher and $c_{12} \sim 75\%$ lower. The calculated c_{11} and c_{44} for AgBr reproduce the data of Marklund *et al.*[53] while c_{12} is again $\sim 75\%$ too low. The frequency f_{0t} for AgBr is $\sim 15\%$ too high. We also noticed that the CCJD potentials fail to reproduce the lattice constant. The equilibrium condition, $c_1 = 0$, can only be satisfied with CCJD parameters if r_0 is $\sim 2\%$ smaller than experiment.

C. Contributions to crystal properties

Good insight into the circumstances which lead to our interaction potentials for AgX, Table III, can be gained from an inspection of the various interaction terms to crystal properties. Table V shows such contributions for AgCl. It is also instructive to compare with alkali halides which are much better understood than AgX. For such a comparison we chose NaCl, because (1) it has the same anion species as AgCl and (2) its neighbor distance[66] ($r_0 = 2.789$ Å) is only 1% larger than in AgCl. The latter property causes very similar Coulomb contributions.

Lattice energies U_0 in Tables V and VI are given in eV and elastic constants and moduli in GPa. Concerning the frequency f_{0t} of transverse optical phonons at Γ, we show contributions from force constants, in units of 10 N m^{-1}, to the quantity $\overline{m}\omega_{0t}^2$ with the reduced mass $\overline{m} = m_1 m_2/(m_1 + m_2)$ and $\omega_{0t} = 2\pi f_{0t}$. Contributions from short-range repulsion are denoted by R and those from vdW interaction by V. As before, the numbers 1 and 2 stand for cations and anions, respectively. The total three-body vdW and Sarkar-Sengupta contributions are labeled with V3B and SS. The Coulomb part and the total of all contributions are given by COU and TOT while the non-Coulombic part is abbreviated with NC [which is the total (TOT) less the Coulombic part (COU)].

The NaCl contributions, Table VI, were obtained from interaction potentials[51] with exact fit to experimental elastic constants,[67] dielectric data,[68] and least deviation from the experimental lattice energy[69] ($U_0 = -8.04$ eV). Because of weak vdW interaction in NaCl we neglected three-body vdW terms and accounted for two-body vdW terms only up to next-nearest neighbors.

TABLE V. Contributions to crystal properties of AgCl (see text for symbols and units).

	U_0	$-c_1$	c_{11}	c_{12}	c_{44}	$\overline{m}\omega_{0t}^2$	K	G
R12	3.19	33.04	300.79			11.112	89.25	133.88
R11	0.01	0.12	0.97	0.49	0.486		0.61	0.18
R22	0.03	0.48	2.97	1.48	1.484		1.82	0.51
V12	−3.55	−27.20	−210.75	−3.41	−3.413	−7.258	−63.46	−90.07
V11	−0.23	−1.76	−7.44	−3.30	−3.304		−4.09	−1.19
V22	−0.88	−6.75	−28.59	−12.70	−12.705		−15.75	−4.57
V3B	1.00	11.46	55.55	35.28	10.433	0.046	38.22	4.41
SS	0.11	2.26	24.24	7.33		0.558	12.21	7.33
COU	−9.13	−11.66	−62.85	13.93	13.927	−2.154	−7.78	−32.56
TOT	−9.45	0.00	74.91	39.08	6.908	2.304	51.02	17.92
NC	−0.32	11.66	137.76	25.15	−7.019	4.458	58.80	50.48

TABLE VI. Contributions to crystal properties of NaCl (see text for symbols and units).

	U_0	$-c_1$	c_{11}	c_{12}	c_{44}	$\overline{m}\omega_{0t}^2$	K	G
R12	1.38	14.40	136.80			5.222	40.80	61.20
R11	0.00	0.00	0.00	0.00	0.00		0.00	0.00
R22	0.09	1.35	8.78	4.39	4.39		5.40	1.52
V12	−0.28	−2.05	−16.43			−0.573	−4.79	−7.19
V11	−0.00	−0.03	−0.12	−0.06	−0.06		−0.07	−0.02
V22	−0.29	−2.14	−8.56	−4.28	−4.28		−4.99	−1.07
SS	−0.02	−0.41	−3.32	−2.08		−0.187	−2.36	−0.42
COU	−9.02	−11.11	−59.84	13.26	13.26	−1.857	−7.40	−31.00
TOT	−8.15	0.00	57.33	11.23	13.31	2.606	26.60	23.05
NC	0.87	11.11	117.17	−2.03	0.05	4.463	34.00	54.05

Starting our inspection with U_0 in Table V, we see a negative NC which indicates a dominance of non-Coulombic attraction in AgX. Contrast this with the positive NC in Table VI which results from a dominance of short-range repulsion in NaCl. Within the framework of our model the strong NC attraction in AgCl can only be accounted for by very strong overall vdW interaction. On the other hand, we can expect stronger nearest-neighbor repulsion in AgCl than in NaCl. This is because there are 46 electrons in Ag^+ and only 10 electrons in Na^+, while the nearest-neighbor distances r_0 of both crystals are very close. In fact R12 is ~2.3 times as large as in NaCl. The strong repulsion in AgCl is more than compensated by very strong two-body vdW attraction as expected from the negative NC. It is known from the theory of vdW interaction[24] that large two-body vdW energies are accompanied by substantial three-body vdW energies. This is also confirmed in Table V. Note that the overall contribution V3B from all three-body vdW terms is of a repulsive nature.[28]

Next we turn to c_{44} in Table V. Since in tangential shear the nearest-neighbor distances change only in second order, we have no R12 and only moderate V12 contributions (from third neighbors in AgCl) to the (linear) elastic constant c_{44}. The total c_{44} is about one-half of the Coulomb part. This is caused by a strong vdW attraction V22 between Cl^- ions which is partly compensated by correcting three-body vdW repulsion. In NaCl, Table VI, on the other hand, small non-Coulombic contributions from second neighbors cancel almost completely, leaving c_{44} very close to its Coulomb part.

The large difference $c_{12}-c_{44}$ of AgCl can only be accounted for by many-body terms such as V3B and SS since all two-body central potentials satisfy the Cauchy relation. Table V shows that the three-body vdW contribution to c_{12} is about 5 times as large as the Sarkar-Sengupta term. We found that SS remained comparatively small if we used, as an alternative, a fixed ratio $q=-4$ in order to simulate a quadrupolar deformability of Ag^+.

More about quadrupole deformation in AgX can be learned from the binormal shear modulus[57] $G=\frac{1}{2}(c_{11}-c_{12}+c_1)$. This quantity characterizes elastic stiffness in response to axial stress equal and opposite in two orthogonal directions. From the right-hand columns in Tables V and VI we see that the NC contributions to G of AgCl and NaCl agree within 10%. This shows that in binormal shear AgCl behaves essentially similar to NaCl rather than "usually."

The three-body vdW lattice sum[28] to G was found to be very small. This explains the small V3B contribution in Table V. Also, the other three-body term, SS, is 1 order of magnitude smaller than the entire NC contribution and causes a small stiffening effect on G of AgCl. Thus three-body potentials play only a minor role in G of AgCl. As a consequence the amount of G results mainly from a counteraction of repulsive and attractive forces between nearest neighbors such as in G for NaCl. If the Ag^+ ion were easily deformable in quadrupolar (volume conserving) E_g symmetry,[8] this should show up most clearly in a substantial negative (softening) SS contribution[51] to G. Our interaction potentials cannot confirm such softening contributions.

Another combination of elastic constants is the bulk modulus[57] $K=\frac{1}{3}(c_{11}+2c_{12}+c_1)$, representing stiffness in response to isotropic compression. The NC part of the AgCl bulk modulus, Table V, is ~70% larger than the NaCl value, Table VI. Here again we see one of the "unusual" properties of silver halides, namely, strong resistance against compression (small compressibility). Table V reveals that the very large terms from two-body vdW attraction cancel most of the even larger contribution from short-range repulsion. The small difference, ~15% of K, is almost completely offset by the attractive Coulomb part. This leaves the three-body terms V3B and SS which furnish ~75% and ~25%, respectively, of K.

We find a similar situation among the contributions to $-c_1$ representing the equilibrium condition. Here short-range repulsion balances essentially two-body vdW attraction, while the three-body terms balance the Coulomb part. It is also interesting to compare the sum of short-range repulsion and two-body vdW attraction in the quantitites U_0, $-c_1$, and K, all of which correspond to perfect cubic crystal configurations. The values of -1.43 eV, -2.07 GPa, and 8.38 GPa, respectively, show the dominance of vdW attraction in the lattice energy but increasing influence from short-range repulsion in the first-[57] and second-order elastic constants c_1 and K. This comes from the "harder" distance dependence of the repulsive potentials, whose second derivatives yield relatively larger contributions to c_1 and K than those from vdW attraction.

Finally we turn to contributions to the quantity $\overline{m}\omega_{0t}^2$

which is related to transverse optical phonons at Γ. We found the corresponding three-body vdW lattice sum[28] to be extremely small. This explains the very small V3B contribution in Table V. The SS term is an order of magnitude smaller than the NC part. This leaves the non-Coulombic two-body terms from nearest neighbors whose large amounts counteract such that NC comes very close to NC of NaCl, Table VI. This shows that optical Γ point phonons in AgCl behave essentially as "normally" as in NaCl.

Much information about the quadrupole deformability of Ag^+ has been deduced by different authors from the phonon dispersion of AgX and in particular from the frequencies at the L point.[8,10] We have calculated these frequencies with our interaction potentials. Lacking reliable effective charges for L-point phonons, we used $Z=1$ in the Coulomb contribution to the frequencies. This is, of course, a crude approximation particularly since the Coulomb contribution and the non-Coulombic contributions other than from nearest neighbors (i.e., the forces which distinguish L-point from Γ-point phonons) are of the same order of magnitude. Thus we cannot expect more than qualitative trends from an inspection of contributions to frequencies of phonons at L. Our calculated values in THz for AgCl (AgBr) are $f_{1l}=3.37$ (3.26), $f_{1t}=1.69$ (1.75) $f_{2l}=5.59$ (3.85), and $f_{2t}=2.28$ (1.56). Agreement with experimental data in Table I is not good (up to 10% deviation) as expected. The contributions from three-body vdW interaction to frequencies of transverse phonons at L (not listed) are very small according to extremely small lattice sums.[28] We found that very large contributions from three-body vdW repulsion to frequencies of longitudinal phonons at L were mainly compensated by attractive vdW terms between second neighbors of the vibrating sublattice. This leaves as the dominant terms the same nearest-neighbor contributions as in f_{0t} accompanied by the insufficiently known Coulomb terms. We could not find any clear indication for easy quadrupole deformalibilty of Ag^+ among the contributions to the frequencies of L-point phonons.

D. Applications

Our interaction potentials have been applied in atomistic calculations of simple crystal defects in AgX (Refs. 70–72). Potstada's calculated Frenkel energy of 1.39 eV for AgCl is in excellent agreement with the experimental value[73] of 1.45 eV. Calculated formation energies for hypothetical Schottky defects in AgCl (AgBr) of 1.79 (2.05) eV by Potstada and 1.83 (1.89) eV obtained by Leutz with a different method confirm the observed predominance of Frenkel defects in AgX. The calculated Frenkel energy for AgBr of 1.48 eV compared to the experimental value[73] of 1.13 eV is less satisfying. As discussed in Sec. III, we suspect that our potentials for AgBr are subject to uncertainties among the elastic constants used in their derivation and hope that this article may stimulate new measurements of elastic constants of AgBr.

V. CONCLUSION

We present interaction potentials for AgCl and AgBr fitted to experimental data of the lattice constant and energy, elastic and dielectric constants, and the frequency of optical phonons at Γ. The long-range Coulomb interaction appears well represented by integer ionic charges, $Z=1$. We saw no necessity to account for partial ionicity as suggested by Pauling,[4] and Phillips,[6] Van Vechten[5] or used in interaction potentials for AgI by Vashishta and Rahman.[74,75] The presence of integer ionic charges in contributions to the lattice energy and elastic constants must not be confused with the occurrence of effective charges in lattice vibrations whose origins are well understood within the ionic framework.[29–38]

The non-Coulombic terms for short-range repulsion and vdW interaction are backed by quantum-mechanical appoximations. The Löwdin approximation[22,23] and London's theory of vdW interaction[24,26,27] provided relations which were used to reduce the number of interaction parameters. We included one phenomenological potential proposed by Sarkar and Sengupta[49,50] which allowed us to simulate a quadrupole deformability of the Ag^+ ion. Our interaction parameters, Tables II and III, appear reasonable in comparison with other authors[15,17,18] and in their contributions to crystal properties, Table V. First applications of our interaction potentials in atomistic calculations of crystal defects[70–72] showed acceptable results.

In regard to the nature of bonding in AgX, our potentials exhibit very strong vdW interaction. This aspect seems to explain many of the "unusual" features of AgX. So does the very strong two-body vdW attraction cause the observed small lattice constant and large lattice energy as well as the small elastic stiffness c_{44} in tangential shear. Considerable repulsive effects from three-body vdW interaction cause the severe deviation from the Cauchy relation and contribute to the large bulk modulus K. The elastic stiffness G for binormal shear and the frequencies of optical phonons at Γ are found to be "usual" compared to alkali halides.

Our results do not confirm an easy quadrupole deformability of Ag^+. This finding is based on (1) the parameters obtained for the Sarkar-Sengupta potential, (2) inspections of contributions to $c_{12}-c_{44}$ and G, and (3) the trend among contributions to frequencies of L-point phonons. It is possible that indications from lattice dynamics[8–10] in support of quadrupole deformation of Ag^+ actually result from three-body vdW interaction. We must bear in mind that these indications are based only on force constants, i.e., second derivatives, rather than on explicit interaction potentials. It is also possible that hints from Pauling's and Phillips–Van Vechten's ionicity schemes toward covalent contributions in silver halides actually reflect the presence of strong vdW interaction.

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