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Brief Reports

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Lattice spacing of hypothetical AgCl and AgBr with "switched-off" van der Waals interactions

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Model calculations show that reduction of van der Waals interactions in AgCl and AgBr to the strength of those in comparable alkali halides leads to hypothetical silver halide crystals with properties similar to those of alkali halides. In particular, the nearest-neighbor distances agree with the sum of Pauling ionic radii. The findings support previous indications that the peculiar cohesive properties of silver halides originate from very strong van der Waals forces rather than from partial covalency.

A longstanding puzzle in the field of ionic crystals concerns the almost equal lattice spacing of AgCl and NaCl. Both materials have the same anion species, Cl^-, and both crystallize in the rocksalt structure. The puzzle arises from the deviating behavior of AgCl from the clear trend among the alkali chlorides where an increase in the electron number of the cations coincides with a larger nearest-neighbor (NN) distance. Although Ag^+ ions have 46 electrons, compared to the 10 electrons of Na^+, an AgCl crystal actually has a slightly (1%) smaller lattice constant than NaCl.

A widely used explanation for the peculiar properties of silver halides, including their lattice spacing and the failure of the additivity rule of ionic radii, is the notion of partially covalent bonding in these materials.[1,2] However, in a former analysis[3] of orbital moments of free ions and their relation to short-range forces, we found indications that the failure of the additivity rule of ionic radii to explain the observed lattice spacing in silver halides originates from a dominance of van der Waals (vdW) interactions over short-range repulsion. The presence of very strong vdW interactions in silver halides, rather than partial covalency, was later confirmed by a determination of semiempirical interaction potentials.[4]

If the peculiar properties of silver halides do originate from dominating vdW interactions, then "switching off" these forces or, better, reducing their strength to those in alkali halides, should result in hypothetical silver halides with properties similar to alkali halides. In particular, we would expect in such hypothetical silver halides NN distances close to the sum of Pauling ionic radii. In this study we present such a test.

In our interaction potentials[4] for AgCl and AgBr we assume ions with charges $\pm Ze$ where $Z=1$ and e is the elementary charge. Short-range repulsion up to next-nearest neighbors (NNN's) is expressed through Born-Mayer potentials with exponential distance dependence. Van der Waals forces are taken into account up to fourth neighbors in both the two-body terms, with a distance dependence of r^{-6}, and the three-body terms of the Axilrod-Teller form.[5] An additional exponential three-body potential, introduced by Sarkar and Sengupta,[6] accounts for short-range deformations of ions. The strength coefficients of these interactions are fitted to experimental values of the lattice constant and energy, elastic and dielectric constants, and special phonon frequencies.[7]

In the first set of model calculations we neglect all vdW and deformation interactions. The resulting NN distances r_0^0 of such hypothetical AgCl and AgBr are shown in Table I. The values of r_0^0 are 17% larger than the experimental NN distances r_0 and 5% larger than the sum of Pauling ionic radii r_0^P.

In order to see the effect of switching-off vdW interactions in the more familiar alkali halides, e.g., in NaCl and NaBr where the additivity rule of ionic radii holds within 2% (see Table I), we repeat the calculations for these crystals with corresponding interaction potentials.[8] Again, the values of r_0^0 are $\sim$7% larger than r_0^P. This shows that both the selected silver halides and alkali halides exhibit similar behavior through an increase of the hypothetical NN distance r_0^0, around 6% over the sum of ionic radii r_0^P, when vdW interactions are completely neglected.

In a second set of calculations we reduce the strength of cation-anion and anion-anion vdW interactions in AgCl and AgBr to those in NaCl and NaBr, respectively. Our choice of these sodium halides was motivated by the nearly equal values of experimental NN distances r_0 of AgCl and NaCl (see Table I). This coincidence causes very similar Coulomb contributions which, in turn, permit an immediate association of different crystal properties with different short-range forces.

As a further modification of the vdW interactions in hypothetical silver halides, we scale the vdW strength between silver ions down from the strength between anions

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TABLE I. Nearest-neighbor distances (at $T=0$) of silver and sodium halides. See the text for full descriptions of the model calculations presented in the last three lines. All distances in Å.

Basis	AgCl	AgBr	NaCl	NaBr
r_0 (experimental values)	2.76[a]	2.87[b]	2.79[c]	2.95[c]
r_0^P (sum of Pauling radii)	3.07	3.21	2.76	2.90
r_0^0 (no vdW interactions)	3.22	3.36	2.93	3.12
r_0^* (vdW interactions like NaX)	3.11	3.19	2.79	2.95
r_0^q (vdW interaction like KX)	3.00	3.12		

[a] J. Vallin, Ark. Fys. **34**, 367 (1967).

[b] E. Vogl and W. Waidelich, Z. Angew. Phys. **25**, 98 (1968).

[c] P. B. Ghate, Phys. Rev. A **139**, 1666 (1965).

in sodium halides with a reduction factor h^{*2}. The basis for the reduction is obtained from a former study of polarizabilities of ions in these crystals.[9] Here $h^* = \alpha_+^*/\alpha_-$ is the ratio between the polarizability of a silver ion in a hypothetical silver halide crystal (with NN distance $r_0^* = r_0^P$, see below) and the polarizability of an anion in an alkali-halide crystal. In that study[9] we obtained $h^{*2}=0.50$ for AgCl and $h^{*2}=0.26$ for AgBr. Whereas the two-body vdW coefficients are modified, all three-body vdW and Sarkar-Sengupta interactions are now neglected.

The resulting NN distances r_0^* of hypothetical AgCl and AgBr with reduced vdW interactions, listed in Table I, agree within 1% with the sum of ionic radii r_0^P. Calculations of r_0^* of NaCl and NaBr reproduce, of course, the experimental r_0 to which the corresponding interaction potentials were fitted.[8]

In a third set of calculations we reduce the strength of vdW interactions in AgCl and AgBr to those in KCl and KBr. The reason for this choice is indicated by applying the analysis of orbital moments[3] to the additivity rule for ionic radii. This analysis showed that the ratios $q=(R^{(2)})^{1/2}/\hat{r}$ between the root of the total second orbital moment $R^{(2)}$ and the first moment of the outermost orbital $\hat{r}$ of free alkali and halide ions are closely grouped around $q_0=3.23$, whereas $q=4.31$ for Ag$^+$. We then observed that the additivity rule of (Pauling) ionic radii holds when the moment ratios q of the ions which constitute a crystal are near q_0. Thus we expect Ag$^+$ to behave in hypothetical silver halides (with additive ionic radii) as if it had a total second moment of $R^{(2)*}=(q_0\hat{r})^2=5.56$ Å^2 instead of $R^{(2)}=(q\hat{r})^2=9.82$ Å^2 of an actual Ag$^+$ ion. This value of $R^{(2)*}$ coincides with $R^{(2)}=5.52$ Å^2 of K$^+$. Since vdW strength coefficients are proportional to $R^{(2)}$ (see Ref. 3), such coefficients should then be similar in potassium halides and in hypothetical silver halides.

We have to keep in mind, however, that the above consideration of radii additivity and moment ratio takes into account only nearest neighbors. Therefore, we adapt in our third set of model calculations the strength coefficients for vdW interactions between NN's in hypothetical silver halides to those of potassium halides while neglecting all other vdW interactions. The resulting NN distances r_0^q in Table I agree within 3% with the sum of ionic radii r_0^P. Thus additivity of ionic radii in hypothetical silver halides can be obtained by using a larger vdW strength, similar to that in potassium halides, acting between NN's only, or, more appropriately, by using weaker strength coefficients, similar to those in sodium halides, but acting between NN and NNN ions.

The finding that hypothetical silver halides show additivity of ionic radii when the vdW strengths are between those of sodium and potassium halides coincides also with the intermediate value of the Pauling ionic radius[10] $r^P(\text{Ag}^+)=1.26$ Å between $r^P(\text{Na}^+)=0.95$ Å and $r^P(\text{K}^+)=1.33$ Å. As pointed out earlier,[3] $r^P(\text{Ag}^+)$, obtained by Pauling from a combination of quantum-mechanical calculations with experimental data of Ag$^+$ in solution, reflects features of a nearly free silver ion similar to ionic radii of alkali and halide ions. This behavior is confirmed in the present study. The Goldschmidt ionic radius of silver, $r^G(\text{Ag}^+)=1.13$ Å, on the other hand, which has been empirically fitted to reproduce the observed lattice spacing of AgF without further justification on theoretical grounds,[3] is less suited than the Pauling radius $r^P(\text{Ag}^+)$ in revealing influences from interatomic forces in silver halides.

Figure 1 shows the lattice energy of AgCl, NaCl, and of two hypothetical silver chlorides as a function of the lattice spacing. Most striking is the lowermost curve reflect-

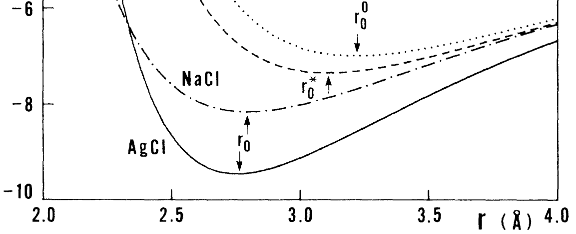

FIG. 1. Lattice energy of AgCl, NaCl, and of two hypothetical silver chloride crystals vs NN distance r. Symbols for the equilibrium NN distances correspond to those in Table I.

ing the very strong vdW attraction in AgCl. The rapid decrease of short-range repulsion at larger r leaves the curves separated by almost constant gaps originating from the medium-range nature of vdW forces. Similar vdW strengths in AgCl* and NaCl account for the quick merging of the dashed and dash-dotted curves at large r. At smaller r, the curves of the three silver chlorides rise at larger distances than the curve of NaCl because of the exponential strength dependence of short-range repulsion on ionic radii.[3]

The most remarkable aspect for our comparison is the overall resemblance of the curves of AgCl* and NaCl. Such curves are typical for alkali halides reflecting dominant Madelung attraction at large lattice spacing and dominant short-range repulsion (nearly-hard-sphere behavior) at small r. The balance of these forces in the transitional region results in a shallow minimum (at r_0^* for AgCl* and at r_0 for NaCl), in sharp contrast to the deep minimum of AgCl caused by interfering vdW attractions. These features show, once more, an emulation of alkali halide properties in hypothetical silver halides.

In conclusion, the results from all three sets of model calculations in this study confirm that reduction of vdW interactions in silver halides to the strength of those in comparable alkali halides gives rise to hypothetical silver halide crystals with properties similar to alkali halides. These findings support previous indications that the peculiar cohesive properties of silver halides originate from very strong vdW forces.

Although a direct experimental verification of switched-off vdW forces does not seem feasible, some indirect evidence may be inferred from the miscibility gap in solid solutions of NaCl-AgCl at low temperatures.[11] This miscibility gap is similar to the one of NaCl-KCl alloys.[12,13] Despite very similar lattice constants for pure NaCl and AgCl, reduced vdW interactions in NaCl-AgCl mixed crystals,[14] compared to pure AgCl, give rise to larger Ag^+-Cl^- than Na^+-Cl^- distances. When these distances differ more than the mixed crystals can accommodate (at low T) through lattice mismatch, lattice instability and precipitation of two phases occur.

The concept of switched-off vdW forces may also be tested independently by a first-principles calculation with the pseudopotential and local-density techniques which have become available in recent years.[15–17] Since vdW interactions can be regarded as arising from intermolecular electron correlation, such an alternative test could be carried out, in a crude fashion, by setting the correlation potential (in local-density approximation[18]) deliberately to zero in the interionic region and thereby determining hypothetical silver halides from first principles. It would be interesting to compare such calculations with the present study.

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