Orbital-moments analysis of ionic radii in silver and copper halides

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We present a linear relation between traditional ionic radii and *ab initio* orbital moments for Ag^+, Cu^+, halide, and, for comparison, alkali ions. Based on the connection of first and second orbital moments with repulsive and attractive interionic forces, respectively, we introduce a quantity q which indicates an ion's contribution to the dominant short-range interaction in a crystal. Some peculiar properties of silver and copper halides are interpreted in terms of strong van der Waals interaction.

I. INTRODUCTION

Knowledge of the "size" of atoms or ions is extremely helpful for an understanding of properties of molecules and condensed matter on a microscopic level. Systematic differences among observed crystal lattice constants and a priori assumptions on the size of F^- and O^{2-} originally led to Goldschmidt's empirical set of ionic radii.[1] Particularly in the case of alkali halides (AX), the underlying hard-sphere model representing the spatial extension of the ions works remarkably well. This shows up in an approximate additivity of the ionic radii r_+ and r_- to the nearest-neighbor (NN) distance r_0 of the crystal:

$$r_0 = r_+ + r_- . \tag{1}$$

Goldschmidt's ionic radius concept fails, however, to satisfy the additivity requirements of Eq. (1) for silver halides (AgX) by predicting too large NN distances r_0 (see Tables I and II). The difference d between hypothetical and experimental r_0 in Table II increases from AgCl to AgI, i.e., with larger anions. Thus the apparent radius of Ag^+, defined by $r_0(\text{expt}) - r_-(G)$, depends sensitively on the actual AgX crystal. This, however, interferes with the assumed hard-sphere model of the ionic radius concept. Goldschmidt's Ag^+ radius of 1.13 Å, obtained from measured lattice constants of a large variety of silver compounds, can be regarded as an average of

strongly compound-dependent apparent radii of Ag^+ ions.

Marking a new phase, a semiempirical ionic radius scale was introduced by Pauling.[2] It is based on quantum-mechanical calculations of screening constants for a hydrogenlike treatment of noble-gas atoms and free noble-metal ions assuming screened nuclear charges. Screening parameters for corrections and extrapolation to other ions are obtained by fitting to experimental values of polarizabilities. Pauling's ionic radii are then determined with the assumption of inverse proportionality between screened nuclear charges and ion sizes and with the requirement of approximate radii additivity for AX.[3] As a consequence, Pauling's ionic radii for Ag^+ and Cu^+ given in Table I do not involve any experimental data of crystalline silver or copper compounds. The corresponding screening constants were fitted to and extrapolated from observed polarizabilities of Ag^+ and Zn^{2+} ions in solution. Thus they essentially reflect features of nearly free ions.

Adding the Pauling ionic radii yields considerably too large NN distances r_0 for AgX and copper halides (CuX) (see Table II). The failure of the additivity of the traditional ionic radii for AgX and CuX together with the occurrence of these crystals in different crystal structures has led to various suggestions concerning the properties of the constituent ions and the nature of their chemical bonding. Among those, highly deformable cations and partly

TABLE I. Goldschmidt and Pauling ionic radii of silver, copper, and halogen ions; all in Å.

	Ag^+	Cu^+	F^-	Cl^-	Br^-	I^-
Goldschmidt[a]	1.13		1.33	1.81	1.96	2.20
Pauling[b]	1.26	0.96	1.36	1.81	1.95	2.16

[a]Reference 1.
[b]Reference 2.

TABLE II. Nearest-neighbor ion distance r_0 of silver and copper halides and difference d between experimental[a] (expt.) and hypothetical values of Goldschmidt (G), Pauling (P), and this investigation (i); all in Å.

	AgF	AgCl	AgBr	AgI
r_0(expt.)	2.46	2.77	2.89	2.80
r_0(G)	2.46	2.94	3.09	3.33
d(G)	0.00	0.17	0.20	0.53
r_0(P)	2.62	3.07	3.21	3.42
d(P)	0.16	0.30	0.32	0.62
	CuF	CuCl	CuBr	CuI
r_0(expt.)	1.84	2.34	2.46	2.62
r_0(P)	2.32	2.77	2.91	3.12
d(P)	0.48	0.43	0.45	0.50
r_0(i)	2.42	2.87	3.01	3.22
d(i)	0.58	0.53	0.55	0.60

[a]R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Wiley, New York, 1963), Vol. 1, pp. 86 and 110.

covalent bonding have been proposed.

A third phase for ionic radii began when their connection to short-range (SR) interionic forces were realized. In particular their role in the empirical Born-Mayer (BM) interaction potentials for AX has been investigated by Pauling,[2] Huggins,[4] and intensively by Fumi and Tosi.[5] Concerning the dominant cation-anion repulsion, this potential

$$U^{BM}_{+-}(r) = b \exp\left[\frac{r_+ + r_-}{\rho}\right] \exp\left[-\frac{r}{\rho}\right] \qquad (2)$$

is a function of the interionic distance r with two parameters, ρ and b, to be fitted to the experimental lattice constant and bulk modulus of the crystal. For the most relevant NN repulsion we insert $r = r_0$ in Eq. (2). For AX the exponential terms cancel almost completely since the radii additivity of Eq. (1) is approximately fulfilled. The remaining strength coefficient b has been found to be a nearly constant quantity around 0.25 eV for the entire AX family. This finding demonstrates nicely that the use of ionic radii, which now together with the hardness parameter ρ enter the exponential function, creates an appropriate scale for representing SR repulsive interaction. This new interpretation of the ionic radius concept appears physically more realistic than the formerly associated hard-sphere model.

As for AgCl and AgBr crystals, we have found from our semiempirical interaction potentials[6] that a value of the strength coefficient b around 0.25 eV is also obtained if the Pauling radius for Ag^+ is used in Eq. (2). This recent finding brings forth two interesting aspects. On the one hand, it shows that the role of ionic radii representing repulsive interaction strength can be adequately extended from AX to

these silver halides. On the other hand, the failure of the additivity requirement of Eq. (1) in the case of AgX indicates that strong attractive forces counterbalancing the BM repulsion may cause the unusually small lattice constants in these crystals.

The dominant SR repulsive and attractive interactions between ions are closely related to first and second orbital moments, respectively. In this paper we want to present such orbital moments and their relation to traditional ionic radii for Ag^+, Cu^+, halogen, and alkali ions. The orbital moments have been obtained from first-principles calculations and they may provide a more reliable background featuring the peculiar properties of AgX and CuX than semiempirical or model-dependent quantities do.

II. ORBITAL MOMENTS

We have caclulated first and second orbital moments

$$\langle r^k \rangle = \int \psi^* r^k \psi \, d\tau \quad (k = 1,2) \qquad (3)$$

of orbital wave functions ψ for closed-shell ions in their ground state. The self-consistent nonrelativistic solutions of the central field all-electron problem were carried out in the local density approximation[7] with the correlation interpolation of Gunnarson and Lundqvist[8] and the self-interaction correction of Perdew and Zunger.[9] For convenience we denote the first orbital moment of the outermost orbital, i.e., the orbital with the least bound energy eigenvalue (e.g., $2p$ for Na^+, $3d$ for Cu^+), by $\hat{r}$. Similarly we abbreviate the total second orbital moment, which is the sum over the second moments of all orbitals of the ion, by $R^{(2)}$. Both, $\hat{r}$ and $R^{(2)}$, of alkali, halogen, Cu^+, and Ag^+ ions are listed in Table III.

TABLE III. Outermost first orbital moment $\hat{r}$, total second orbital moment $R^{(2)}$, and ratio q [see Eq. (5)] for univalent closed-shell ions.

	$\hat{r}$ (Å)	$R^{(2)}$ (Å^2)	q
Li$^+$	0.30	0.25	1.67
Na$^+$	0.42	1.81	3.20
K$^+$	0.76	5.52	3.09
Rb$^+$	0.91	8.95	3.29
Cs$^+$	1.11	14.70	3.45
F$^-$	0.67	4.63	3.21
Cl$^-$	1.09	11.10	3.06
Br$^-$	1.23	15.35	3.19
I$^-$	1.44	22.69	3.31
Cu$^+$	0.52	5.33	4.44
Ag$^+$	0.73	9.82	4.29

In Fig. 1 Goldschmidt and Pauling ionic radii are plotted versus $\hat{r}$. We see that the alkali ions, with the exception of Li$^+$, fall very close to a straight line. Pauling's radius for Ag$^+$ agrees very well with that relation. The Pauling radius for Cu$^+$ is somewhat off that line which may result from extrapolat-
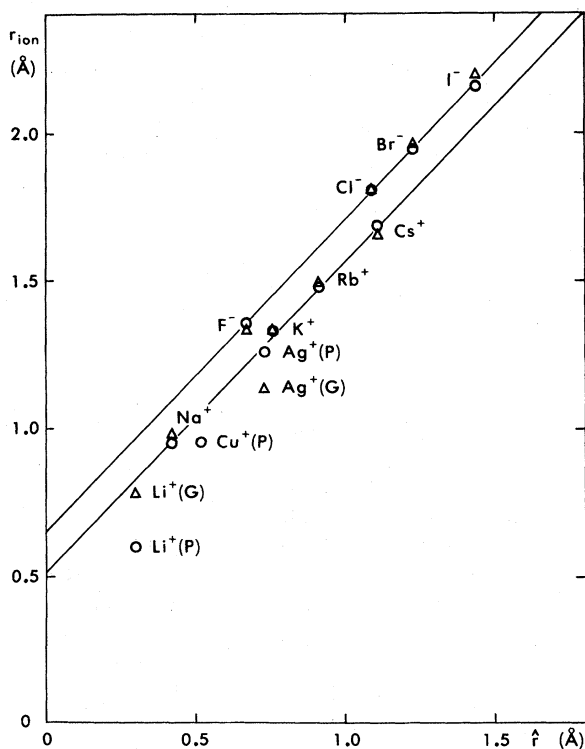

FIG. 1. Goldschmidt (G, triangle) and Pauling (P, circle) ionic radius r_{ion} vs outermost first orbital moment $\hat{r}$ of univalent closed-shell ions.

ing this value from the polarizability of Zn^{2+} in solution. The linear relation in Fig. 1 suggests rather an ionic radius of 1.06 Å for Cu$^+$. This value together with Pauling's halogen radii was used for our hypothetical NN distances $r_0(i)$ for CuX in Table II.

Concerning Li$^+$, both Goldschmidt's and Pauling's radii are empirical values obtained from lattice constants of lithium compounds. However, these compounds represent a somewhat peculiar case as exhibited by the radii additivity for lithium halides (LiX) which show the largest deviations among all AX. This behavior is a consequence of relatively strong interactions between next-NN anions in LiX. The linear relation in Fig. 1 suggests an ionic radius of 0.83 Å for Li$^+$. The significance of this value, however, requires confirmation through further investigation.

Figure 1 finally shows that the halogen ions fall very close to a second straight line which runs parallel to the cation line.[10]

The linear relation between the outermost first orbtial moments of free closed-shell ions and the ionic radii which represent the BM repulsive interaction indicates that the dominant contributions to SR repulsion in a crystal arise from (overlapping) outermost orbitals. The counteracting SR interionic attraction, on the other hand, originates mainly from electron correlation and is approximately expressed by the London formula[11] for van der Waals (vdW) interaction due to mutually inducing fluctuating dipoles. The leading term accounting for cation-anion attraction reads

$$U^{vdW}_{+-}(r) = -\frac{C_{+-}}{r^6} = -\frac{2}{3}\frac{R^{(2)}_+ R^{(2)}_-}{E_+ + E_-}\frac{1}{r^6} . \tag{4}$$

The vdW strength coefficient C_{+-} depends on the total second orbital moments $R^{(2)}$ and mean dipole excitation energies E of the ion pair. The sum $E_+ + E_-$ varies only moderately[12] (around 80 eV) for alkali, Ag$^+$, Cu$^+$, and halogen ions. This leaves the essential dependence of the vdW strength to the second orbital moments $R^{(2)}$.

The actual crystal equilibrium and lattice constant is the result of a balance of all interionic forces. Significant insight, however, is gained by considering the counterbalance of the SR repulsion and attraction between NN only. The BM repulsion is proportional to the exponential function of $\hat{r}$ due to Eq. (2) and Fig. 1. The vdW attraction increases with $R^{(2)}$ because of its proportionality with the strength coefficient C_{+-}, but also with decreasing interionic distances r according to the inverse r^6 dependence in Eq. (4). Thus strong vdW attraction can be expected for ions with large $R^{(2)}$ but relative small spatial ex-

tension as expressed by small $\hat{r}$.

We have found the ratio

$$q = \frac{(R^{(2)})^{1/2}}{\hat{r}} \qquad (5)$$

to be a useful expression reflecting an ion's contribution to the counterbalance between SR repulsive and attractive forces in crystalline environment. So are small and large values of q indicative of the dominance of repulsive and attractive interactions, respectively. Such quantities q are listed in Table III. Their values form three groups: The small value for Li^+ results from small $R^{(2)}$ as a consequence of the only two electrons in Li^+. All other alkali as well as the halogen ions, i.e., with outermost p^6 shells, show q values around 3.23. The large q values of Ag^+ and Cu^+ come mainly from the larger electron numbers in those ions' outer regions, i.e., their outermost d^{10} shell.

An interesting detail concerns the values of q for Na^+ and F^- which are larger than the subsequent values for K^- and Cl^-, respectively, thus breaking the otherwise monotonous increasing sequences. The reason for this anomaly can be seen in the relatively small p orbitals of Na^+ and F^-, in comparison to their outermost s orbitals, since there are no other p orbital shells in these ions causing (radial) orthogonality restrictions. The same reason, though now concerning d orbitals, explains why Cu^+ has a larger q value than Ag^+.

For a binary ionic crystal we expect the dominant SR interactions between NN to be related to the q values of the constituent ions. Since the q values for anions do not vary much, simple algebraic combinations of cation and anion q data fall again in three groups, namely (1) LiX, (2) other AX, and (3) CuX and AgX. It is interesting to note that in the other AX, repulsive and attractive forces counterbalance such that the additivity requirement of Eq. (1) is approximately fulfilled. The deviations of the ionic radii additivity for AgX and CuX as well as for LiX coincide with large and small q values of the ion pairs which in turn indicate a dominance of vdW attraction and BM repulsion between nearest neighbors, respectively.

III. COMMENTS

Many of the peculiar properties of AgX and CuX which distinguish them from AX may be explained by strong vdW interaction as reflected by their large q values. Among the most striking features is the crystallization of AgF, AgCl, and AgBr in octahedral but of AgI and CuX in tetrahedral coordina-

tions. A theoretical prediction of the realized crystal structure by means of the minimal free energy is of course a delicate endeavor since the structure-determining part may be as small as 10^{-3} of the total energy.[13] Calculations of such high accuracy are subject to sophisticated investigations of all interactions involved but are well beyond our present orbital moments consideration focusing on NN interactions only. Nevertheless, we would like to point out that there are two kinds of higher-order effects which, together with the discussed dominant NN interactions, could determine the realized crystal structures and lattice constants.

The first effect concerns repulsive and, more important, attractive interactions between like ions. The earlier noted increasing differences d between hypothetical and observed ion distances r_0 of AgX and CuX in Table II and also peculiarities of LiX may be due to considerable additional vdW attraction between anions with large electron numbers.

The second higher-order effect concerns three-body vdW interactions.[14] Besides the leading (two-body) vdW pair attraction, like in Eq. (4), strong vdW interaction also gives rise to significant three-body terms which, in their net effect, are of repulsive character. Such repulsion has to be investigated in detail by corresponding three-body vdW lattice sums. Concerning the dominant contributions from interacting triples of near-neighbor ions, however, less three-body vdW repulsion occurs in tetrahderally coordinated than octahedral crystals. For crystals with sufficiently strong vdW interaction, like AgX and CuX, three-body vdW contributions are in favor of tetrahedral structures. This aspect also suggests the possiblity that chemical bonding of some tetrahedral crystals, heretofore explained mainly in terms of covalency, may be interpreted by strong vdW interaction which was formerly underestimated.

IV. CONCLUSION

We have found evidence that ionic radii for Ag^+ and Cu^+ are helpful quantities representing the repulsive strength of the ions by means of BM interaction potentials. This interpretation of the ionic radius concept is regarded to be more realistic than the formerly associated hard-sphere model with its consequent radii additivity requirement. We have presented a linear relation between the repulsion-related traditional ionic radii and first-order orbital moments. Using the connection between vdW attraction and second orbital moments we have introduced a quantity q, obtained from first-principles calculations of free ions. This quantity indicates an

ion's contribution to the dominance of SR repulsive or attractive interactions for ions in a crystalline environment. By means of q, strong vdW interaction is predicted for AgX and CuX which, in turn, is held to account for the failure of the ionic radii additivity in these crystals. Finally some consequences of strong vdW interaction on crystal structures are considered.

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