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Short-range-force indicator for closed-shell ions based on orbital moments: Crystal-structure preference

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We relate the dominance in the balance of short-range repulsion and van der Waals attraction between closed-shell ions to first and second orbital moments of free ions. Consequences lead to the rule that dominant van der Waals attraction (short-range repulsion) favors a small (large) number of neighbor coordination. As an example we show a coincidence of the positions of ions ($Z=1,2,3$) in a chart of orbital moments with crystal structures of RX-type compounds.

I. INTRODUCTION

What determines the crystal structure of a compound? This question is as old as solid-state physics. For most materials the answer is fairly complicated since the crystal structure depends delicately on a variety of competing mechanisms. Hence there seems to be a continuous need for simplifying descriptions which still capture the most relevant factors. This holds true even in the presence of the enormous progress made during recent years in predicting crystal structures and other cohesive properties from first-principles calculations with pseudopotential techniques and local-density approximations[1] since the task still remains of interpreting the results in terms of tangible concepts.

Prominent models to meet this need are, e.g., Goldschmidt's and Pauling's ionic radius scales[2] to explain the spacing of crystal lattices; or Pauling's electronegativity scale,[2] the ionicity-covalency scheme of Phillips and Van Vechten,[3] and Harrison's bond-orbital model[4] to interpret structural properties. More recent examples are orbital-radii models by St. John and Bloch,[5] Zunger,[6] and Andreoni *et al.*[7] which show coincidences with crystal structures and molecular configurations, respectively.

A limitation in many of these models is their neglect or under-representation of electron correlation (van der Waals) interaction in properties which are determined by interatomic short-range forces. Consequences show up, for example, in the above ionic radius scales,[8] whose additivity requirements are excellently satisfied for ions with outermost $1s^2$ or p^6 shell, but which are less successful for ions with outermost d^{10} shell such as Cu^+, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, or $d^{10}s^2$ shells like Tl^+ and Pb^{2+}. Because of properties deviating from those of classical ionic crystals (alkali halides), closed d-shell compounds are often referred to as "partially covalent." This terminology implies the danger of regarding the bonding in these materials in a dualistic ionicity-covalency scheme,[2,3] ignoring again contributions from van der Waals (vdW) interactions.

In a previous study[8] on alkali, silver, and copper halides we proposed a unitless quantity

$$q=(R^{(2)})^{1/2}/\hat{r} \tag{1}$$

which indicates an ion's contribution to the balance of vdW attraction and short-range (SR) repulsion. Here $R^{(2)}$ is the total second orbital moment of an ion and $\hat{r}$ is derived from the first moment of its outermost orbital. In

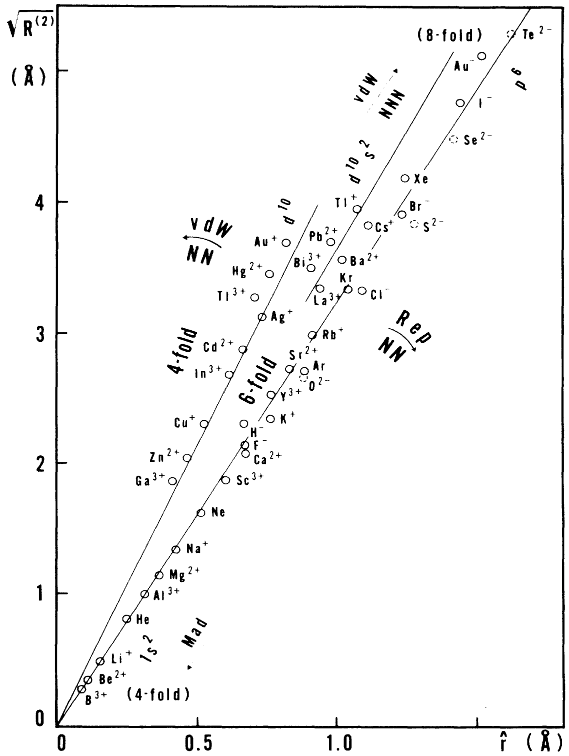

FIG. 1. Root of total second orbital moment $R^{(2)}$ vs. first moment of the outermost orbital, $\hat{r}$, of free ions and atoms with closed electron shells. (See text for definition of $\hat{r}$ and for approximation with divalent anions.) Solid arrows show increasing dominance of short-range repulsion or van der Waals attraction between nearest neighbors. Dashed arrows show increasing influence from Madelung interaction and from van der Waals attraction between next-nearest neighbors. These four interaction mechanisms coincide with a crystallization preference of RX-type compounds in (nearest neighbor) coordinations as shown in the chart.

this paper we present a chart of orbital moments $[R^{(2)}]^{1/2}$ versus $\hat{r}$ for 42 relevant free ions and atoms with closed electron shells (see Fig. 1 above). The positions of the ions in the chart show their main contribution to the strength coefficients of vdW attraction and repulsive SR interaction. These strength coefficients determine structural and cohesive properties of pure compounds,[9] ionic impurities, and even of solvated ions.[10] As an example, we demonstrate a coincidence between the crystal structures of binary compounds of the RX type[11] and the position of the constituting ions in the chart.

II. ORBITAL MOMENTS AND SHORT-RANGE FORCES

The chart is based on a first-principles calculation of first and second orbital moments, $\langle \psi r^k \psi \rangle$ $(k=1,2)$, of orbital wave functions ψ for free closed-shell ions in their ground state. The self-consistent nonrelativistic solutions of the central-field all-electron problem were carried out in local-density approximation[12] with the correlation interpolation of Gunnarson and Lundqvist[13] and the self-interaction correction of Perdew and Zunger.[14] The sum over the second moments of all orbitals of an ion is the quantity $R^{(2)}$ introduced above. With $\hat{r}$ we denote the first moment of the outermost orbital if this is a p or d orbital. For ions with outermost $1s^2$ shell, $\hat{r}$ is half of the first moment of a $1s$ orbital.[15] If an ion has outermost $d^{10}s^2$ shells, $\hat{r}$ is the average of the first moments of such a d and s orbital. The divalent ions of the chalcogenides, O, S, Se, Te, which form interesting and important II-VI compounds, are not stable in a free state. Therefore we calculated (as rough approximations for crystal-stabilized ions) orbital moments of isoelectronic free X^{z-} ions with a hypothetical (fractional) nuclear charge adjusted to yield $z \simeq 1.45$ near the ions' stability limit. The moments $\hat{r}$, $R^{(2)}$, and the ratio q of 42 closed-shell atoms and ions are listed in Table I.[16]

Short-range interactions between closed-shell ions i and j are conveniently expressed in terms of Born-Mayer potentials[17] with repulsive contributions $B_{ij}\exp(-r_{ij}/\rho_{ij})$ (Ref. 18), and attractive vdW terms $-C_{ij}^{(n)}/r^n$ $(n=6,8,\ldots)$ (Ref. 19). Here B_{ij} and $C_{ij}^{(n)}$ are strength coefficients, r_{ij} interionic distances, and ρ_{ij} hardness parameters. Because of their simplicity such potentials have been widely and successfully used in calculations of structural and cohesive properties of ion configurations, mostly for alkali halides and alkaline-earth oxides, but also for silver halides and other d^{10} compounds, ranging from lattice statics to molecular dynamics.[20]

From a conceptual point of view the most appealing aspect of Born-Mayer potentials is that the strength coefficients B_{ij} and C_{ij} can be related to the orbital moments $\hat{r}$ and $R^{(2)}$ which simply characterize the ions by extension and number of their orbital wave functions. The relation between the repulsion coefficients and first moments may formally be expressed as

$$B_{ij} = b_{ij}\exp[(\hat{r}_i + \hat{r}_j)/\rho_{ij}] \ . \tag{2}$$

TABLE I. Outermost first orbital moment $\hat{r}$, total second orbital moment $R^{(2)}$, and ratio q [see Eq. (1)] of free atoms and ions with closed electron shells. (See text for definition of $\hat{r}$ and for approximation with divalent anions.)

Atom	$\hat{r}$ (Å)	$R^{(2)}$ (Å^2)	q
He	0.25	0.67	3.32
Ne	0.51	2.66	3.20
Ar	0.88	7.39	3.08
Kr	1.04	11.17	3.22
Xe	1.24	17.56	3.39
Li^+	0.15	0.25	3.30
Na^+	0.42	1.81	3.20
K^+	0.76	5.52	3.10
Rb^+	0.91	8.95	3.27
Cs^+	1.11	14.70	3.46
H^-	0.67	5.33	3.46
F^-	0.67	4.63	3.21
Cl^-	1.09	11.10	3.06
Br^-	1.23	15.35	3.17
I^-	1.44	22.69	3.31
Be^{2+}	0.11	0.13	3.29
Mg^{2+}	0.36	1.33	3.21
Ca^{2+}	0.67	4.34	3.12
Sr^{2+}	0.83	7.49	3.31
Ba^{2+}	1.02	12.71	3.51
O^{2-}	0.81	7.08	3.30
S^{2-}	1.27	15.54	3.09
Se^{2-}	1.42	20.15	3.17
Te^{2-}	1.62	28.10	3.27
B^{3+}	0.09	0.08	3.28
Al^{3+}	0.31	1.02	3.22
Sc^{3+}	0.60	3.54	3.13
Y^{3+}	0.76	6.43	3.35
La^{3+}	0.94	11.22	3.56
Cu^+	0.52	5.33	4.41
Ag^+	0.73	9.82	4.31
Au^+	0.82	13.60	4.49
Zn^{2+}	0.46	4.20	4.48
Cd^{2+}	0.66	8.30	4.38
Hg^{2+}	0.75	11.92	4.58
Ga^{3+}	0.41	3.48	4.54
In^{3+}	0.61	7.23	4.44
Tl^{3+}	0.70	10.69	4.65
Tl^+	1.07	15.59	3.69
Pb^{2+}	0.98	13.66	3.78
Bi^{3+}	0.91	12.24	3.85
Au^-	1.51	26.24	3.38

For calculational and particularly for conceptual purposes these expressions can be further simplified: The finding[9] that in almost all practically occurring configurations SR repulsion between cations is very small allows one to neglect those contributions. Since the hardness parameters ρ_{ij} for both anion-anion and cation-anion repulsion are predominantly determined by the outer orbitals of the (softer) anion, they may be approximated by one value, ρ, which varies only moderately for different anions. Also the coefficients b_{ij} are found[17] to be approximately constant, $b_{ij} \simeq b(Z_i, Z_j)$, for ion pairs ij with the same net charges $Z_i e$ and $Z_j e$. This leaves the $\hat{r}$ moments as the most ionspecific quantities determining the strength of SR repulsion. Since these $\hat{r}$ represent average distances of the outermost orbitals from free ions' nuclei, these moments serve also as a measure for the distance between nuclei and the (repulsion generating) orthogonality holes which arise from overlapping outer (free) wave functions of ions in condensed configurations.

The vdW coefficient of the leading dynamical dipole-dipole interaction ($n=6$) is related to total second moments as

$$C_{ij} = \tfrac{2}{3} e^4 R_i^{(2)} R_j^{(2)} / (E_i + E_j) \ . \tag{3}$$

Here e is the elementary charge and E_i and E_j are mean dipole excitation energies, the sum of which varies again only moderately for ion pairs with the same net charges $Z_i e$ and $Z_j e$. This leaves the moments $R^{(2)}$, which are closely related to ion polarizabilities, as the most ion-specific properties affecting the vdW coefficients. Thus strong vdW attraction can be expected between ions with a large number of electrons, particularly in outer electron shells such as d^{10} shells.

III. IONIC NEIGHBOR COORDINATION

Besides the above relations between interaction strength coefficients and ionspecific orbital moments, the distance dependence of Born-Mayer potentials implies an important tendency for neighbor coordination around an ion. Consider for simplicity N neighbor ions located on a spherical neighbor shell of radius d. The assumption that the density of neighbors on such a shell remains constant when d varies implies $N \sim d^2$. Since both SR repulsion and vdW attraction between a central ion and the neighbor shell change with d more than quadratically, minimization of their sum leads to a large (small) equilibrium radius d_e and large (small) coordination number N_e of the shell when the coefficient B of SR repulsion (C of vdW attraction) is large. Although too crude for quantitative predictions, this model supports the tendency that an increase in repulsion strength favors more neighbors at a larger distance, whereas an increase in vdW strength favors fewer neighbors at a closer distance. This behavior may be regarded as an energetically favorable distribution of (free ion wave function) overlap in small portions over many distant neighbors or of intense electron correlation with a few near neighbors, respectively.

We now consider the crystallization preference of binary crystals of the RX type, i.e., with $|Z_+| = |Z_-| = Z$. The structure of a crystal is, of course, determined by minimal Gibbs free energy which, for low temperature and pressure, may be approximated by minimal interaction energy of the ions. Although the Coulomb interaction between point ions (Madelung energy), $U_{\mathrm{Mad}} = -\alpha_r Z^2 e^2 / r_0$, is by far the largest contribution to the lattice energy of an ionic compound, *differences* between Madelung energies for different structures with the same nearest-neighbor (NN) distance r_0 are usually small due to similar Madelung constants α_r. Thus Coulomb interaction between point ions plays only a minor role in the preference of crystallization except for ions of very small size and with large charge such as Be^{2+}, B^{3+}, and Al^{3+}. The major influence on crystal structure preference arises from SR interaction, particularly between NN. Next-nearest neighbors (NNN) can become influential through large vdW attraction in compounds with large ions as a consequence of large $R^{(2)}$ moments.

Whenever the sum of SR repulsion and vdW interaction energy between closed-shell ions is positive (negative) we say that SR repulsion (vdW attraction) is dominant. Well-known examples with dominant SR repulsion are the alkali halides and alkaline-earth chalcogenides.[17] A direct consequence is the hard-sphere behavior of the constituting ions with outer p^6 or $1s^2$ shell leading to additivity of their ionic radii. Most common among p^6 and/or $1s^2$ compounds is the $B1$ (NaCl) structure with sixfold NN coordination. Two groups of exceptions are (1) beryllium chalcogenides, MgTe, AlSb, and III-V compounds of B and Al with N, P, and As (fourfold coordination) and (2) CsCl, CsBr, and CsI (eightfold).

The $B1$ phase, although exceptional for d^{10} compounds, is also realized in AgF, AgCl, AgBr, and CdO. Semi-empirical interaction potentials[9] have shown a clear dominance of vdW attraction in AgCl and AgBr. A similar situation can be expected for AgF and CdO, and an even more pronounced vdW dominance for the other d^{10} compounds (of RX type) all of which, except AuI and HgO, crystallize in ZnS or ZnO structure (fourfold NN coordination). AuI and HgO both show chainlike cation-anion configurations with twofold NN coordination.

Of the $d^{10}s^2$ compounds lead chalcogenides and TlF crystallize in $B1$ phase while TlCl, TlBr, and TlI, as well as the exotic insulators RbAu and CsAu (with Au^- anion) crystallize in $B2$ (CsCl) structure. An exception is fourfold-coordinated PbO.

The chart of orbital moments (see Fig. 1) shows the closed-shell ions scattered closely along three lines. The slopes of the lines give the indicator q, Eq. (1), for each ion's contribution to dominant SR interaction between NN. Accordingly, ions along the right ($1s^2$ and p^6) line give rise to dominant SR repulsion with hard-sphere behavior and ions along the left (d^{10}) line to dominant vdW attraction which causes deeper ion penetration and thereby destroys their hard-sphere display.

The q values show a noticeable coincidence with the NN coordination of RX-type compounds. Since all anions (except Au^-) have an outermost p^6 or $1s^2$ shell, a compound's crystal structure is mostly determined by the position of its cation species. Cations from the middle part of the right line form $B1$ crystals and those near the left line form tetrahedral structures. Silver halides and cadmium chalcogenides are borderline cases as reflected by the position of Ag^+ and Cd^{2+} on the left line. In these cases secondary effects from NNN and Madelung interaction become decisive. Considerable NNN vdW attraction from large $R^{(2)}$ of ions high in the chart supports the strong vdW attraction between NN and thus favors a smaller coordination of NN. The group of AgF, AgCl, and AgBr with sixfold coordination, but AgI with fourfold coordination is a typical example. Even stronger support from NNN vdW attraction in AuI causes twofold NN coordination.

Since Madelung interaction also supports vdW attraction in the counterbalance against SR repulsion, large ion charges and small ion sizes favor again small NN coordination. The combined secondary effects from NNN vdW and Madelung interaction can be seen in the NN coordination of cadmium chalcogenides. Here only CdO (isoelectronic with AgF) has sixfold coordination, whereas CdS, CdSe, and CdTe (isoelectronic with AgCl, AgBr, and AgI, respectively) have fourfold coordination. The support of Madelung interaction to vdW attraction becomes crucial for the very small cations with large charge at the lower part of the right line in the chart. We may visualize this support by "Madelung shifts" of these ions slightly to the left with small displacements proportional to their charge, so that Be^{2+}, B^{3+}, and Al^{3+} would fall into the region of fourfold coordination left of the d^{10} line. It is likely that a combination of "Madelung shift" and NNN vdW attraction also accounts for the fourfold coordination of MgTe.

Interestingly, the eightfold NN coordination in CsCl, CsBr, CsI, TlCl, TlBr, TlI, RbAu, and CsAu is also a result of very strong NNN vdW attraction due to the very large $R^{(2)}$ of ions high in the chart. In fact the sum of very large vdW attraction and moderate SR repulsion between NNN offsets now the dominant SR repulsion between NN of these p^6 and $d^{10}s^2$ compounds. According to the coordination rule stated above a small coordination number of NNN rather than of NN becomes favorable here. Since p^6 and $d^{10}s^2$ ions maintain the same NN distance r_0 due to their hard-sphere character, the $B2$ phase has six NNN at a distance $d=1.15r_0$ compared to twelve NNN at $d=1.41\ r_0$ in $B1$ phase. Thus NNN vdW attraction overcoming SR interaction between NN hard-sphere ions favors the CsCl structure. The same mechanism accounts also for the transition from $B1$ to $B2$ phase for most alkali halides under high pressure.

IV. CONCLUSION

In conclusion, we have demonstrated that an interpretation of counterbalancing SR repulsion and vdW attraction in terms of orbital moments, i.e., of spatial electron structure of free ions, provides a viable concept for structural and cohesive properties of compounds. The distance dependence of these interactions implies the rule that dominating vdW attraction (SR repulsion) favors a small (large) number of neighbor coordination. Our orbital-moments consideration of crystal structure preference, based on closed-shell ions, covers besides the classical alkali halides and alkaline-earth chalcogenides, monovalent and divalent d^{10} and $d^{10}s^2$ compounds which are widely regarded as "partially covalent," and, surprisingly, even some III-V compounds. Of course the latter finding does not imply that all III-V compounds consist of trivalent cations and (crystal-stabilized) anions. The possibility rather arises that directed molecular orbitals ("bonds"), originating from open-shell electrons with unpaired spins, enhance the coordination tendency imposed by counteracting SR repulsion and vdW attraction. Further investigation should provide better insight into the cooperation of these bonding mechanisms.

At any rate, the casual use of the term "covalency" should be reconsidered, particularly when it tacitly refers to features which merely deviate from alkali halides. The latter interpretation appears to be of little value since it does not reveal any mechanism. Shortcomings of dualistic ionicity-covalency schemes and associated problems with a definition of charge transfer have been repeatedly noted in the literature.[21,22] By pointing out the role of vdW interaction we add with this paper one more argument against such covalency concepts.

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[15] Note that in Ref. 8, $\hat{r}$ for Li^+ was defined as the first moment of the $1s$ orbital but here $\hat{r}$ is defined half that value. This new definition shifts Li^+ in Fig. 1 of Ref. 8 so that Li^+ becomes included in the linear relation between $\hat{r}$ and Pauling ionic radii.

[16] The ratios q in Table I supersede those in Ref. 8 which were calculated from rounded-off values of $\hat{r}$ and $R^{(2)}$.

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[18] The simple exponential repulsion term of the Born-Mayer potential accounts only for overlap of outer orbitals of closed-shell ions. When ions strongly penetrate one another, supplementary correction terms of inverse-power distance-dependence arise leaving SR repulsion between very near ions

always stronger than vdW attraction. Such correction terms can become important for very close ion configurations (e.g., in molecular-dynamics calculations) to avoid artificial "vdW catastrophies."

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