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Relation between interatomic distances and sizes of ions in molecules and crystals

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Bond lengths and dissociation energies in alkali halides and alkaline earth oxides and fluorides have been analysed. Ions are considered as static deformable spheres, where an essential part of the electron density is concentrated. In molecules, they are compressed. Moving from molecules to crystals, the bond lengths are extended to such an extent that closed electron shells of ions in alkali halide crystals are separated by distances of ~20 pm owing to weakened Coulomb attractive forces acting in opposite directions in a crystal. Short-range repulsion is important only within a few surface layers. Some ionic radii are approximately estimated.

1. Introduction

Bond lengths or the shortest interatomic distances (IDs) in molecules and crystals are determined by the character of the interatomic interactions and the sizes of the atoms (ions). Ions cannot be assigned definite radii because of their quantum-mechanical nature. Both semiempirical (Pauling, 1960) and quantum-chemical (Bader, 1990) considerations state that neighbouring cations and anions have a common boundary. All experimental and theoretical estimations of the distribution of electron density in ionic crystals and molecules show that it is not equal to zero anywhere along the bond line between a cation and an anion, and the effective charges of the ions are always less than their formal oxidation states (Brown & Spackman, 1991; Tsirelson *et al.*, 1998; Vidal-Valat *et al.*, 1978; Witte & Wolfel, 1958). However, there are difficulties with determining the boundaries of ions and ionic charges (Bader, 1990; Clark, 1985; Tsirelson & Ozerov, 1996).

In the empirical crystal chemistry of ionic solids, the ID is determined by the radii of the cation (R_c) and the anion (R_a), which are considered as hard or soft (deformable) spheres, being in close contact or compressed (Pauling, 1960; West, 1988). This simplest classical model implies that in both molecules and crystals the equilibrium IDs are governed mainly by electrostatic attraction and elastic repulsion of the electron shells according to the equation (Kittel, 1956; Animalu, 1977)

$$U(r) = E_q(r) + E_{\rm rep}(r), \qquad (1)$$

where U is the potential of interaction. $E_q = -\alpha k q_1 q_2 / r$ and $E_{\rm rep} = b\exp(-r/\rho)$ are the Coulomb or Madelung and the Born–Mayer (B–M) potentials, respectively; α is the Madelung constant of an infinite crystal lattice, $\alpha = 1$ for diatomic molecules; q_1 and q_2 are the formal ionic charges; b and ρ are empirical parameters; $k = 9 \times 10^9$ N m^2 K^{-1}.

In the case of diatomic molecules, (1) has a transparent physical meaning: derivatives of the Coulomb and B–M potentials are the forces acting in opposite directions and balancing each other at the equilibrium point.

However, in a large crystal that exhibits no widening of X-ray diffraction lines, every ion is surrounded by millions of other ions. In fact, any crystal lattice can be considered as an almost infinite static one, where the equilibrium positions of ions are a result of attractive electrostatic forces acting in opposite directions. In an infinite electrostatic lattice, ions can have *any definite* size in the range $R_{ca} \leq \mathrm{ID}$, where $R_{ca} = R_c + R_a$. This paper is concerned with just the static approach to the interatomic interactions in a crystal lattice, because the observed IDs are static quantities. Since the work of J. J. Thompson, it has been well known that any finite electrostatic system is unstable and should collapse in a finite time while dynamically any system of point charges is unstable (Jeans, 1946; Tsirelson & Ozerov, 1996). Therefore, repulsion of electron shells should always be present in crystals, even within the framework of the static approach. Does it act on *every* ion or only on *some* ions? The scalar potential (1) implies that it acts on every ion, but this is not obvious.

Therefore, whereas in molecules the contact of ions (atoms) is obligatory because of the polar character of the attractive forces that act on a given ion, in crystals the ions might not have common boundaries and therefore (1) might not provide the true equilibrium conditions. In order to define a sufficiently accurate relationship between the sizes of ions and the IDs in a crystal, one should start by analysing the relationship in molecules where possible.

In this paper, the equilibrium parameters of ion–ion interactions in molecules and crystals of some of the most ionic substances (alkali halides *MX*, alkaline earth oxides *M*O and fluorides $M\mathrm{F}_2$) have been compared in order to find a physically meaningful empirical model of the interrelation between the IDs and sizes of ions.

2. Theoretical procedure

2.1. Diatomic ionic molecules

Based on the observations of Slater (1964, 1965) on the interrelation between atomic and ionic radii, one can conclude that the sum of the radii of the cation and the anion is the same in a molecule and in a crystal, despite changes in the sizes of ions with the degree of charge transfer (Batsanov, 1986). This allows one to apply to a free diatomic molecule a simple model of deformable or overlapped spheres (Pauling, 1960). This is a good approximation at least for alkali halide molecules, in which the bonding is presumably ionic (Pauling, 1960; Hofer & Ferreira, 1966; Solomonik & Sliznev, 1998). The model takes into account that both the repulsion and the covalent binding depend on overlapping of the wave functions (Kittel, 1956; Slater, 1965; Kumar *et al.*, 1986; Tsirelson & Ozerov, 1996; Marks *et al.*, 2001; Fernandez Rico *et al.*, 2002). Thus the ID in a molecule is given by

$$R_{\rm m} = R_{\rm ca} - {\rm d}R_{\rm m}, \qquad (2)$$

where ${\rm d}R_{\rm m}$ is the deformation (overlap) of electron shells of ions and $R_{\rm ca}$ is the sum of ionic radii as defined in §1. Deformation means the length of the area of overlap of two spheres along the bond line, but it is expressed as (and equals, if the ions are spherical) the difference of IDs: ${\rm d}R_{\rm m} \simeq R_{\rm ca} - R_{\rm m}$.

Obviously, (2) is approximate because ions are not exactly spherical (Bader, 1990; Gibbs *et al.*, 1998). However, according to the Bader (1990) model of ion polarization, based on the Hellmann–Feynman electrostatic theorem, the charge increase in the binding region of anion X^- exceeds that in its antibinding region (the X^- ion is polarized towards the M^+ ion) and the charge distribution of the M^+ ion is polarized away from the anion. Consequently, the interrelation of internuclear distances and the degree of overlap of spherical electron clouds is not substantially different to that for polarized electron clouds. Besides, these polarizations are a necessary requirement for the attainment of electrostatic equilibrium in the face of a complete charge transfer from cation to anion. However, the charge transfer is not complete in alkali halide single molecules (Bader, 1990) and dimers (Solomonik & Sliznev, 1998).

One of the objectives of the present work is to argue that the ions' closed electron shells are separated in alkali halide crystals. That is, the aim is to prove the following equation:

$$R_{\rm cr} = R_{\rm ca} + {\rm d}R_{\rm cr}, \qquad (3)$$

where $R_{\rm cr}$ is the ID and ${\rm d}R_{\rm cr}$ is the distance between boundaries of counterions in a crystal.

However, as a starting point it is reasonable to accept the close-packing model, according to (1). Provided that in a crystal *MX* (high-temperature phase *B*1) the ions touch or slightly compress each other, one may consider the difference ${\rm d}R_{\rm crm}$ between IDs in the crystal and in the corresponding molecule as the deformation of ions (${\rm d}R_{\rm m}$) in the latter:

$${\rm d}R_{\rm crm} = R_{\rm cr} - R_{\rm m} = {\rm d}R_{\rm cr} + {\rm d}R_{\rm m}, \qquad (4)$$

$${\rm d}R_{\rm crm} \simeq {\rm d}R_{\rm m},\ {\rm d}R_{\rm cr} \leq 0. \qquad (5)$$

To check the validity of the equality ${\rm d}R_{\rm crm} = {\rm d}R_{\rm m}$, one can analyse the covalent contribution to the dissociation energy of molecules as a function of the deformation. In general, the magnitude of the ground-state dissociation energy of a diatomic molecule (D_0) equals the algebraic sum of four main terms (Hofer & Ferreira, 1966; Urusov, 1995):

$$-U(r,i) = E_q(r,i) + E_{\rm cov}(r,i) - E_{\rm rep}(r,i) - \Delta E(i),$$
$$D_0 \equiv -U(R_{\rm m}, i) \qquad (6)$$

where $E_q = kq_{\rm c}q_{\rm a}/r$ is the magnitude of the Coulomb energy; $q_{\rm c}$ and $q_{\rm a}$ are the net charges of the cation and the anion, respectively; $E_{\rm cov}$ and $E_{\rm rep}$ are the undefined energies of the covalent attraction and of the repulsion of electron shells, respectively, although they can be taken in the form of the Morse potential:

$$E_{\rm M}(r) = D[\exp(2\sigma\Delta r) - 2\exp(\sigma\Delta r)]. \qquad (7)$$

D is the numerical value of the covalent binding energy, $\Delta r = R - r$ (*R* is the sum of the covalent radii of the atoms),

$\sigma = -(2\rho)^{-1}$ is an empirical parameter and ρ was defined in (1). ΔE is the energy of charge transfer,

$$\Delta E(i) = i(I - \mathrm{EA}), \tag{8}$$

where I is the ionization energy of the metal, EA is the electron affinity of the electronegative atom and i is the ionicity of the bond. The difference Δr in the Morse potential equals the deformation $\mathrm{d}R_\mathrm{m}$ if $R = R_\mathrm{ca}$.

To discover how the covalent contribution to the bonding depends on the deformation $\mathrm{d}R_\mathrm{m}$ in a set of molecules, one can analyse the difference of the terms E_cov and E_rep,

$$\begin{aligned}\mathrm{d}E(R^j_\mathrm{m}, i) &= E_\mathrm{cov}(R^j_\mathrm{m}, i) - E_\mathrm{rep}(R^j_m, i)\\ &= D_0(R^j_\mathrm{m}, i) + \Delta E(i)^j - E_q(R^j_\mathrm{m}, i),\end{aligned} \tag{9}$$

as a function of $\mathrm{d}R_\mathrm{crm}$. This is feasible for alkali halides, because there is a complete set of accurate experimental data for ionization and electron-affinity energies of atoms and interatomic distances, dissociation energies and dipole moments (μ) of molecules from which the net ionic charges q_c and q_a can be derived (Batsanov, 1986):

$$q_\mathrm{c} = q_\mathrm{a} = ie = e^* = \mu / R_\mathrm{m}. \tag{10}$$

Also, the term E_rep does not significantly affect the dependence $E_\mathrm{cov}(\mathrm{d}R_\mathrm{crm})$, because it is expected to be small compared with E_cov and because both the covalent attraction and the electron-shell repulsion certainly depend on the deformation in the same fashion: the greater $\mathrm{d}R_\mathrm{m}$, the greater E_cov and E_rep. Finally, the difference $\mathrm{d}E$ itself may be regarded as the magnitude of the effective covalent energy, like the coefficient D in the Morse potential. It is natural to assume that at distances where $\mathrm{d}E \leq 0$, covalent bonding is absent and the repulsion is very weak compared with the electrostatic attraction.

The trends in the variations of the ID differences in molecules M_NX and $M_{N+1}X$,

$$\Delta R_\mathrm{m} = R_{\mathrm{m}(N+1)} - R_{\mathrm{m}N}, \tag{11}$$

and in corresponding crystals,

$$\Delta R_\mathrm{cr} = R_{\mathrm{cr}(N+1)} - R_{\mathrm{cr}N}, \tag{12}$$

where $N = 1, 2, 3, \ldots$ for the first, second, third, ... row main group cations of the periodic table, seem to provide some information on the polarization and other effects that are beyond the static model of deformable spheres.

2.2. Crystal lattice

The objective of lattice calculations is to determine how the long-range electrostatic forces influence the ID and the deformation of ions. To understand the process of extension of ID, one has to model sets of ions beginning with a diatomic molecule $(MX)_1$ through clusters $(MX)_n$ to a crystal $(MX)_{n\to\infty}$. *A priori*, it is evident that there are two factors affecting the ID in the bulk of a crystal lattice:

(i) the weakening of the attraction between the cation and anion that formed the initial molecule due to electrostatic cation–cation and anion–anion repulsions;

(ii) the action of attractive forces on an ion in opposite directions.

While it is difficult to quantify the influence of the latter factor, one can compare values of electrostatic forces that act on an ion along the bond line in a diatomic molecule with those for the corresponding crystal with the same ID and ionic charges. The author failed to find any references on the summation of static force vectors within crystal lattices, possibly because of the existence of well developed methods of Madelung summations (Kittel, 1956; Mestechkin, 2000) and the general rule that force is the first derivative of potential. However, this statement cannot be applied to the relationship between the Madelung potential and the force. As it is impossible to calculate the magnitude of the force directly from the Madelung potential, one needs to sum the force vectors of pairwise interactions.

The force acting on an ion in the structure of halite ($B1$) along the [001] polar direction within a hemispace can be calculated by the formula

$$\begin{aligned}F_{001} &= ke^2 \sum \left[(-1)^j \cos\psi_j / R_j^2\right]\\ &= (ke^2/R^2_\mathrm{cr}) \sum \left[(-1)^j p / \left(m^2 + n^2 + p^2\right)^{-3/2}\right]\\ &= \alpha_f ke^2 / R^2_\mathrm{cr},\end{aligned} \tag{13}$$

where ψ_j is the angle between the [001] axis and the radius vector $\mathbf{R}_j$ connecting the ion placed at the origin of the Cartesian system with the jth ion [R_j in (13) is the magnitude of the vector]; $j = m + n + p$ where $m, n, p = 0, 1, 2, 3\ldots$ are the coordinates of the ions; α_f is the static force constant for the [001] direction. Equation (13) is very simple and was deduced using a standard procedure for addition of projections of vectors on the [001] axis.

It is well known that the results of a summation in real space depend on the area of summation. The magnitudes of the sum and convergences of the series may be quite different. In this paper, two electroneutral areas were selected: cubes and areas restricted by a surface where every term (t_j) in brackets in (13) is less than a given small number, $\delta t \to 0$, that is within sequential infinite layers perpendicular to the [001] axis. In the author's opinion, the latter procedure is more correct. Manual calculations have been performed. At present, a homemade computer program that allows the calculation of the magnitudes of forces acting along the [001] and [111] directions within the $B1$ structure is being tested and developed.

3. Results

3.1. Correlation between differences of interatomic distances in molecules and crystals, dissociation energies, and ionic charges in molecules of alkali halides

Table 1 presents experimental data for D_0, e^* and $\mathrm{d}R_\mathrm{crm}$ accompanied by calculated $\mathrm{d}E$. The data for D_0, e^* and ID are retrieved from Batsanov (1986), with references therein to thermochemical data from NBS Technical Notes (Wagman *et al.*, 1973), CODATA (1978), *Termicheskie Konstanty Veschestv* (1981) and Pedley & Marshall (1983), on dissocia-

Table 1
Differences of interatomic distances (pm)†, effective ionic charges (e) and dissociation energies of molecules (kJ mol^{-1}) of alkali halides.

Calculated quantities are in italics.

		Cation								
Anion	Quantity	Li$^+$		Na$^+$		K$^+$		Rb$^+$		Cs$^+$
F$^-$	d$R_{\rm crm}$	45		38		50		55		65
	e*	*0.84*		*0.88*		*0.82*		*0.78*		*0.70*
	$\Delta R_{\rm m}$		37		24		10		8	
	$\Delta R_{\rm cr}$		30		36		15		18	
	D_0	573.2		477.0		494.0		502.0		510.4
	dE	*106*		*67*		*138*		*188*		*254*
Cl$^-$	d$R_{\rm crm}$	55		46		48		50		56
	e*	*0.73*		*0.79*		*0.80*		*0.78*		*0.74*
	$\Delta R_{\rm m}$		34		31		12		12	
	$\Delta R_{\rm cr}$		25		33		14		18	
	D_0	472.8		408.4		422.6		427.0		440.2
	dE	*231*		*157*		*147*		*167*		*199*
Br$^-$	d$R_{\rm crm}$	58		49		48		48		55
	e*	*0.70*		*0.79*		*0.78*		*0.77*		*0.73*
	$\Delta R_{\rm m}$		33		32		13		12	
	$\Delta R_{\rm cr}$		24		31		13		19	
	D_0	420.1		376.1		385.0		393.7		396.0
	dE	*243*		*165*		*159*		*175*		*192*
I$^-$	d$R_{\rm crm}$	61		53		48		51		51
	e*	*0.65*		*0.71*		*0.74*		*0.75*		*0.73*
	$\Delta R_{\rm m}$		32		34		13		14	
	$\Delta R_{\rm cr}$		24		29		14		16	
	D_0	349.4		306.7		321.3		324.2		333.7
	dE	*249*		*191*		*163*		*160*		*169*

† d$R_{\rm crm}$ for CsCl, CsBr and CsI in the $B2$ structure are 65, 65 and 63 pm, respectively.

tion energy, and to Lovas & Tiemann (1974) on dipole moments. The data for D_0 do not differ from those listed by Huber & Herzberg (1979) except for slightly lower values of the dissociation energy (by 0.00–0.07 eV) of RbX compared with KX. This discrepancy demonstrates the level of accuracy of D_0 thermochemical measurements. It is high enough for the interpretation of the data of Table 1, which do not differ significantly from earlier data by Cottrell (1958). The biggest discrepancy is observed for the NaF molecule (448 kJ mol^{-1} against 477 kJ mol^{-1} in Table 1). Even this error does not disturb the general trend of variation of D_0: it decreases from fluorides to iodides and from sodium to caesium halides (Table 1).

The IDs are measured with an error not larger than 1.0 pm (WWW-MINCRYST, 2000; Batsanov, 1986; Sutton, 1958; Gray, 1965; Hartley & Fink, 1987, 1988; Lapshina & Girichev, 1991; Lapshina *et al.*, 1989). From analysis of the literature, it is seen that the largest scatter is observed in the dipole moment measurements. Corresponding values of ionic charges differ by up to 0.11e. For example, according to the data of McClellan (1963), the dipole moments of KF and KI molecules are 8.60 D and 9.24 D, respectively. Corresponding charges are 0.89e and 0.62e, in contrast to 0.82e and 0.73e in Table 1. It is reasonable to assume that the data by Lovas & Tiemann (1974), obtained using the molecular-beam electric-resonance method for the whole set of alkali halide molecules, are more reliable. The author failed to find more recent data, except for LiF and BeO molecules (Yoshioka & Jordan, 1981), and these agree with the previous data. According to the calculations of Bader (1990), ionic charges in lithium, sodium and potassium fluoride and chloride molecules vary from 0.91 to 0.94.

The trends of variation of D_0 from lithium to caesium halides and from fluorides to iodides (Table 1) are strongly influenced not only by the electrostatic energy but also by the charge-transfer energy and, hence, by the electronegativities of atoms. Pauling's electronegativity rule is a traditional explanation of experimental data for alkali halide and other polar molecules (Pauling, 1960; Gray, 1965; Matcha & King, 1976; Batsanov, 1986; Allen, 1989; Gibbs *et al.*, 1997, 1998). From this point of view, the charge transfer from metal to halogen atom is most complete in the CsF molecule, and the low values of the dipole moment and the effective charge e* of the molecule are due to polarization of the metal atom (Matcha & King, 1976).

Table 1 demonstrates a correlation between the three independently measured experimental quantities: D_0, e* and d$R_{\rm crm}$. It is well defined in fluorides and chlorides and to a lesser extent in bromides and iodides. This allows us to suppose that the interaction between atoms in the molecules is governed by charge transfer due to the large differences between the electrochemical potentials of the atom species, but the charge transfer is limited by the plasticity of atoms compressed by the electrostatic attraction. The simple model of overlapped spheres is in fairly good agreement with this supposition and the observed correlation. According to the model, the covalent energy depends on the magnitude of the deformation and would not differ significantly in various molecules for the same deformation. However, the Coulomb attraction depends on the interatomic distance and decreases from LiF to CsI. Consequently, the covalent contribution to the cohesive energy tends, in general, to increase from fluorides to iodides and from LiX to CsX, whereas the decrease of ionicity of the bond is not obligatory. The equilibrium state of an alkali halide molecule results from competition between the degrees of charge transfer and overlapping, which in turn depend on intrinsic properties of the ions' electron shells. In both the dynamic and the static cases, the decrease in overlapping leads to an increase in the electrostatic attraction that compresses the ions. *Vice versa*, a decrease of the electrostatic attraction due to a larger ID results in a decrease of the overlap and corresponding covalent energy. The role of this factor is manifested by the smallest ionic charges and the largest d$R_{\rm crm}$ in CsF among other caesium halides (Table 1). The conventional opinion on the highest ionicity of the NaF molecule (Sanderson, 1976; Batsanov, 1986) is also in good agreement with the data of Table 1.

Within the framework of the proposed model, the considerable increase of d$R_{\rm crm}$ and decrease of e* from the left to the right of Table 1 in Li and Na halides and from KF to CsF is caused by the increasing radii (hence, plasticity and polarizability) of halogen and metal ions and a sufficiently strong electrostatic attraction due to moderate IDs. Variation of d$R_{\rm crm}$ and e* in the K, Rb, Cs series from fluorides to iodides tends to be in the opposite direction because of a weaker electrostatic attraction. Actually, both I and EA are closely related to the radii of the atoms. When atoms form a molecule, the degree of overlapping of electron shells also depends on their radii. One could say that a larger atom has a more plastic or soft electron shell (Butterfield & Carlson, 1972). Therefore, CsF or CsCl might not be the most ionic molecules despite having minimal ΔE and the highest differences between the electronegativities of the atoms.

Table 1 presents the numerical values of dE calculated according to (9) using the values of D_0 and e^* in Table 1. It is seen that, in general, the behaviour of dE is the inverse of that of e^*, and it decreases by a factor of 3.8 from CsF to NaF. As mentioned in §2.1, the repulsive energy would be small compared with the covalent energy. Actually, the covalent bonding is controlled by the Coulomb attraction and its energy would be, in general, lower or approximately equal to the Coulomb energy. The range of dE (Table 1) satisfies this statement. Only in LiI does the increment dE (249 kJ mol^{-1}) slightly exceed E_q (245 kJ mol^{-1}). It seems realistic to impose a maximal $E_{\rm rep}$ of 50 kJ mol^{-1} in the strongly deformed CsF and LiI molecules and a minimal value of 20 kJ mol^{-1} in NaF. Since $E_{\rm cov}$ and $E_{\rm rep}$ increase with increased deformation, the trends of variation of dE certainly reflect those of $E_{\rm cov}$ to a large extent. Hence, dE is an accurate indicator of the covalent bonding as assumed in §2.1.

Fig. 1 shows a plot of dE *versus* d$R_{\rm crm}$, which was obtained using standard Microsoft Excel 5 facilities. From the attached equations in Fig. 1, it follows that the dependence dE(d$R_{\rm crm}$) is well approximated by a straight line that intersects the abscissa at $({\rm d}R_{\rm crm})_0 = 27$ pm. The fitting parameter R^2 for the exponential curve is notably smaller than that for the straight line. If the extrapolation of the dependence down to d$E = 0$ using this straight line is valid, the interval to the left of the intersection point is the mean distance between counterions' electron shells in alkali halide crystals $({\rm d}R_{\rm cr})_0$ while the remaining intervals on the right are the deformations of the ions in molecules $({\rm d}R_{\rm m})_j$. According to Table 1 and Fig. 1, the latter values vary from 11 pm in NaF to 38 pm in CsF. However, one cannot be fully confident of the accuracy of such an extrapolation. In view of the above discussion, this uncertainty can be diminished by a small shift of the intersection point to a nearly arbitrarily chosen value $({\rm d}R_{\rm crm})_0 - 7 = 20$ pm.

It is worth noting that the range of d$R_{\rm m}$ includes that of the empirical parameter ρ in the B–M potential (1). This parameter varies from 23 pm in CsF to 38 pm in CsI molecules (Varshni & Shukla, 1963). Within the model of deformable spheres (Butterfield & Carlson, 1972; Gilbert, 1968; Narayan & Ramaseshan, 1978) it consists of the parameters of individual ions: $\rho = \rho_j + \rho_i$. The sum $\rho_j + \rho_i$ varies bewteen 25.7 pm (LiF) and 36.2 pm (KI) and tends to increase from LiF to CsI, in general (Narayan & Ramaseshan, 1978). The parameter ρ has the dimensionality of length and indicates the softness of the bond (Butterfield & Carlson, 1972): it gives the distance at which the B–M potential decreases $e \simeq 2.73$ times. Although ρ is not a variable in the repulsion potential, it is determined only for the equilibrium state of molecules and could be referred to as the deformation d$R_{\rm m}$.

Thus, there are grounds to assume that within the empirical model, *extension of IDs in alkali halides from diatomic molecules to crystals leads to the separation of closed electron shells of counterions* and (2) and (3) are valid. This allows one to obtain a novel set of approximate values of ionic radii. With regard to the conventional accuracy of the determination of radii, about ±5 pm (Batsanov, 1986), and the roughness of the proposed model, it is allowable to accept the value obtained above, d$R_{\rm cr} = 20$ pm, as being constant for all alkali halide crystals.

As a starting point in estimating the ionic radii, the crystal radius of the F$^-$ ion (119 pm) (Fumi & Tosi, 1964) was chosen, based on the analysis of electron-density maps (Witte & Wolfel, 1958; West, 1988), with the goal of comparing the results with the crystal radii (CR) and effective ionic radii (IR) for the coordination number (CN) 6, represented in Table 1 of Shannon (1976). It is worth remembering that CR differs from IR only by a constant factor of 14 pm: for cations CR > IR and for anions CR < IR (Shannon & Prewitt, 1969; Shannon, 1976). The cation radii were derived by applying (2) to fluorides. Then the radii of Cl$^-$, Br$^-$ and I$^-$ were estimated and averaged.

The results of the evaluation are presented in Table 2. The derived radii of the cations are smaller by 5–14 pm than the corresponding IR radii, but agree to within ±4 pm, on average, with the respective Pauling (1960) radii. The mean values of the anion radii are very close to the corresponding CR radii of the Shannon–Prewitt system. Equations (2) and (3) imply that $R_{\rm c}$ and $R_{\rm a}$ are the radii of the free ions. For cations, the free-ion electron densities have usually been found to be sufficient to evaluate the interaction energy in crystals by the Hartree–Fock equations (Allan & Mackrodt, 1994). The obtained values of ionic radii agree with those estimated by Butterfield & Carlson (1972) for a definite level of charge density (BCR): 69, 95, 125, 137 and 153 pm for respective cations and 118, 145, 154 and 166 pm for anions. Comparatively lower values of the BCR radii of the larger ions, especially of the anions, correspond to the increase of the

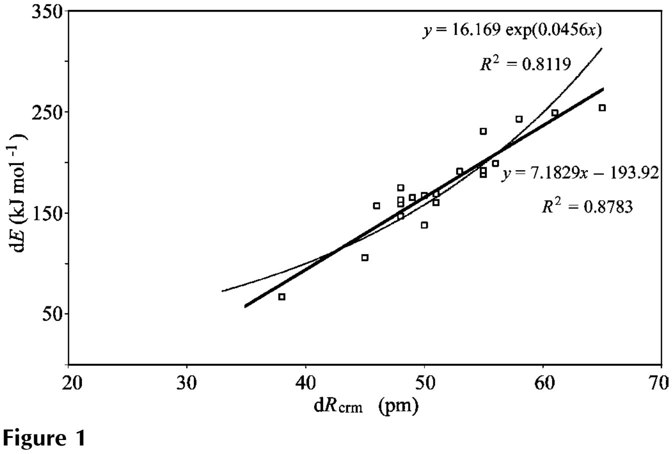

Figure 1
Correlation between dE and d$R_{\rm crm}$.

Table 2
Deformations and radii of monovalent ions (pm).

IR_c and CR_a are the effective ionic radius (IR) of a cation and the crystal radius (CR) of an anion (Shannon, 1976), respectively; $\langle R_a \rangle$ and $\langle \Delta R_a \rangle$ are the mean arithmetic values of an anion radius and its deviation. Entries in bold are the final calculated values.

	Anion											
	F^-			Cl^-			Br^-			I^-		
Cation	R_m	dR_m	R_c (IR_c)	R_m	dR_m	R_a	R_m	dR_m	R_a	R_m	dR_m	R_a
Li^+	156	25	**62** (76)	202	35	175	217	38	193	239	41	218
Na^+	193	18	**92** (102)	236	26	170	250	29	187	271	33	212
K^+	217	30	**128** (138)	267	28	167	282	28	182	305	28	205
Rb^+	227	35	**142** (152)	279	30	167	295	28	181	318	31	207
Cs^+	235	45	**161** (167)	291	36	166	307	35	181	332	31	202
$\langle R_a \rangle$ ($\langle \Delta R_a \rangle$)			**119**			**169 (3)**			**185 (4)**			**209 (5)**
CR_a			119			167			182			206

Table 3
Calculation of the electrostatic force constant in 'clusters' of the ordered $B1$ structure along the [001] direction.

	α_f					
Layer	2 × 2 × 2	4 × 4 × 4	8 × 8 × 8	12 × 12 × 12	16 × 16 × 16	20 × 20 × 20
1	−0.356	−0.318	−0.316	−0.312	−0.311	−0.310
2		+0.140	+0.127	+0.125	+0.125	+0.123
3			−0.077	−0.076	−0.075	−0.073
4			+0.049	+0.049	+0.049	+0.048
5				−0.031	−0.030	−0.030
6				+0.017	+0.016	+0.016
7					−0.017	−0.016
8					+0.007	+0.007
9						−0.013
10						+0.013
Total	−0.356	−0.178	−0.217	−0.228	−0.236	−0.235

Table 4
Calculation of the force constant within an area where $t_j < \delta t$.

	α_f	
Layer	$\delta t = 0.0007$	$\delta t = 0.0002$
First	−0.3010	−0.2991
Second	−0.0023	+0.0006
Total	−0.3033	−0.2985

number of electrons from 0.076 (Li^+) to 0.730 (Cs^+) and from 0.639 (F^-) to 1.500 (I^-) outside a sphere confined by the BCR radius (Butterfield & Carlson, 1972).

Calculated values of the anion radii in Table 2 scatter widely and the deviations increase from Cl^- to I^-. This may be caused by polarization of the ions and by the quantum-mechanical uncertainty in ion sizes, neither of which are accounted for by the static model of deformable spheres. It is likely that the observed tendencies of variation of increments ΔR_m and ΔR_{cr} (Table 1) have the same nature. For instance, an increase of the deformation dR_m from 25 pm (LiF) to 35 pm (LiCl) in comparison with the respective values 18 pm (NaF) and 26 pm (NaCl) would extend ΔR_m from 37 pm (NaF–LiF) to 39 pm (NaCl–LiCl), but it actually decreased to 34 pm (Table 1). In the sodium/lithium bromide and iodide pairs this difference is even smaller. Similar changes are characteristic for ΔR_{cr}. In contrast, the K—Na halide pairs demonstrate a considerable increase of ΔR_m and a decrease of ΔR_{cr} from fluorides to iodides (Table 1).

3.2. Comparison of the forces acting between cations and anions in molecules and crystals

The results of calculations for a set of cubic 'clusters' of the ordered $B1$ structure, made according to (13), show that in clusters with volumes larger than $V = (16 \times 16 \times 16)R_{cr}^3$, the resulting force of electrostatic attraction is approximately constant and 4.25 times weaker than that in a free molecule given that other parameters are equal (Table 3). If F_{001} is calculated within an area restricted by a surface where $t_j < \delta t$ (13), its value is 3.35 times[1] less than that in the initial molecule (Table 4). From comparison of α_f of layers 1 and 2, one can see that in the final crystal structure *only attraction to the nearest-neighbour layer is important*.

Furthermore, ions from the other hemispace attract the given ion with a force of the same magnitude. One can approximate this situation by the interaction between a central cation and two anions in a linear triatomic $X—M—X$ pseudomolecule. The first significant difference between the usual MX_2 molecules and this pseudomolecule is the absence of electrostatic repulsion between the anions in the latter. Actually, Table 4 demonstrates that there is a very weak interaction between a given ion and the second layer. One can now predict the extension of ID due to the weakening of the electrostatic attraction, given that the repulsion potential for the corresponding molecule is correct. If the B–M repulsion potential (1) and the value $\alpha_f = 0.299$ (Table 4) are used, this distance equals 1.2ρ, which does not differ significantly from the recommended values dR_m and certainly is shorter than dR_{crm} in alkali halides (Tables 1 and 2).

The phenomenon of the lengthening of IDs from molecules to crystals is well studied experimentally and theoretically. Electron diffraction measurements (Hartley & Fink, 1988; Lapshina & Girichev, 1991; Lapshina *et al.*, 1989) and *ab initio* calculations (Solomonik & Sliznev, 1998) of diatomic molecules MF and dimers M_2F_2 (M = Li, Na, K) show that the IDs increase from 156.39, 192.60 and 217.15 pm to 173.7, 207.2 and

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[1] Note that the sum (α_f) is close but not equal to the Madelung sum divided by the coordination number ($\alpha/6 = 0.291$).

Table 5
Results of evaluating the increments dR_m and dR_{cr} in alkaline earth fluorides.

Cation	R_m (pm)	dR_{crm} (pm)	D_0 (kJ mol^{-1})	IR (pm)	dR_m (pm)	dR_{cr} (pm)
Be^{2+}	140	21	635.4	45	24	−3
Mg^{2+}	177	22	517.9	72	14	8
Ca^{2+}	210	27	560.5	100	9	18
Sr^{2+}	220	31	549.0	118	17	14
Ba^{2+}	232	36	566.0	135	22	14

Table 6
Results of evaluating the increments dR_m and dR_{cr} in alkaline earth oxides.

Cation	R_m (pm)	dR_{crm} (pm)	D_0 (kJ mol^{-1})	IR (pm)	dR_m (pm)	dR_{cr} (pm)
Be^{2+}	133	32	446	45	38	−6
Mg^{2+}	175	35	423	72	23	12
Ca^{2+}	182	58	477	100	44	14
Sr^{2+}	192	66	469	118	52	14
Ba^{2+}	194	82	569	135	67	15

236.4 pm, respectively. Rhombic geometries with IDs ranging from 274 pm to 337 pm were observed in dimers Na_2Br_2, K_2Br_2, Rb_2Br_2 and Cs_2Br_2 in the vapour phase (Hartley & Fink, 1987), in contrast to the range 250–307 pm in respective monomers (Table 2). A study of the X-ray absorption spectra of the Na_4Cl_4 cluster shows that the ID is about 250 pm compared with 236 pm in a NaCl molecule (Yalovega *et al.*, 2000). In $(MgO)_{1/13}$ clusters, the interatomic distance increases from 175 pm to 199 pm (de la Puente *et al.*, 1997). Similar structural relaxations were predicted for alkali halide clusters $(MX)_{1/10}$ (Aguado *et al.*, 1997). These data demonstrate the leading role played by the electrostatic repulsion in the increase of ID from diatomic molecules to small clusters. The lower values of dR_{crm} in alkaline earth fluorides MF_2 (Table 5) compared with those in alkali halides MX (Table 1) and alkaline earth oxides MO (Table 6) are also caused by this effect.

There is another crucial difference between the usual MX_2 molecules and the $X—M—X$ pseudomolecule. In the former, the cation is certainly a centre of attraction. In the latter, it is not. Here anions are also attracted by all other ions in *opposite* hemispaces. The most natural way to demonstrate the effect of the phenomenon on ID is to compare IDs in the bulk and at the surface of a crystal. Madelung (1919) predicted the shortening of ID between the first and second surface layers. There are many experimental facts implying the relaxation of the surface layer(s) inward (Brown *et al.*, 1999; Jona & Marcus, 1988; Somorjai, 1981, 1990). Most of the work was carried out with metals, although some oxides were also studied. In metals, the relaxation of the ID is up to 15% (Jona & Marcus, 1988). The effect of contraction is usually small (4–5% of the bond lengths) and is sometimes presumably obscured by the experimental [low-energy electron diffraction (LEED), extended X-ray absorption fine structure (EXAFS) and other methods] and theoretical uncertainty (Somorjai, 1981). According to Somorjai (1981), the precision is about ±10 pm. The amplitudes of the atomic oscillations are of the same order. The bond-length contractions at surfaces are consistent with the observations made when adsorbates are deposited on these surfaces: the shortened bond lengths are systematically lengthened again (Somorjai, 1981). The different wavelengths of IR absorption (λ_a) and reflection (λ_r) spectra in alkali halides also indicate a shortening of IDs on the surface: $\lambda_r < \lambda_a$ (Kittel, 1956).

So, the positions of ions in the outermost surface layer are governed by the polar electrostatic and, because of the inevitable shortening of ID and overlapping of ions' electron shells, covalent attractions and by repulsion of the electron shells. As mentioned above, every ion in any electroneutral layer within a hemispace of the ordered structure is attracted only by the *nearest-neighbour* layer. It is evident that the altered bonding at the surface would slightly affect the equilibrium conditions of ions only in *several* near-surface layers, although it is difficult to provide a rigorous mathematical proof. An unlimited shortening of ID in a finite system of point charges would be caused by the merging of the negative and positive point charges at the surface. This maintains the polar character of the attraction. In crystals, the ions do not merge and continue to attract inner ions/layers. Therefore, in the bulk of the structure, the equilibrium positions of ions and IDs are not governed by repulsion of the electron shells but by attractive forces acting in opposite directions. This is the classical condition of equilibrium of ions in a crystal lattice. Consequently, dR_{cr} appears mainly as a result of the action of attractive forces in opposite directions and R_{cr} does not provide true information about the sizes of ions: it may be smaller, equal to or larger than the sum of the ionic radii.

4. Discussion

4.1. Molecules

The results obtained in §3.1, support the validity of the simple static model of deformable spheres for alkali halide molecules as a first-order approximation. Corrections can be made to account for the polarizability of ions. According to Bader *et al.* (1987), the net charge and the polarizability affect the value of the dipole moment, μ, in an approximately equal measure. From the analysis made in § 3.1, particularly from the observed correlation between the values of the deformation dR_m ($= dR_{crm} - 20$), dissociation energy D_0 and net ionic charge e^* (Table 1 and Fig. 1), one may conclude that polarization plays a subordinate role in the alkali halide molecules and, probably, contributes to the overlapping. Thus, the charge transfer in these molecules is not complete and the experimental values e^* exhibited in Table 1 closely relate to real ionic charges. Accordingly, there are grounds for assuming that the interatomic interaction in molecules cannot be described solely in terms of the scalar energy and electronegativity (electrochemical potential). One should also account for geometrical constraints of the charge transfer, namely for the polar character of electrostatic attraction, which compresses the ions.

It is impossible to fulfil similar analyses for the alkaline earth fluoride and oxide molecules. However, there is an interrelation between the dissociation energies and differences $dR_{\rm crm}$ (Tables 5 and 6), similar to that in alkali fluoride molecules (Table 1). The strongest deformations of the oxide molecules (Table 6) qualitatively correspond to relatively small values of their dipole moments (Huber & Herzberg, 1979; Yoshioka & Jordan, 1981) and are in a satisfactory agreement with the proposed model, which assumes that the degree of deformation (overlapping) and charge transfer are governed by electrostatic attraction of ions.

4.2. Crystals

The obtained results indicate that the extension of bonds in alkali halides results in the appearance of an empty space between the cation's and anion's electron shells in crystals, from the viewpoint of covalent bonding. The same seems to be valid for alkaline earth fluorides and oxides. The more electronegative small Be^{2+} cation definitely tends to preserve covalent bonding in crystals. This could be explained not only by its ionization potential and electronegativity but also by the high ionic strength (q/R_c) and hence the polarization effect of the cation on the anion and by residual compression of the ions. In alkali halide crystals, polarization is also important, but it might not relate to covalent bonding, which is absent according to the results obtained in §3.1 and §3.2. Actually, the range of variation of the refraction index (n_D) decreases from lithium to caesium halides (Batsanov, 1986): 1.392 (LiF)–1.955 (LiI), 1.326 (NaF)–1.774 (NaI), 1.352 (KF)–1.667 (KI), 1.396 (RbF)–1.647 (RbI), 1.478 (CsF)–1.661 (CsI). The higher values of the refraction index for higher CNs (Batsanov, 1986) point to a dependence of n_D on ID, and the given values of the index indicate some intrinsic properties of ions (note the lowest index for NaF, which consists of the hardest ions according to the data of Table 1). However, the highest value of n_D in LiI apparently indicates that the iodine ion is strongly polarized.

Gibbs *et al.* (1997) concluded that the average separations between bonded atoms in oxide, fluoride and other kinds of crystals are largely independent of the long-range forces. Based on the data obtained and the considerations presented in §3.2, one can conclude that it is necessary at least to take into account the action of attractive forces in opposite directions. The relative magnitudes of electrostatic forces might also be important. For example, the larger cation–anion ID and the lower difference between cation–anion and anion–anion IDs in CsCl for the denser *B*2 structure compared with the eutactic *B*1 structure (O'Keeffe, 1977) could be caused by the weaker forces of electrostatic attraction and repulsion. The variation of IDs within irregular coordination polyhedra also could somehow relate to the different values of attractive electrostatic forces. The proposed model of extension of ID from diatomic molecule (CN = 1) to crystal (CN = 6) is closely related to the known 'bond-strength–bond-length' relationships (Pauling, 1960; Brown, 1988; O'Keeffe & Brese, 1991; Gibbs *et al.*, 1998). For instance, the lengths of a bond in various crystal structures can be estimated by the following equation:

$$R = R_0 - 0.37 \ln S, \tag{14}$$

where $S = V/{\rm CN}$, V is the cation oxidation state (formal charge), R_0 is a distance constant for the appropriate cation–anion pair and ${\rm CN} \geq 2$ (Brown, 1988). This equation is connected to the short-range B–M potential (Jansen *et al.*, 1992; Urusov, 1995) and does not account for the possible empty space between ions. When applied to ionic crystals, (14) reflects, to some extent, just the dependence between the interatomic distance $R_{\rm cr}$ and the long-range Coulomb force of attraction. Therefore, it would be worthwhile to compare the resulting electrostatic forces acting along a given direction in a crystal. The resulting forces are easily calculated based on standard crystallographic formulae.

If CNs do not depend on the cation–anion ratio, as in the antifluorite structure, cations coordinated in crystals with up to four anions would be deformed and would retain covalent bonding. For instance, one can conclude that there is a considerable covalent contribution to the attraction between magnesium and oxygen in spinel (sp), $MgAl_2O_4$, because its $dR_{\rm cr}$ is negative: using the data in Table 6 for periclase (pr), MgO, $dR_{\rm cr}({\rm sp}) = R_{\rm cr}({\rm sp}) - (R_{\rm cr} - dR_{\rm cr})({\rm pr}) = 192 - (210 - 12) = -6$ pm. It is concordant with the small coordination number of the cation (CN = 4) and the high hardness of spinel (Frye, 1981). Conversely, increasing CN from 4 to 8 and above would lead to a greater increase in the separation of the counterions' electron shells. In these terms, the dependence of cations' sizes on coordination numbers (Shannon & Prewitt, 1969; Shannon, 1976) can be reinterpreted. For instance, the effective radius (IR) of a sodium ion varies from 102 pm to 139 pm for CN = 6–12 (Shannon, 1976). This is a straightforward consequence of the quantum-mechanical uncertainty of ions' sizes. However, it is obvious that such a wide range would result in a corresponding difference between the strengths of electron densities and hence of covalent binding and/or repulsion. Altogether, the combination of more or less constant ionic radii with the deformations $dR_{\rm m}$ and intershell intervals $dR_{\rm cr}$ is as flexible as the system of Shannon–Prewitt tailor-made radii, but it is believed to have a more correct physical ground. It is worth mentioning that Zachariasen (cited by Kittel, 1956) in an unpublished work proposed an equation like (2) and (3) and obtained values of the increment Δ_N ($\simeq dR_{\rm m}$ and $dR_{\rm cr}$, $N \simeq {\rm CN}$) varying within the range [−50, 0, 19 pm] for CN = 1, 6 and 12, respectively.

According to the proposed model and obtained data, bonds of monovalent and, in most of the structures, divalent ions with halogens and oxygen have purely or essentially ionic character. In the bonding of highly charged cations (Si^{4+}, Ti^{4+}, Al^{3+} *etc.*) with oxygen, there should be a constantly present covalent contribution, regardless of the coordination number. It is difficult to decide where the wavefunctions or electron density of ions can be neglected. The radii and deformations obtained in §3.1 and Appendix *A* can be used as a zero-order approximation and should be specified based on quantum-mechanical calculations of the radii of free ions and accurate analyses of electon-density maps of crystals and molecules.

It is noteworthy that there are two different ways to describe empirically the static equilibrium condition of ions in a crystal: equalizing either the attractive electrostatic forces acting in opposite directions or the electrostatic and short-range repulsion forces as derivatives of the respective potentials as in (1). In general, these models deal with different sizes of ions. While the former is physically more correct, the latter is mathematically more suitable. Many excellent simulations of crystal structures and calculations of their properties have been made during the past three decades, for example, by C. R. A. Catlow's group with the help of empirical repulsion potentials (Freeman & Catlow, 1992; de Leeuw *et al.*, 2000; Wright *et al.*, 1994). On the other hand, the empirical potentials are rather crude (Crocombette, 1999), and to simulate a wide range of chemical compositions in layer silicates by transferable potentials (Sainz-Diaz *et al.*, 2001), for example, is hardly possible.

5. Conclusions

The most essential difference between the interatomic interaction in ionic crystals and molecules is the action of considerably weakened attractive electrostatic forces in opposite directions in the former.

In molecules, the charge transfer cannot be complete because the Coulomb attraction is polar and there is an interdependence between the electrostatic attraction, covalent bonding and electronic repulsion. Here the interatomic distance certainly depends on the sizes of the ions. Ions considered as static deformable spheres are compressed.

In crystals, the compression is not obligatory for every ion: it is present only in several near-surface layers. In the bulk of a crystal, the ions may not have common boundaries. However, the interaction of highly charged ions in substances like SiO_2, TiO_2 and Al_2O_3 would retain covalent character.

The sum of the radii of the cation and the anion is definitely larger than the ID in the molecule, but it can be smaller, equal to or larger than that in the corresponding crystal.

APPENDIX *A*
Approximate evaluation of increments dR_m and dR_{cr} in alkaline earth fluorides and oxides

Tables 5 and 6 present data for R_m, dR_{crm}, D_0 and the estimated dR_m and dR_{cr} in fluorides and oxides of alkaline earth metals and beryllium. Other alkaline earth halides and chalcogenides have not been analysed because of the variety of structures, the complicated geometry of the molecules, or the lower electronegativity of S, Se and Te. The increments dR_m and dR_{cr} were estimated using the cation IR and anion CR radii (F^- 119 pm, O^{2-} 126 pm) according to Shannon (1976) and (2), (3) and (4).

From comparison of the data in Tables 1, 5 and 6 it follows that alkaline earth fluorides have the smallest values of dR_{crm}. This is evidently caused by the Coulombic repulsion between fluorine ions ($F^{0.n-}$—$F^{0.n-}$) in the molecules. The common feature in all of these tables is the relation between dR_{crm} and D_0. This demonstrates the strengthening of covalent bonding in molecules from MgF_2 and MgO to BaF_2 and BaO like that from NaF to CsF. Comparatively low values of the increment dR_{crm} in BeF_2 and BeO are not an exception. In crystal structures of β-quartz and wurtzite, beryllium is four-coordinated and retains covalent bonding (Blatov *et al.*, 1999; West, 1988). In other words, it is still deformed, though to a lesser extent. For this kind of compound, the inequalities d$R_m >$ dR_{crm} and d$R_{cr} < 0$ hold.

The trends of variation for the obtained values of the increments dR_m from beryllium to barium (Tables 5 and 6) correspond to that of D_0. The values of the increments dR_{cr} demonstrate that in the alkaline earth fluoride and oxide crystals the counterions tend to be separated by an empty space like those in the alkali halide crystals. The increment tends to increase from Be to Ba fluorides and oxides. This tendency satisfies the rules of increasing bond length [Brown (1988); equation (14) in §4.2 of this paper] and ionicity (Pauling, 1960) with increasing CN. The Ca^{2+} ion is probably larger ($R_{Ca} \simeq 105$ pm), because the value of d$R_{cr} = 18$ pm in CaF_2 is too high compared with the values for SrF_2 and BaF_2 (Table 5). The difference between the radii of F^- and O^{2-} ions is probably larger as well, because the attraction between Mg^{2+} and O^{2-} ions in MgO is stronger and dR_{cr} is smaller than between Mg^{2+} and F^- in MgF_2.

Lower values of deformations in Ca, Sr and Ba fluorides compared with those of MgF_2 (Table 5) can be explained by a different relation between the IDs and the overlap of electron clouds in respective molecules. The former molecules are bent (Gillespie & Hargittai, 1991). Both the nonlinearity of the molecules and the great difference between $D_0(CaF_2)$ and $D_0(MgF_2)$ point to the considerable participation of elongated σ-orbitals in bonding. In this instance, the overlap can be strong regardless of the large internuclear distance. In crystals, the ions become spherical. In such a case, the real overlapping (deformation) of counterions' electron shells in molecules is not equal to the deformation of the spheres and dR_{crm} is not a sufficiently reliable parameter. Hence one would expect the true deformations in Ca, Sr and Ba fluoride molecules to be about 10–15 pm larger than the dR_m values exhibited in Table 5.

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