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Perturbation-theoretical-model calculation of the lattice mechanics of the NaF and RbF crystals in the Watson potential approximation

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A simplified version of the perturbation-theoretical-model approach to ionic solids developed by Basu and Sengupta has been employed for calculating the different lattice-mechanical properties of the two low-polarizability ionic crystals. Although this is not a microscopic calculation, the interesting feature of the method is that the only input data necessary for predicting the crystal properties are the Hartree-Fock wave functions of the constituent ions. In addition, the present investigation for the first time makes an attempt to study the effect of the alteration of the free-ion wave functions, when the ions are put in a crystal, on the lattice-dynamical properties. The effect of the crystal environment is thought to be simulated by the Watson potential. The calculated properties with and without the potential give a rough estimate of the order of magnitude of this effect. It is found that certain properties, namely, the dielectric properties and some phonons in the symmetry directions that depend on the excited states of the crystal, are rather sensitive to this effect which varies from crystal to crystal. Apart from this, a unified treatment of the cohesion, the phase transition, and the elastic, the dielectric, and the vibrational properties of the NaF and RbF crystals is presented without any adjustable free parameter. In view of the simplicity of the approach, the overall agreement obtained is satisfactory. Finally the reliability and the limitations of the present method of estimating the effect of the surroundings are critically discussed.

I. INTRODUCTION

Starting from a very general form of the energy expression for an assembly of ions occupying arbitrary configuration the perturbation-theoretical-model approach within the point dipole approximation provides a satisfactory semimicroscopic description of the lattice-mechanical properties of the ionic solids in general.[1–4] Moreover, it has been found that, in addition to describing the lattice-mechanical properties, the calculation employing this perturbation-theoretical-model scheme is also capable of describing the collective response of the electrons, namely, the plasma frequencies in insulators.[5] However, the execution of a full-fledged program of this approach for any crystal still requires quite tedious numerical calculation. On the other hand, we have shown in a recent work[6] that at least for a group of ionic solids, and in particular for the RbF crystal whose polarizability is rather low (characterized by the value of the Szigeti charge), drastic simplification in calculation may be achieved if we totally neglect the short-range polarization effects. Bose *et al.*[6] have discussed in detail the justification of this approximation for a certain group of ionic crystals. Despite this approximation and in view of the fact that the only input data used in the calculation are the Hartree-Fock wave functions of the corresponding free ions the overall description of the lattice mechanics is rather satisfactory except for some of the dielectric properties. Furthermore in recent work we have speculated that the remaining discrepancies between theory and experiment may be solely attributed to the neglect of the short-range polarization effects.[6] This appears to be only partly true according to our present investigation and the earlier calculation of the lattice mechanics of the KCl and NaCl crystals.[1] We shall demonstrate in this work that at least a part of the discrepancy may be explained by including the effect of the surroundings on the wave functions of the free ions.

In all the earlier applications of the perturbation-theoretical-model approach we have neglected the effect of the surroundings on the ionic wave functions when the ions are transferred to a lattice. It is understandable that it is extremely difficult to properly take account of this effect. It is the purpose of this work to first develop a rough idea about the order of magnitude of this effect on the different crystal properties. Within a rather simplified version of the perturbation-theoretical-model approach we shall try to make an estimate of the same through an artificial simulation of the crystal surroundings employing the Watson-spherical-potential approximation.[7] This calculation will provide us with insight particularly into the properties dominantly dependent on the excited states of ions in the crystal. The choice of both the particular version of the perturbation-theoretical-model approach as well as the crystals for which this version is suitable has been motivated by the fact that since other complicating factors are less important in these cases, the effect of the surroundings may be clearly projected through a rather simple calculation.

Before we proceed with our calculation it must be clearly mentioned that the present approach is not a microscopic calculation. It is only a semimicroscopic one in the sense that there is no free parameter and the only input data employed are the Hartree-Fock wave functions of the ions. No crystal data are necessary except the structure.

As we have stated that it is the excited state which will be strongly influenced by the surroundings we shall concentrate on the dipole polarization of an ion in a crystal. Banerjee *et al.*[8,9] have discussed in detail both the general expression and the factors responsible for the change in the polarizability value of an ion when the same is transferred to a lattice. We shall not go here into the details of the mechanism of the change. Speaking roughly there are two types of effects: One is due to the electric field created by the other ions at the site where the ion in question is located, and the other is due to the overlap effects of the neighboring ions. Since in the present application we are not considering the short-range polarization effects, these effects are assumed to be small. However, even the inclusion of the effect of the electric field is too difficult. Watson[7] suggested a method of considering this effect by approximating the real potential experienced by the charge cloud of an ion in a crystal by a spherical potential. There is some arbitrariness in selecting the radius of this sphere which is a parameter. Usually this is either kept arbitrary or may be fixed from some physical considerations that we discuss later.

Starting from the Hartree-Fock wave functions of the Rb^+, Na^+, and F^- ions we shall calculate the different lattice-mechanical properties of the RbF and NaF crystals with and without the Watson potential and shall compare the results with each other and with experiment.

From the value of the Szigeti charge of the NaF crystal, which is $0.88e$, we find that its deviation from unity is somewhat larger compared to that of the RbF crystal which is $0.95e$. Although the NaF crystal is not a high-polarizability crystal it is not very low either, and we do not expect the present calculation to be as accurate as in the case of the RbF crystal. Its choice has been dictated by another interesting consideration the investigation of which is one of our main purposes. The effect of the surroundings will be more pronounced in the NaF crystal compared to the RbF crystal. It is due to the large difference in the polarizability values of its constituent ions. The ratio of the free-ion polarizability values of the ions in the NaF crystals, $a_-/a_+ \sim 10$, may be compared with that of the RbF crystal which is ~ 1. Upon comparing the final results of in-crystal calculations of the two solids we shall find that this ratio is an important parameter which conveys an idea before explicit calculation whether the effects of the environments on the positive and the negative ions will mutually cancel in various lattice-mechanical properties. From the present investigation it will be found that the larger the ratio the more pronounced the cancellation effect.

In the next section we shall briefly describe the Watson potential and shall discuss the considerations for fixing its parameter. Then we shall give a broad outline of the basic theoretical framework and the method of calculation. In the last section we shall discuss the two sets of results for each crystal together with the limitations of the present method of estimating the effect of the crystal environment.

II. THEORY

The details of the theoretical considerations and some applications of the approach have been discussed in a series of previous works.[1–6,8,9] The basic idea is to construct an energy expression for a system of interacting ions and then to introduce the approximations systematically to yield a manageable expression without sacrificing the major effects, and finally to extract the parameters describing the interactions from the wave functions of the free ions. In the above calculations we have not considered the effect of the surroundings on the free-ion wave functions. We shall discuss in the present work that certain properties, in particular the polarizability of the ions, some phonon branches in the symmetry directions, and the macroscopic dielectric properties, are rather sensitive to this effect to be simulated by a simple potential. Although it is demonstrated that the free-ion wave-function description of the crystal properties is a reasonable first approximation, for a more accurate calculation this effect needs to be included.

A. Watson potential

Watson[7] suggested a simple model to simulate the solid. In particular he showed that for the O^{2-} ion a spherical potential well of opposite charge around the ion would stabilize it. The free oxygen ion is not a stable ion. The model has been exhaustively used to calculate the various ion properties. Muhlhausen and Gordon[10] have discussed the effect of this stabilizing potential on the charge densities of some ionic crystals and its effect on the static properties, but we shall presently see that this effect is more pronounced when the excited states of the ions in crystal are involved.

The crystal potential is generated by a hollow charged sphere which surrounds the ion. The magnitude of the charge is equal to and opposite in sign to that of the enclosed ion. The form of the potential is given by (see Fig. 1)

$$U_W(r) = \begin{cases} \dfrac{q}{r_0} & \text{for } r \le r_0, \\[2ex] \dfrac{q}{r} & \text{for } r > r_0, \end{cases} \tag{1}$$

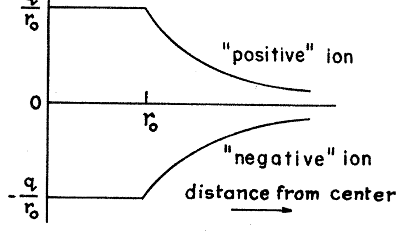

FIG. 1. Watson potential r_0 is the radius of the charged sphere. Beyond r_0 the behavior of the potential is Coulombic.

where r_0 is the radius of the sphere. Instead of keeping r_0 as a free parameter there are several suggestions for fixing r_0 from various physical considerations. For the ionic solids since the actual potential seen by an ion is the Madelung potential, the radius may be simply fixed by the following relation:

$$r_0 = l/M \ , \tag{2}$$

where l and M are the lattice constant and the Madelung constant for the appropriate structure. It may be mentioned here that the radius remains the same for both the positive and the negative ions while the charge changes sign with the ion. From the nature of the potential chosen it is apparent that this will cause a reduction and an enhancement of the free-ion polarizability values of the $-ve$ and $+ve$ ions, respectively. Many other empirical studies[11,12] are also consistent with the above fact.

B. Energy expression

Following our earlier work[6] for low-polarizability ionic crystals the energy of an assembly of interacting ions simplifies to

$$W = \tfrac{1}{2} \sum_{i,j}{}' \frac{z_i z_j}{r_{ij}} - \sum_i \vec{\mu}_i \cdot \vec{\mathrm{E}}_i^m - \tfrac{1}{2} \sum_i \vec{\mu}_i \cdot \vec{\mathrm{E}}_i^\mu + \sum_i \frac{\mu_i^2}{2a_i}$$

$$+ \tfrac{1}{2} \sum_{i,j}{}' \phi(r_{ij}) + \tfrac{1}{2} \sum_{i,j}{}' \phi(r'_{ij}) \ , \tag{3}$$

where, as usual, the first term represents the Coulomb interaction between the ions and the next three terms represent the interaction between the dipole and the monopole field, the dipole and the dipole field, and the dipolar self-energy, respectively. The last two terms give the overlap interaction between the nearest neighbors and between the next-nearest neighbors (considered for anions only).

For the first set of calculations the different parameters describing the interactions in (3) are evaluated using the free-ion wave functions as in Ref. 6. For the second set of calculations employing the Watson potential, Eq. (3) may be interpreted as follows. The assembly of ions considered whose energy is given by Eq. (3) no longer refers to those of the free ions. We may think of each ion in this assembly to be described by the wave functions which have undergone alteration due to the effect of the Watson potential. The spherical symmetry being preserved, there is no charge transfer and each ion maintains its total charge as in the free ion. It implies that the first term alone remains unchanged, while all other terms are affected. Now, the assembly of these so-called dressed ions is our starting point. Hence if we simply reinterpret the parameters occurring in Eq. (3) as referring to these dressed ions instead of the free ions all the relevant equations remain formally unchanged. With this new interpretation Eq. (3) is sufficient to calculate all the lattice-mechanical properties provided we obtain the parameters for the dressed ions. The method of determination of the parameters will be discussed in a later section. Equation (3) with the following adiabatic condition,

$$\frac{\partial W}{\partial \mu_i} = 0 \ , \tag{4}$$

will be used for the investigation of the dynamical properties.

C. Dynamical and dielectric properties

Expanding r_{ij} in Eq. (3) about the equilibrium configuration and retaining terms up to second order in energy, the dynamical equation is obtained in the usual six-vector notation,

$$\omega^2 m \underline{U} = \underline{R}\,\underline{U} + \underline{R}'\underline{U} + \underline{Z}\underline{C}[Z - (\mathbb{1} - \alpha\underline{C})^{-1}\alpha\underline{C}\underline{Z}]\underline{U} \ , \tag{5}$$

where the symbols have the same significance as in Ref. 6.

The corresponding dielectric equations are similarly derived in the $\vec{\mathrm{q}} \to \vec{0}$ limit of the dynamical equation, and the relevant Huang relations are given by

$$b_{11} = -\frac{1}{\overline{m}} \left[R_0 - \frac{(4\pi/3)Z_1^2}{v_0(1 - 4\pi\alpha_e/3v_0)} \right]$$

and

$$b_{22} = \frac{\alpha_e}{v_0} \frac{1}{1 - 4\pi\alpha_e/3v_0}, \quad b_{12} = \frac{Z_1}{(\overline{m}v_0)^{1/2}} \frac{1}{1 - 4\pi\alpha_e/3v_0} \ , \tag{6}$$

where $\overline{m}$ is the reduced mass of the ion pair, $R_0 = -R\,|_{q \to 0}$ and $\alpha_e = \alpha_1^c + \alpha_2^c$; α^c's are not the free-ion polarizabilities as assumed earlier, but they represent the in-crystal values of the same obtained by subjecting the free ions to the Watson spherical potential. The three macroscopic dielectric properties, the high- and the low-frequency dielectric constants, ϵ_∞ and ϵ_0, and the reststrahlen frequency ω_0, are related to b's by

$$\epsilon_\infty = 1 + 4\pi b_{22}, \quad \epsilon_0 = \epsilon_\infty - 4\pi b_{12}^2/b_{11}, \quad \omega_0^2 = -b_{11} \tag{7}$$

D. Static properties

In order to calculate the static properties we use the parameters given in Table I. The specific properties we have considered are the equilibrium lattice constant, the cohesive energy, the second-order elastic constants, the polymorphic phase transition, and the consequent volume change. All calculations refer to harmonic values. Assuming the potential parameters remain unchanged we have arranged the ions on a CsCl lattice and have solved numerically for the equilibrium configuration of the crystal in that phase. Since the relevant equations are well known we do not reproduce them here.

E. Determination of the parameters

The parameters involved in the different interactions are derived from the Clementi wave functions of the corresponding ions.[13] They belong to two groups. One group, namely those describing the overlap interactions, depends solely on the ground-state wave functions of the ions. The other group depends critically on the excited states. We have followed the method described in our ear-

TABLE I. Values of parameters.

Crystal	b (10^{-8} erg)	ρ (Å)	b' (10^{-12} erg cm^{-1})	a (Å^{-1})	K (Å)	α_+ (10^{-24} cm^3)	α_- (10^{-24} cm^3)
NaF	0.3449	0.250	-0.1577	1.988	2.883	0.140 (F)[a] 0.147 (W)[b]	1.399 (F) 1.033 (W)
RbF	0.4656	0.279	-0.1577	1.988	2.883	1.280 (F) 1.375 (W)	1.54 (F) 1.177 (W)

[a] Free-ion calculation.

[b] Watson potential calculation.

lier work to find the parameters b and ρ of the Born-Mayer potential $\phi = b\exp(-r/\rho)$ representing the nearest-neighbor overlap interaction and the parameters b', K, and a of the potential

$$\phi(r'_{ij}) = b'(r'_{ij} - K)\exp[-a(r'_{ij} - K)] \tag{8}$$

representing the next-nearest-neighbor anion overlap interaction[14] obtained from a calculation of the overlap charge density. The values of the parameters are given in Table I. For consistency, however, we should have determined these parameters not from the free-ion charge densities but from the densities stabilized by the Watson potential. But it has been found that there is practically no change in the cation density in the Watson potential approximation and the small change in the anion density is neglected in this preliminary application. Moreover, since the overlap interactions do not involve the excited states and we do not expect an exact fit with experiment and some other effects, namely, the van der Waals interaction, the many-body interaction, etc., which are at least comparable to and if not more than this effect are neglected, this difference, we believe, is not at all significant in altering our general conclusion. The same is, however, not true for the other group of parameters, namely, the dipole polarizabilities of the ions which are entirely dependent on the excited states.

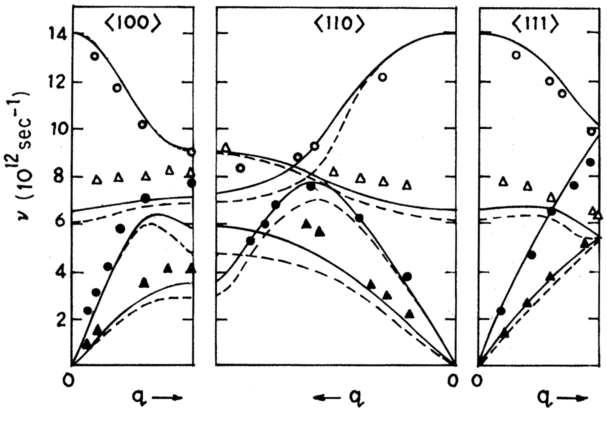

FIG. 2. Phonon dispersion relation of NaF crystal. Dashed and solid lines represent the free-ion and the Watson potential calculations, respectively. Experimental points are taken from Ref. 26.

For the electronic polarizabilities of the ions we first of all use the free-ion ones. For the Na$^+$ and F$^-$ ions in the NaF crystal we use the results gained from the fully coupled Hartree-Fock (HF) method using the Clementi wave functions.[14] This set corresponds to our calculation using purely the ionic wave functions assumed to remain unaltered in crystal. However, when we use the Watson potential execution of the fully coupled HF calculation becomes formidable. Maessen and Schmidt[15] and Schmidt *et al.*[16] have recently developed a simpler self-consistent HF method followed by a geometrical approximation which ensures higher-order self-consistency contributions. In order to test the validity of the method we may compare the results for the same system by the above two methods. It is found that in the case of free ions where both the results are available, the method of Schmidt *et al.* is comparable in accuracy to that of the coupled HF calculation. In fact, for the cations they agree within 1–2%. For anions it is slightly larger. In the absence of a coupled HF calculation for ions in the Watson potential we use those of Schmidt *et al.* They have extended the method to compute the different properties of the ions with various radii of the potential sphere. From an exhaustive calculation of the dipole polarizabilities of both cations and anions they conclude that the best choice of the Watson-sphere radius seems to be the one implied by the Madelung energy. The corresponding values of the parameters are given in Table I.

We use the results of Schmidt *et al.* for both sets of the RbF crystal, and those of the present paper for the in-crystal polarizabilities of the NaF crystal. It is important to note that the Watson-sphere radii are 1.322 and 1.611 Å for the NaF and the RbF crystals, respectively, which indicates that the change of the polarizability of the anion will be stronger in the previous case since both lattices have the same amount of charge in the sphere. The fractional reduction in the polarizability value of the same anion is approximately 33% and 25% for the NaF and the RbF crystals. The corresponding enhancements in the cation value are only about 5% and 7%. The implications of these changes and also the effect of choice of a different basis on these calculations will be discussed in Sec. III.

III. RESULTS AND DISCUSSION

The results obtained for the different lattice static and dynamic properties of the NaF crystal are shown in Fig. 2

TABLE II. Cohesion, phase transition, and elastic properties. All calculations refer to harmonic values.

Lattice constants (Å)		Cohesive energy (10^{-12} erg/mol)		Elastic constants (10^{12} dyn/cm)						Phase-transition pressure (GPa)		Phase-transition volume (%)	
				C_{11}		C_{12}		C_{44}					
Calc.	Expt.	Calc.	Expt.[a]	Calc.	Expt.[b]	Calc.	Expt.[b]	Calc.	Expt.[b]	Calc.	Expt.[c]	Calc.	Expt.[c]
4.670	4.566	−15.62	−15.35	1.21	1.14	0.33	0.22	0.33	0.30	15.57	21.0–27.0	11.6	9

[a]Reference 22.
[b]Reference 23.
[c]Reference 18.

and in Tables II–IV. For the RbF crystal we only show the calculation in the crystal potential. All calculations refer to harmonic values. In view of the fact that the calculation does not contain any adjustable parameter, and despite some drastic approximations the overall broad description of both the statics and dynamics of both the crystals is satisfactory. However, we must mention that the quantitative agreement is still not satisfactory for the static dielectric constant the cause of which we shall discuss presently.

Before we discuss the results of the Watson potential approach we indicate, in brief, the situation with respect to the static properties of the NaF crystal. The cohesion and the equilibrium lattice separation and the elastic constants considered individually are well reproduced. However, the model fails to take account of the Cauchy violation since this is a two-body central-interaction model. This difference in the elastic constants C_{12} and C_{44} is known to be explained by invoking many-body interactions.[17] The polymorphic phase-transition behavior of the NaF crystal is also qualitatively well reproduced. In contrast to the Rb halides the Na halides show some peculiarities in their transition behaviors. All the Rb and the K halides transform from the $B1$ phase to the $B2$ phase within the pressure range 0.5 to about 4 GPa, while the Na halides have been known not to undergo any transformation up to about 20 GPa. Recently Yagi *et al.*[18] have detected a transition of the NaF crystal at a still higher pressure (see Table II) with a considerable hysteresis and a volume contraction of about 9%. It is quite well known that the transition pressure critically depends upon the details of the interactions and hence we do not expect a quantitative agreement in this simple calculation. However, our results for the NaF crystal clearly indicate the enhancement compared to that of the RbF crystal (Ref. 6).

It is expected that the general trend of agreement of the static properties will remain more or less the same even if we use the Watson potential approximation. But in the case of dynamics and the dielectric properties this effect is quite important. The two sets of calculations given in Tables III and IV and Fig. 2 indicate that the inclusion of the effect of the potential improves the agreement in the right direction in all properties. For the phonon frequencies of the NaF crystal, in particular the phonons of the acoustic branches in the ⟨100⟩ and ⟨110⟩ symmetry directions, marked improvement is noticed. The major disagreement occurs in the TO branches. This is essentially due to the neglect of the short-range polarization effects. However, the success of the present calculation may be appreciated if we compare it with other existing calculations. Both sets of the present parameter-free calculations may be compared with our previous calculation[19] and that of Singh and Chandra,[20] who used six and twelve free parameters, respectively, and obtained better agreement for the TO branches of the NaF crystal. This is due to the fact that both these calculations included the effect of short-range polarization through the shell model, while the present calculation totally neglects it. Further, we

TABLE III. Macroscopic dielectric properties. All calculations refer to harmonic values.

Crystal	High-frequency dielectric constant Calc. (F)[a]	High-frequency dielectric constant Calc. (W)[b]	Expt.[c]	Low-frequency dielectric constant Calc. (F)	Low-frequency dielectric constant Calc. (W)	Expt.[c]	Reststrahlen frequency (THz) Calc. (F)	Reststrahlen frequency (THz) Calc. (W)	Expt.
NaF	2.03	1.73	1.72	10.73	8.15	5.1	37.27	40.16	45.86[e] 47.12[f]
RbF	2.21	2.06	1.94	9.37	8.28	5.91	27.62	28.49	29.40[d]

[a]Free-ion calculation.
[b]Watson potential calculation.
[c]Reference 24.
[d]Reference 25.
[e]From infrared measurement, Ref. 26.
[f]From neutron measurement, Ref. 26.

TABLE IV. Some selected phonons. All calculations refer to harmonic values (in THz).

Crystal	$\vec{q}$		LO	LA	TO	TA
NaF	⟨1000⟩	Calc. (*F*)[a]	56.78	28.90	42.07	17.72
		Calc. (*W*)[b]	56.98	35.81	44.67	20.98
		Expt.[c]	56.54	48.38	51.52	26.39
RbF	⟨1000⟩	Calc. (*F*)	41.0	18.03	30.47	10.81
		Calc. (*W*)	39.33	19.16	30.54	11.31
		Expt.[d]	34.2±0.2	20.2±0.1	31.8±0.2	10.9±0.2

[a] Free-ion calculation.
[b] Watson potential calculation.
[c] Reference 26.
[d] Reference 25.

note that the discrepancy in the TO branches of the NaF crystal is more magnified than that of the RbF crystal (Ref. 6) because the short-range polarization is more important here—this may also be ascertained from a comparison of the values of the Szigeti charge for the two crystals. While comparing the results it is found that the Watson potential approximation does not show any substantial improvement for the phonon frequencies of the RbF crystal (see Table IV). As mentioned in the Introduction, the increase and the decrease for the cation and the anion polarizabilities in the crystal mutually tend to compensate for the RbF crystal, whereas for the NaF crystal the change in the cation polarizability is very small and a significant balance remains to affect the frequencies. A rough idea regarding this compensating effect is obtained from the ratio of ionic radii.

On the whole we observe that the use of the Watson potential approximation within the framework of the perturbation-theoretical-model approach shows a somewhat improved description of the lattice mechanics of the low-polarizability ionic crystals without entailing much additional computation. It is also concluded that the remaining discrepancy is mainly due to the short-range polarization effects which we have discussed in detail in our earlier work.[6] The present work also seems to imply that the remaining discrepancy in the static dielectric constant may be entirely due to the first-order exchange interaction determined dipolar distortion. A critical discussion by Roy *et al.*[21] regarding the applicability of the different models implying short-range polarization also supports the above conjecture.

Before concluding let us discuss some of the limitations of the present calculation. The reliability of the estimate of the effect of the surroundings on the lattice-mechanical properties depends upon the two factors. Firstly the radius of the sphere is a very sensitive parameter. In the absence of a more suitable criterion the sphere's radius has been fixed by the Madelung energy for each crystal separately. The next important factor is the choice of the basis. Schmidt *et al.* have considered and discussed several variants, keeping the radius of the sphere the same for all of them. Of them the most important, namely, the self-consistent numerical HF (NHF) and the self-consistent HF-Roothaan (HFR) results agree quite closely both for free ions and for the cations in the potential. But the divergence between the two becomes somewhat pronounced for the anions inside the potential. We have used the results of the former method, which, as emphasized by Schmidt *et al.*, appears to be more reliable since the parameters describing the wave functions in the HFR calculation inside the potential are kept fixed to their free-ion values, whereas in the NHF calculation a full-fledged variation procedure is adopted.

For the two crystals considered here the Watson potential description of the properties shows distinct improvement over that of the free-ion calculation and no inconsistency appears. However, to contribute to a better understanding of the situation and to assert the reliability of the method, one needs to apply it to a few other cases. We may gain confidence in the method if in all cases a systematic trend indicating improvement is discernible.

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