

Unified study of potassium flouride (KF) using perturbation model and Watson potential approximation

U. C. SRIVASTAVA

Amity Institute of Applied Sciences, Amity University-Noida-201301, U.P, India

The present investigation for the alteration of the free-ion wave functions, when the ions are put in a crystal, the effect of the crystal environment is simulated by the Watson potential. The developed perturbation theoretical model for ionic solids by Basu and sengupta has been used for calculation of the different lattice-dynamical properties for the low-polarizability ionic crystal. The feature of used method it requered only input data necessary for the study of (KF) crystal properties are the Hartree–Fock wave functions of the constituent ions. Certain properties like, the dielectric properties and some phonons in symmetry directions, depend on the excited states of the crystal, are rather sensitive to this effect which varies from crystal. A unified study of the phase transition, cohesion, elastic constant, dielectric and vibrational properties of the (KF) crystal is given without using any adjustable free parameter, our approach and overall agreement obtained is well satisfactory. Finally the limitations and reliability of the present model for estimating the effect of the surroundings are critically discussed.

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1. Introduction

The perturbation model within the point dipole approximation provides a semimicroscopic description generally [1,2] for the ionic solids. For describing the lattice mechanical properties, perturbation–model is also capable of describing the collective response of the electrons and plasma frequencies in insulators [3]. For KF whose polarizability is rather low, drastic simplification in calculation may be achieved by neglecting the short range polarization effects complitely. Bose et al [4] have discussed in detail the justification of this approximation for a certain group of ionic crystals. The discrepancies between theory and experiment may be solely attributed to the neglect of the short–range polarization effects [4]. This appears to be only partly true for the lattice mechanics of the KCl and NaCl crystals [1]. In present work a part of the discrepancy may be explained by including the effect of the surroundings on the wave functions of the free ions. In perturbation theoretical –model our approach to neglect the effect of surroundings on the ionic wave functions when ions are transferred to a lattice. On place of simplified theoretical perturbation model we used artificial simulation of the crystal ssurroundings employing the Watson-spherical–potaintial approximation [5]. The present approach is only a semimicroscopic i.e no free parameter and only input data employed are the Hartree-Fock wave functions of the ions. No crystal data necessary except structuer by Banerjee et al [6,7]. In the present application short–range polarization effects are not considering because these effects are assumed to be small. However ,even the inclusion of the effect of the ellectric field is too difficult. Watson [5] suggested a method of using this effect by approximation of the real potential and by a spherical potential. The effect of the surroundings will be more pronounced in the KF crystal due to

polarizability values of its constituent ions. The free polarizability values of the ions in the KF crystals α_{ion} 10 (approxmatily). From the present investigation it will be found that the larger the ratio the more pronounced the cancellation effect.

Theory:

The details theoretical considerations and application of the approach have been discussed in a series of previous workers [1-4,6,7]. 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 present work we shall discuss about the certain properties like the polarizability of 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 need to be included.

Watson potential

Watson [5] 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 [8] have discussed the effect of this stabilizing potential on the charge densities of some ionic crystals and its effect on the

static properties, but presently 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 and magnitude of the charge is equal and opposite in sign to that of the enclosed ion. The form of the potential is given by in Fig. 1.

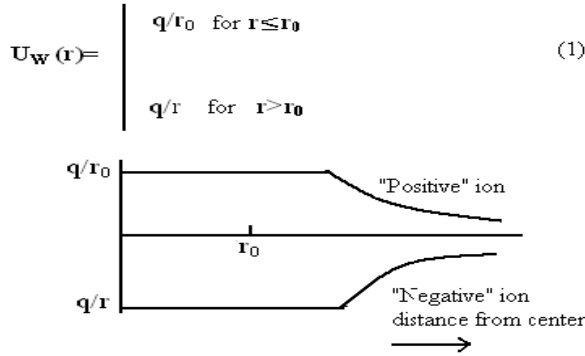


Fig. 1. Watson potential.

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:

$$r_0 = l/M \quad (2)$$

Where l and M are the lattice and Madelung constant for the appropriate structure. It may be mentioned here that the radius remains the same for positive and 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 [9,10] are also consistent with the above fact.

Energy expression:

For low polarizability ionic crystals the energy of an assembly of interacting ions simplifies to

$$W = \frac{1}{2} \sum_{i,j} \frac{z_i z_j}{r_{ij}} - \sum_i \bar{\mu}_i \bar{E}_i^m - \frac{1}{2} \sum_i \bar{\mu}_i \bar{E}_i^d + \sum_i \frac{\mu_i^2}{2\alpha_i} + \frac{1}{2} \sum_{i,j} \phi(r_{ij}) + \frac{1}{2} \sum_{i,j} \phi'(r_{ij}) \quad (3)$$

Where the first term represents the coulomb interaction between the ions and next three terms represent the interaction between dipole and monopole field, dipole and dipole field, and dipole self-energy, respectively. The last two terms give the overlap interaction between the nearest neighbours and between the next-nearest neighbors (consider for anions only). For the first set of

calculation of different parameters describing the interactions are evaluated using the free-ion wave functions as in [4]. 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. 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 remain unchanged while all other terms are affected. Now, the assembly of these so-called dressed ions which is 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 dynamical properties provided we obtain the parameters for the dressed ions. Equation (3) with the following adiabatic condition, will be used for the investigation of the dynamical properties.

$$\frac{\partial W}{\partial \mu_i} = 0 \quad (4)$$

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,

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

Where the symbols have the same significance as in [4].

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

$$b_{11} = -\frac{1}{m} \left[R_0 - \frac{(4\pi/3) Z_1^2}{\nu_0 (1 - 4\pi\alpha_e / 3\nu_0)} \right] \quad (6)$$

and

$$b_{22} = \frac{\alpha_e}{\nu_0} \left[\frac{1}{\nu_0 (1 - 4\pi\alpha_e / 3\nu_0)} \right]$$

$$b_{12} = \frac{Z_1}{(m\nu_0)^{1/2}} \left[\frac{1}{\nu_0 (1 - 4\pi\alpha_e / 3\nu_0)} \right]$$

Where m is the reduced mass of the ion pair, $R_0 = -R_{lq=0}$ 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

$$\begin{aligned} \epsilon_{\infty} &= 1 + 4\pi b_{22}, \\ \epsilon_0 &= \epsilon_{\infty} - 4\pi b_{12}^2 / b_{11}, \omega_0^2 = -b_{11} \end{aligned} \quad (7)$$

Static properties:

In order to calculate the static properties we use the parameters given in Table 1. 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.

Determination of the parameters:

The parameters involved in the different interactions are derived from the Clementi wave functions of the core 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 to find the parameters.

Table 1. Values of parameters.

Crystal	b (10^{-8} erg)	ρ (A^0)	b' (10^{-8} erg cm^{-1})	a (A^0)	K (A^0)	α^+ ($10^{-24} cm^3$)	α^- ($10^{-24} cm^3$)
KF	2.648	0.2552	-0.9541	2.648	1.830	1.201 (F) ^a	0.759 (F)
						1.315 (W) ^b	0.074 (W)

^aFree-ion calculation

^bWatson potential calculation

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

Representing the next-nearest-neighbour anion overlap interaction [14] obtained from a calculation of the overlap charge density. The values of the parameters are given in Table 1. 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 other group of parameters, namely dipole polarizabilities of the ions which are entirely dependent on the excited states.

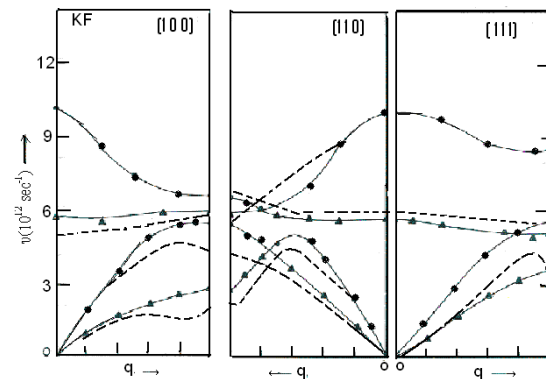


Fig. 2. Phonon dispersion relation of KF crystal.

Dashed and solid lines represent the free-ion and the Watson potential calculations, respectively. Experimental points are taken from Ref [24].

For the electronic polarizabilities of the ions we first of all use the free ion ones. For [KF] we use the results gained from the fully coupled Hartree-Fock (HF) method using the Clementi wave functions [12]. It is found that in the case of free ions where both the results are available, the method of the Schmidt et al. [13,14] is comparable in accuracy to that of the coupled HF calculations. 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. We use the result of Schmidt et al. for polarizabilities of KF

crystal. It is important that the Watson-sphere radii are 1.100 \AA^0 for the KF, which indicates that the change of the polarizability of the anion will be stronger in the previous case same amount of charge in the sphere of lattice. The fractional change in polarizability value of the same anion

is approximately 30% for the KF. The corresponding enhancements in the cation value are only about 4%. The implications of these changes and also the effect of choice of a different basis on these calculations will be discussed in result.

Table 2. Cohesion, Phase transition, and elastic properties. All calculations refer to harmonic values.

Lattice Constant (\AA^0)		Cohesive energy (10^{12}erg/mol)		Elastic constants (10^{12}dyn/cm)				Phase transition pressure		Phase transition volume			
Calc.	Expt.	Calc.	Expt. ^a	C_{11}		C_{12}		C_{44}		Calc.	Expt. ^c	Calc.	Expt. ^c
3.75	3.65	167	158	0.658	0.757	0.149	0.135	0.128	0.133	17.75	22-29	13.6	11

^aReference 20

^bReference 21

^cReference 16

2. Results and discussion

The result obtained for the different lattice static and dynamic properties of the KF crystal are shown in Fig. 2 and in Table 2-4. Over all broad description for KF crystal both statics and dynamics 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 KF 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 [15]. The KF halides have been known not to undergo any transformation T. Yagi et al [16] have detected a transition of KF crystal at a still pressure in Table 2 with a considerable hysteresis and a volume contraction of about 7%. 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. 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 calculation given in Table 3 and 4 and Fig. 2 indicates 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 KF crystal, in particular the phonons of the acoustic branches in the $\langle 100 \rangle$ and $\langle 110 \rangle$ 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 [17] and that Singh Chandra [18], who used six and twelve free parameters, respectively, and obtained better agreement for the TO KF crystal. This is due to the fact that both these calculations include the effect of short range polarization through the shell model, while the present calculation totally neglects it.

Table 3. Macroscopic dielectric properties. All calculations refer to harmonic values.

Crystal	High-frequency dielectric constant			Low-frequency dielectric constant		Reststrahlen frequency (THz)			
	Calc.(F) ^a	Calc.(W) ^b	Expt. ^c	Calc.(F)	Calc.(W)	Expt. ^c	Calc.(F)	Calc.(W)	Expt.
KF	2.13	1.97	1.96	9.73	8.23	5.43	30.22	33.46	38.76 ^e 40.21 ^d

^aFree-ion calculation, ^bWatson potential calculation

^c[22], ^d[23], ^{e,f}[24]

Table 4. Some selected phonons. All calculations refer to harmonic values (in THz).

KF	q		LO	LA	TO	TA
	<1000>	Calc.(F) ^a	6.45	5.71	5.50	2.75
		Calc.(W) ^b	6.60	5.90	5.65	2.90
		Expt. ^c	6.56	5.97	5.52	2.83

^aFree-ion Calculation, ^bWatson potential calculation, ^c[24], ^d[23].

On the whole we observe that by using of Watson potential approximation in the framework of the perturbation-model approach shows a some what improved description of the lattice dynamics 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 discussed in [4]. The present work the remaining discrepancy in the static dielectric constant may be entirely due to the first order exchange interaction determined dipolar distortion. A critical discussion given by Roy et al [19]. Before concluding let us some of the limitations of the present calculation. The reliability of the estimate of the surroundings on the lattice dynamical properties depends upon the two factors. Firstly the radius of the sphere is a very sensitive parameters and choice of the basis Schmidt et al [14] have discussed several variants, keeping the radius of the sphere the same for all of them.

In KF crystal considered 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 few other cases a systematic trend indicating improvement is discernible. For some metal oxide this theory applicable and satisfactory [25].

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*Corresponding author: ucsrivastava@amity.edu