Comments and Addenda

Comment on the pressure-induced off- to on-center transition of Li$^+$ in KCl

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The nature of the pressure-induced off- to on-center transition of a substitutional Li$^+$ impurity in KCl is examined. Dielectric-response and far-infrared absorption measurements are interpreted by means of a simple two-parameter barrier model and found to be consistent. The experimental results provide evidence for a rather sharp on- to off-center transition as the hydrostatic pressure is increased. In contrast, recent shell-model calculations yield a gradual decrease of the off-center displacement with pressure. Thus, static ionic potentials do not provide an accurate description of the strain dependence of the local environment of small substitutional impurities in alkali halides.

I. INTRODUCTION

The properties of substitutional impurities in alkali halides have been extensively studied.[1,2] The experimental results provide a wealth of detail concerning the local environment of the impurity in its host lattice which is a challenge for theory to explain. The most energetically favorable location for an impurity can be either on-center or, for an impurity of sufficiently small size, a number of equivalent off-center sites. Thus, the behavior of an impurity has been classified as: (1) strongly off center (thermally activated reorientation among equivalent sites), (2) quantum-mechanical tunneling between sites, (3) anharmonic on center, or (4) harmonic on center.[3]

Hydrostatic pressure is a unique parameter because it can be used to study transitions between these regions of behavior. Kahan *et al.*[4] studied the pressure dependence of the lattice resonant modes in KCl: Li$^+$ by far-ir spectroscopy and interpreted their data as evidence for an off- to on-center transition. The present authors[5] have analyzed the data of Kahan et al.[4] in terms of a simple two-parameter barrier model and found that the off-center displacement of the impurity, defined as the distance of the potential-energy minima from the original cation site, undergoes an abrupt collapse as the pressure is increased. Recently, Holland and Lüty[3] performed dielectric-response measurements on KCl: Li$^+$ under hydro-

static pressure and also found evidence for the off- to on-center transition.

The pressure tuning of an off-center impurity into an on-center configuration presents perhaps the most stringent test to theoretical models of the interionic forces in alkali halides. The shell-model calculations of Catlow *et al.*[6] are the most sophisticated application to date of static ionic potentials to the off- to on-center transition.

The purpose of this comment is to examine the recent experimental and theoretical work on KCl: Li$^+$ for consistency in order to gain insight into the nature of the off- to on-center transition. Section II is a brief review of the two-parameter barrier model and the fits to the data of Kahan *et al.*[4] In Sec. III, we compare Holland and Lüty's[3] results with our fits to the barrier model and find them consistent. In Sec. IV, we examine the results of Catlow *et al.*[6] and conclude that static ionic potentials do not provide a sufficiently accurate description of the local environment of Li$^+$ in KCl to predict the transition. Section V summarizes our conclusions.

II. SIMPLE BARRIER MODEL

In the absence of hydrostatic pressure, the potential energy for a substitutional Li$^+$ ion in KCl has equivalent minima in each of the eight [111] directions.[7,8] The simplest potential function with this property is the separable potential:

$$V(x, y, z) = v(x) + v(y) + v(z), \tag{1}$$

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where the one-dimensional potential $v(x)$ is a symmetric double well. We form the Hamiltonian matrix for the one-dimensional problem using a set of harmonic oscillator functions as a basis and numerically diagonalize the matrix to compute the energy eigenvalues and eigenvectors. For each value of the pressure, a search program varies the parameters of $v(x)$ to find the best fit to the far-infrared absorption frequencies measured by Kahan et al.[4] Perhaps the simplest choice for $v(x)$ that can describe both off- and on-center configurations is

$$v(\xi) = \tfrac{1}{2}\hbar\beta(v_4\xi^4 + v_2\xi^2); \quad \xi = (m\beta/\hbar)^{1/2}x, \tag{2}$$

where $\tfrac{1}{2}\hbar\beta$ is the ground-state energy of the basis harmonic oscillator, ξ is the displacement in dimensionless units, m is the mass of the Li$^+$ ion, and v_2 and v_4 are variable parameters. For comparison, we also performed fits with a harmonic oscillator perturbed by a Gaussian barrier:

$$v(x) = Ax^2 + B\exp(-Cx^2), \quad A, B, C > 0. \tag{3}$$

The value of A was chosen as the harmonic part of the potential for KBr: Li$^+$ at zero strain,[9] while B and C were variable parameters. For further details, see Ref. 5.

Kahan et al.[4] observed four distinct absorption frequencies throughout most of their range of pressure. The fits of the two-parameter barrier model to the data were inadequate at the highest pressures, for which the Li$^+$ ion is expected to behave most nearly as a particle in a harmonic well. Indeed, the barrier potentials are nearly harmonic, but the splitting in the excited-state band observed experimentally (two lines are observed) indicates the presence of additional anharmonicity in the true potential. The lowest-order term consistent with cubic symmetry that we have ignored is of the form $x^2y^2 + x^2z^2 + y^2z^2$. As a crude estimate we calculated in first-order perturbation theory that the two T_{1u} multiplets of the tenfold degenerate $n = 3$ level of the three-dimensional harmonic oscillator are split by roughly a factor of 2.5 times the shift in energy of the $n = 1$ T_{1u} triplet induced by this cubic anharmonicity. In addition, an anharmonic term of this type should improve the fit to the isotope effect at high pressures.[5]

The important results of the barrier-model fits to the data of Kahan et al.[4] for our purposes are: (1) The barrier height V_0 decreases linearly with lattice strain and (2) the off-center displacement x_m is weakly strain dependent for low pressures, but collapses abruptly to zero at the pressure for which the barrier disappears. The relationship between lattice strain, $-dr/r$ in percent, and pressure, in kbars, according to Kahan,[10] is

$$-dr/r \ (\%) = 0.163P - 0.0023P^2 \tag{4}$$

for KCl.

III. DIELECTRIC RESPONSE

In this section we compare the far-infrared data, as interpreted by the two-parameter barrier model, with the dielectric-response measurements of Holland and Lüty[3,11] on KCl: Li$^+$.

Holland and Lüty[3] found that ϵ_D, the dipolar (i.e., impurity) contribution to the dielectric function, is consistent with a two-level model. In the low-field limit $\langle p\rangle E \ll k_B\Delta$, the polarizability of a two-level system is given by[12]

$$\alpha_D = \frac{2\langle p\rangle^2}{3\Delta}\tanh\left(\frac{\Delta}{2T}\right), \tag{5}$$

where Δ is the splitting between the lowest two levels in K and $\langle p\rangle$ is the dipole moment. Holland and Lüty[3] use the Clausius-Mossotti relation to obtain the approximation

$$\epsilon_D \simeq (\epsilon_p + 2)^2\tfrac{4}{9}\pi N\alpha_D, \tag{6}$$

where ϵ_p is the dielectric constant of the pure alkali halide crystal and N is the density of impurities. Equations (5) and (6) can be combined to yield the expression for the pressure dependence of the dipolar contribution to the dielectric function:

$$\frac{\epsilon_D(P)}{\epsilon_D(0)} = \frac{\alpha_D(P)}{\alpha_D(0)} = \left(\frac{\langle p\rangle(P)}{\langle p\rangle(0)}\right)^2\left(\frac{\Delta(0)}{\Delta(P)}\right)\frac{\tanh[\Delta(P)/2T]}{\tanh[\Delta(0)/2T]}, \tag{7}$$

where P is the pressure. Equation (7) was used to extract $\langle p\rangle(P)$ and $\Delta(P)$ from the data.

In the two-parameter barrier model, the polarizability of the substitutional impurity is

$$\alpha_D = \frac{2e^2}{Z}\sum_{n\neq m}\frac{x_{nm}x_{mn}}{E_m - E_n}e^{-E_n/k_BT}, \tag{8}$$

where

$$x_{nm} \equiv \int_{-\infty}^{\infty}\phi_n(x)x\phi_m(x)dx \tag{9}$$

is the dipole matrix element connecting states m and n of the one-dimensional double well, E_n is the energy of the nth level, and Z is the partition function:

$$Z = \sum_n e^{-E_n/k_BT}. \tag{10}$$

We have assumed that the applied electric field $\vec{E}$ is in the x direction. The calculation reduces to a one-dimensional problem because the potential is separable and we let $\vec{E}$ lie along a symmetry axis. Note that Eq. (8) reduces to Eq. (5) if we retain only the lowest two levels of the double well potential.
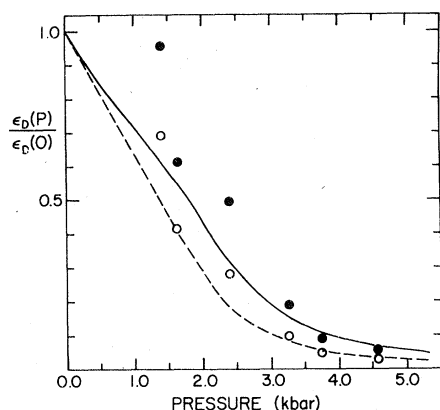
Figure 1 shows the pressure dependence of the

FIG. 1. Pressure dependence of the dipolar contribution to the dielectric function of $KCl:Li^+$ for two values of the temperature. The solid (dashed) line represents the fit of the quartic-harmonic potential to the far-infrared data for $T=4$ K (2 K). The solid (open) circles were obtained from dielectric data (Ref. 3) for $T=4$ K (2 K).
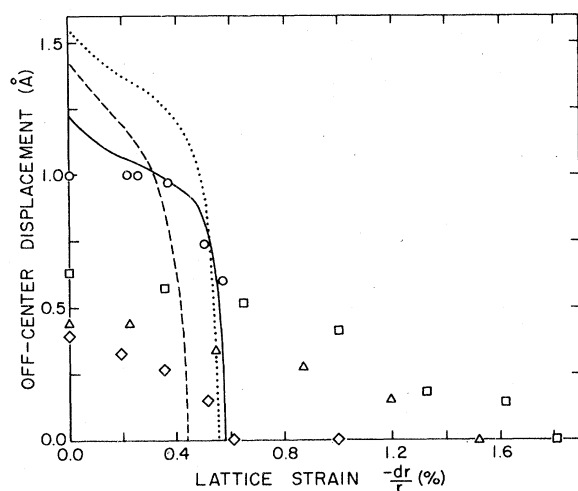

FIG. 2. Strain dependence of the off-center displacement of Li^+ in KCl. The dotted (solid) line represents the fits of the quartic-plus-harmonic (Gaussian barrier) potential to the far-infrared data. The dashed line is the displacement of maximum probability density along the [111] direction for the ground-state wave function obtained by fitting the quartic-harmonic potential to the far-infrared data. The open circles show the strain dependence of the dipole moment, normalized to 1 Å at zero strain for convenience, obtained from dielectric-response measurements (Ref. 3). The squares (diamonds) represent the results of shell-model calculations using Catlow et al. (Ref. 6) potential I (II). The triangles are the results of polarizable point ion calculations by Quigley and Das (Ref. 17). The experimental results imply an abrupt off- to on-center transition, whereas the static ionic-potential calculations predict a gradual decrease of off-center displacement with increasing strain.

reduced dielectric function $\epsilon_D(P)/\epsilon_D(0)$ for two values of the temperature. The circles represent the dielectric data, which are taken from Holland and Lüty's[3] Fig. 19. The lines represent the fits for the quartic-plus-harmonic barrier potential [Eq. (2)] to the far-infrared data. The far-infrared and dielectric data are consistent within the barrier model.

Figure 2 displays the strain dependence of the normalized dipole moment, taken from Fig. 20 of Holland and Lüty,[3] and the strain dependence of the off-center displacement for the fits of the barrier potentials to the far-infrared data. The dipole moment rolls over at about the same strain that the off-center displacement collapses. The sharpness of the collapse of the dipole moment is unclear because of the large error bars indicated by Holland and Lüty[3] for the data points taken at the highest pressures and owing to possible strain dependence of the effective charge which must be divided out of the dipole moment to obtain an off-center displacement. However, there is no inconsistency between the far-infrared data and the dielectric data revealed by this comparison. Holland and Lüty[3] present more convincing data for an abrupt off- to on-center transition from dielectric and ultraviolet absorption measurements on $RbBr:Ag^+$, $RbCl:Ag^+$, and $NaBr:Cu^+$.

In Fig. 2 we also show the strain dependence of the position of the maximum of the probability density for the ground-state wave function of $KCl:{}^6Li^+$ along the [111] direction for the fits of the data of Kahan et al.[4] to the quartic-harmonic
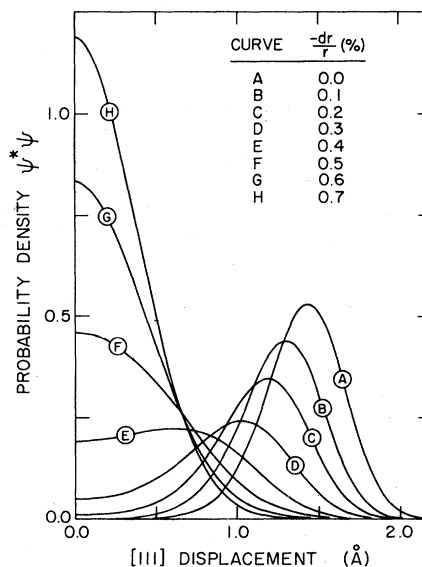

FIG. 3. Strain dependence of the probability density $|\psi|^2$ in the [111] direction for the ground state obtained by fitting the quartic-plus-harmonic potential to the far-infrared data.

potential. The probability density is given by

$$|\psi(x, y, z)|^2 = |\phi_0(r/\sqrt{3})|^6 , \tag{11}$$

where $\phi_0(x)$ is the ground-state wave function of the one-dimensional quartic-harmonic potential and $r^2 = x^2 + y^2 + z^2$. Figure 3 shows explicitly the strain dependence of the probability density. At low pressures, the Li$^+$ ion is off center and $|\psi|^2$ possesses a pocket in each of the [111] directions. As the pressure is increased, the peak of $|\psi|^2$ moves gradually towards the center of the cavity and probability density begins to accumulate at the center. A further increase in pressure induces the maximum of $|\psi|^2$ to move rapidly on center. The Li$^+$ is quite delocalized at the pressure for which $|\psi|^2$ first peaks on center, but as the pressure is further increased, the ion becomes strongly localized on center. The on-center peak is much larger than the off-center peak because it is formed by the coalescence of all eight off-center pockets of probability density. Thus, this plot of the strain dependence of $|\psi|^2$ indicates a rather gradual transition from off- to on-center for a Li$^+$ impurity treated quantum mechanically in the simple barrier model. This result is in contrast to the sharp transition we obtained for the off-center displacement (Fig. 2) in this model.

IV. STATIC IONIC POTENTIALS

There have been a number of attempts to calculate the properties of substitutional ions in alkali halides, particularly Li$^+$ in KCl, using static ionic model potentials.[13,14] In general, the small substitutional ion is placed at some location along a symmetry direction in the cavity formed by the removal of a host ion. Then the surrounding ions, and perhaps the substituent ion itself, are permitted to relax and the configuration of minimum energy is computed.

The recent work of Catlow et al.[6] has been especially successful when compared with the experimental evidence for off- or on-center configurations and the direction of off-center displacements of substitutional cations in alkali halides. In fact, their only serious disagreement with experiment, RbCl: Li$^+$, was resolved by recent experiments of Thörmer and Lüty.[15] The improvement of the Catlow et al.[6] results over previous work is largely due to the replacement of the polarizable point ion model by the shell model.[16]

Catlow et al.[6] simulated the effects of hydrostatic pressure on the local environment of a Li$^+$ impurity in KCl by varying the lattice constant. They found that the barrier heights in the [100], [110], and [111] directions follow the ratio 1 : 2 : 3
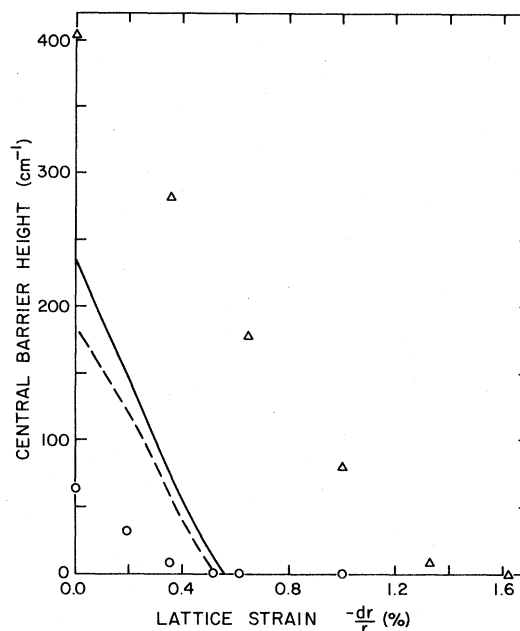

FIG. 4. Strain dependence of the central barrier height. The solid (dashed) line represents the fit of the quartic-plus-harmonic (Gaussian barrier) potential to the far-infrared data. The triangles (circles) were obtained by shell-model calculations of Catlow et al. (Ref. 6) for their potential I (II).

quite closely. Since a 1 : 2 : 3 ratio of barrier heights is a consequence of the assumption that the potential is separable [Eq. (1)], this result lends further support to the applicability of the two-parameter barrier model to off-center KCl: Li$^+$. Figure 4 shows the strain dependence of the central barrier height obtained by Catlow et al.[6] for their potentials I and II in comparison with the results of the barrier model fits to the far-infrared data. In all cases, the barrier height depends linearly on strain for low strains, but there is some rounding at higher strains, especially for the Catlow et al.[6] potential I.

Figure 2 shows the available results on the strain dependence of the off-center displacement in KCl: Li$^+$. In addition to the shell-model results,[6] we have included the results of polarizable point ion calculations by Quigley and Das[17] for completeness. The off-center displacement gradually decreases to zero for the static ionic calculations in contrast to the two-parameter-barrier fits to far-infrared data and the roll-off in the dipole moment observed by Holland and Lüty.[3] The extreme delicacy of the balance of forces in this problem requires significant (and perhaps inordinately difficult) improvements to the ionic potentials to obtain results which would permit a reasonable estimate of the tunneling splitting as well as the excited-state levels of an off-center

system. We took the Catlow *et al.*[6] values for the barrier height and off-center displacement for both their potentials I and II and estimated that the tunneling splitting at zero pressure should be 17.7 cm^{-1} and 66.7 cm^{-1}, respectively, using the quartic-plus-harmonic potential. The experimental value[18] for the tunneling splitting in $KCl:^7Li^+$ is 0.82 cm^{-1}. The large discrepancy clearly demonstrates the sensitivity of the spectroscopic information to the local environment of the impurity. In addition, there may be some physics underlying the abrupt off- to on-center transition which cannot be explained with any reasonable choice of static ionic potentials. For example, the transition could be related to the defect-phonon interaction and the "small polaron" self-trapping effect.[19]

V. CONCLUSION

We have examined the strain dependence of the off-center displacement of a Li^+ substitutional impurity in KCl by analyzing the available experimental data within a simple two-parameter barrier model and comparing the results with sophisticated shell-model calculations. We conclude that the far-infrared and dielectric data are consistent within the barrier model and suggest a rather abrupt off- to on-center transition. The transition cannot be explained by calculations based on static ionic potentials which successfully predict the configuration of the impurity at zero pressure. Thus, further work is necessary to determine whether modifications of the ionic models or a completely new process is required to explain the data.

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