

$(\omega_1+3\omega_2)$ and $p_1(1)=0$. By decomposing into two series of odd and even powers, one has

$$\begin{aligned} \sum_{m=0}^{\infty} p_1(m) &= \sum_{n=0}^{\infty} p_1(2n) + \sum_{n=0}^{\infty} p_1(2n+1) \\ &= \sum_{n=0}^{\infty} h^n p_1(0) + \sum_{n=0}^{\infty} h^n p_1(1). \end{aligned} \quad (\text{A7})$$

By substituting the value of $p_1(0)$ and $p_1(1)$ and summing the series $\sum_n h^n$, one has

$$\hat{p}_1 = \sum_{m=0}^{\infty} p_1(m) = \frac{(\omega_2' + 3\omega_B)(\omega_1 + 3\omega_2)}{\omega_1\omega_2' + 3\omega_B(\omega_1 + 3\omega_2)}, \quad (\text{A8})$$

which is Eq. (17). One can similarly obtain Eq. (18).

Dependence of KCl:Li⁺ and KBr:Li⁺ Off-Center Behavior on Lattice Parameter*

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Minimum-energy configurations for impurity displacements along the $\langle 111 \rangle$ crystal axis in KBr:Li⁺ and KCl:Li⁺ systems were calculated over a range of lattice-parameter (LP) values: 3.200 to 3.315 Å for KBr:Li⁺, and 3.070 to 3.180 Å for KCl:Li⁺. The nearest-neighbor Born-Mayer model previously applied by the authors was utilized. The minimum-energy curves and configurations were found to be rather sensitive to the lattice parameter. Thus, in contrast to the room-temperature LP (3.293 Å) results for KBr:Li⁺, where the $\langle 111 \rangle$ off-center well was 0.015-eV deep, the depth for the liquid-helium LP (3.26 Å) was only 0.002 eV. The latter depth is comparable to the zero-point energy for Li⁺ vibration, indicating that the Li⁺ ion should not be localized at an off-center site at liquid-helium temperatures. This agrees with current experimental evidence at this temperature, which indicates that Li⁺ is on center in KBr; it also supports the low-barrier interpretation due to Bowen, Gomez, and Krumhansl for this system. Estimates are made of the dependence of the $\langle 111 \rangle$ motional frequencies on lattice parameter and show that the frequencies are quite sensitive, in agreement with results due to Clayman, Nolt, and Sievers. For KCl:Li⁺, the off-center configuration is found to persist for the liquid-helium-temperature KCl lattice parameter (3.117 Å). An applied hydrostatic pressure of 7 kbar is found to be sufficient to restore an on-center configuration. The electric field gradient at the Li⁷ nucleus was calculated over the entire range of KCl lattice parameter considered.

I. INTRODUCTION

IT is now known that substitutional impurities smaller than the replaced host species can have equilibrium positions off the perfect lattice site.^{1,2} KCl:Li⁺ has been the most thoroughly investigated¹⁻⁷ example of this phenomenon, but recent⁸ experimental work indicates that RbCl:Ag⁺ is another off-center system. In a previous paper,⁶ referred to here as QD, results of ionic-model calculations on KCl:Li⁺ were given and indicated that the Li⁺ ion is off-center in KCl along

one of the eight $\langle 111 \rangle$ directions of the crystal.^{3,4} The potential energy which was calculated for KBr:Li⁺ also has a $\langle 111 \rangle$ off-center well, but one which is only half as deep as that found in KCl:Li⁺. Experimental results,¹⁻⁵ on the other hand, are consistent with an on-center KBr:Li⁺ configuration. In particular, Harrison, Peressini, and Pohl⁹ measured the specific heat of KBr:Li⁺ at 2°K in an attempt to observe tunneling splitting of the magnitude (~ 1 cm⁻¹) to be expected for an off-center system, but no tunneling effects were found.

The calculations of QD were not expected to be quantitative in view of the semiempirical repulsive potential used; nevertheless, the qualitative disagreement between experiment and theory, over whether Li⁺ is on-center in KBr, is disturbing, since we have no explanation for why the model should be any less applicable to KBr:Li⁺ than it is to KCl:Li⁺, and yet the model had appeared to provide a satisfactory explanation of the KCl:Li⁺ behavior. We note, however, that the room temperature KBr lattice parameter (3.293 Å) was used in the KBr:Li⁺ calculations of QD,

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¹ G. Lombardo and R. O. Pohl, Phys. Rev. Letters **15**, 291 (1965); Bull. Am. Phys. Soc. **11**, 213 (1966).

² H. S. Sack and M. C. Morianity, Solid State Commun. **3**, 93 (1965).

³ N. E. Byer and H. S. Sack, Phys. Rev. Letters **17**, 72 (1966); N. E. Byer, F. S. Welsh, and H. S. Sack, Bull. Am. Phys. Soc. **11**, 229 (1966).

⁴ M. Gomez, S. P. Bowen, and J. A. Krumhansl, Phys. Rev. **153**, 1009 (1967).

⁵ I. G. Nolt and A. J. Sievers, Phys. Rev. Letters **16**, 1103 (1966).

⁶ R. J. Quigley and T. P. Das, Phys. Rev. **164**, 1185 (1967).

⁷ S. Kapphan and F. Lüty, Bull. Am. Phys. Soc. **13**, 500 (1968).

⁸ W. Dreybrodt and K. Fussgaenger, Phys. Status Solidi **18**, 133 (1966).

⁹ J. P. Harrison, P. P. Peressini, and R. O. Pohl, Phys. Rev. **171**, 1037 (1968).

whereas the experiments have been carried out at liquid-helium temperatures where the KBr lattice parameter is actually 3.26 Å. This is only a 1% difference, but the work of Clayman, Nolt, and Sievers¹⁰ has shown that such small differences in lattice parameter can be important in determining off-center behavior.

Clayman, Nolt, and Sievers¹⁰ (CNS) studied the effects of a change in lattice parameter (LP) on the sharp low-frequency (16.2 cm⁻¹) absorption associated with an on-center Li⁺ resonant mode in KBr:Li⁺. They changed the average lattice parameter by alloying: To reduce the average lattice spacing KCl (up to 14.2 mole %) was alloyed with KBr:Li⁺, and to enlarge the spacing KI (up to 4.5 mole %) was used. Vegard's law¹¹ states that the average lattice parameter of a solid solution of two ionic species lies between the lattice parameters of the two components and varies linearly with the concentration of each component. Using Vegard's law, CNS were able to compute the average lattice parameters of their alloy samples. The changes in the resonant-mode infrared-absorption curve could thus be followed as the lattice parameter was varied. The absorption broadened for both decreases and increases of spacing (the broadening is presumably a side effect of adding Cl⁻ and I⁻ ions), but the frequency of maximum absorption shifted in opposite directions: upward with the addition of KCl, and downward with the addition of KI. CNS concluded that decreasing the lattice parameter strengthens the on-center character of the KBr:Li⁺ resonant mode, whereas increasing the lattice parameter destabilizes this mode.

The purpose of the present work is twofold: (1) to resolve the disagreement between theory and experiment over whether Li⁺ is off-center in KBr; and (2) to see if the model of QD will yield well depths which can explain the trends observed by CNS. We hope that the results will lead to a better insight into the physical effects which determine off-centrism.

II. DESCRIPTION OF THE MODEL

The model is described in detail in QD.⁶ An abridged description will be given here. The sum of the repulsive, electrostatic, and polarization energies of the impurity and its nearest neighbors is calculated as a function of their displacements. All other ions are held rigid and unpolarizable. The displacements and induced dipoles of the nearest neighbors are constrained to be radial with respect to the position of the impurity (see Fig. 1). A Born-Mayer repulsive potential of the form $A \exp(-r/\rho)$ is taken for the repulsive energy between two ions whose centers are a distance r apart. The electrostatic energy of a displaced ion is a sum over

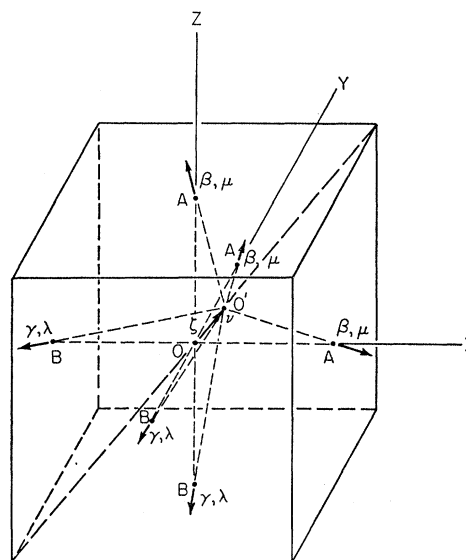


Fig. 1. Displacements ζ , β , and γ , and induced electronic dipoles ν , μ , and λ for the $\langle 111 \rangle$ geometry.

the Coulomb terms contributed by the other displaced ions together with the interaction of the ion with the surrounding rigid lattice. This lattice contribution is expressed as a cubic harmonic expansion in the displacement of the ion. Terms up through sixth order were kept. The polarization energy consists of the energy necessary to polarize the impurity and its nearest neighbors, the dipole-dipole interaction energies, and the dipole-monopole interaction energies. The induced dipoles are evaluated self-consistently. The equilibrium configuration is determined by minimization of the total energy ΔE (measured relative to the energy of the perfect crystal). To find the minimum, ΔE is evaluated for the 10^p configurations which result when 10 likely values are assigned to each of the p displacement parameters. The lowest energy for each value of the impurity displacement ζ is plotted. In the present work, ζ will always represent an impurity displacement along a $\langle 111 \rangle$ symmetry axis of the cubic crystal, since in QD this direction was found to always have the lowest energy. A few calculations were carried out for the $\langle 110 \rangle$ and $\langle 100 \rangle$ orientations for both the large and small extremes of the KBr and KCl lattice parameters, and the results showed that the $\langle 111 \rangle$ direction consistently had the lowest energies. Since it was found in QD that no polarization catastrophe occurs in the $\langle 111 \rangle$ geometry calculations, there was no need to use the Born-Mayer-Verwey potential or to adjust the anion polarizability in the manner described in QD. The lattice parameters investigated in each material ranged from about 1% larger than the room-temperature value down to just small enough to yield a centrosymmetric configuration ($\zeta=0$).

A short discussion of the values of the constants used in the calculations is given in the Appendix.

¹⁰ B. P. Clayman, I. G. Nolt, and A. J. Sievers, Phys. Rev. Letters **19**, 111 (1967).

¹¹ L. Vegard, Z. Physik **5**, 17 (1921).

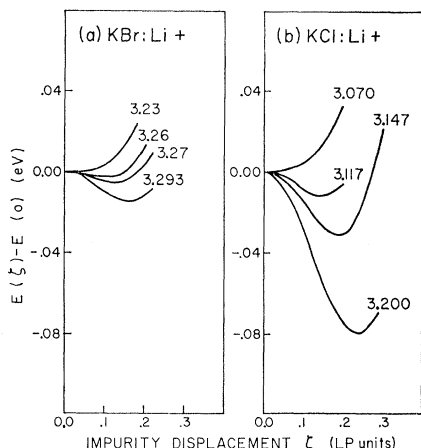


FIG. 2. Energies of the impurity and its nearest-neighbor cluster as a function of the $\langle 111 \rangle$ displacement ζ of the impurity ion. The energies are measured relative to those of the corresponding centrosymmetric configurations ($\zeta=0$). (a) KBr:Li $^+$ energies for the four lattice-parameter values indicated (in units of Å). 3.293 is the normal KBr lattice parameter. (b) KCl:Li $^+$ energies for the four lattice parameters indicated. 3.147 is the normal KCl lattice parameter.

III. KBr:Li $^+$ RESULTS AND DISCUSSION

The KBr:Li $^+$ and KCl:Li $^+$ minimum energy configurations along with their corresponding energies are given in Table I over the respective ranges of lattice parameter. In this section, we shall analyze the KBr:Li $^+$ results.

Use of the room-temperature⁷ KBr lattice parameter (3.293 Å) leads to an off-center potential well whose energy is 0.015 eV lower than that of the centrosym-

TABLE I. Energies and displacements of minimum-energy configurations.

Material	LP (Å)	ζ_0^a (LP)	ΔE_0^b (eV)	E_0^c (eV)	β_0^d (LP)	γ_0^d (LP)
KBr:Li $^+$	3.200	0.00	0.000	-0.908	-0.06	-0.06
	3.230	0.02	-0.0005	-0.811	-0.06	-0.05
	3.260	0.11	-0.002	-0.737	-0.07	-0.02
	3.270	0.14	-0.005	-0.716	-0.08	-0.01
	3.280	0.14	-0.009	-0.697	-0.08	-0.01
	3.293	0.17	-0.015	-0.684	-0.08	0.00
	3.306	0.19	-0.022	-0.663	-0.08	0.01
	3.315	0.19	-0.028	-0.662	-0.08	0.01
KCl:Li $^+$	3.070	0.00	0.000	-0.973	-0.06	-0.06
	3.080	0.05	-0.000	-0.940	-0.07	-0.04
	3.090	0.09	-0.002	-0.910	-0.08	-0.03
	3.100	0.11	-0.005	-0.883	-0.08	-0.02
	3.110	0.14	-0.008	-0.857	-0.09	-0.01
	3.117	0.14	-0.012	-0.841	-0.09	-0.01
	3.133	0.17	-0.022	-0.806	-0.09	0.00
	3.147	0.19	-0.031	-0.780	-0.09	0.01
	3.160	0.20	-0.041	-0.758	-0.09	0.01
	3.170	0.21	-0.049	-0.743	-0.10	0.02
	3.180	0.22	-0.059	-0.730	-0.10	0.02

^a ζ_0 is the $\langle 111 \rangle$ displacement, in units of the lattice parameter (LP), of the impurity ion at its minimum-energy position.

^b ΔE_0 is the minimum energy measured relative to the energy of the centrosymmetric configuration.

^c E_0 is the minimum energy measured relative to the perfect crystal.

^d β_0 and γ_0 are the displacement parameters of the nearest neighbors for the minimum-energy configuration. See Fig. 1.

metric configuration ($\zeta=0$). On the other hand, when the 2°K lattice parameter (3.26 Å) is used, the off-center well depth is only 0.002 eV. Thus, a 1% reduction in lattice parameter produced a sevenfold reduction in off-center well depth. In addition, the impurity displacement ζ decreased by 35%, and the total dipole moment of the defect system was reduced to 3.07 D (the room-temperature value was 5.90 D). The predicted KBr:Li $^+$ behavior at 2°K is thus dramatically less off-center than the behavior predicted for the room-temperature LP system. The dependence of the impurity potential on lattice parameter is graphically presented in Fig. 2(a): The configuration energy is plotted for four lattice-parameter values as a function of the impurity displacement ζ .

Bowen, Gomez, and Krumhansl⁴ have suggested that KBr:Li $^+$ fits the low-barrier region of their model, i.e., that the Li $^+$ ion in KBr behaves more like a spherical oscillator than like a particle tunneling about from one off-center well to another. Our calculated potential supports their interpretation. For a KBr lattice parameter of 3.26 Å (the 2°K value), the central barrier between diametrically opposite $\langle 111 \rangle$ wells is only 0.002 eV, and the barrier between adjacent wells is even smaller, 0.0007 eV. But estimates of the zero-point energy can be made in several ways (for example, by assuming a double harmonic oscillator, a spherical oscillator, or a particle in a box), and all of them yield a zero-point energy of at least 0.002 eV. Thus, in KBr the Li $^+$ ion is not even quasilocized in an off-center well, since the ion has enough zero-point energy to overcome all the barriers. An applied electric field of even 50 000 V/cm will not be able to change this situation, since this field can favor the $[111]$ well by at most 0.0006 eV over the $[\bar{1}\bar{1}\bar{1}]$ well (assuming a Lorentz local field); this does not increase the central barrier by enough to significantly block the zero-point motion. Thus, we find in agreement with the conjecture of Bowen, Gomez, and Krumhansl, that the KBr:Li $^+$ barriers at 2°K are too weak to localize the impurity ion in any one of the shallow $\langle 111 \rangle$ off-center wells. Tunneling splittings on the order (~ 1 cm $^{-1}$) of those which Harrison, Peressini, and Pohl⁹ attempted to observe, would also require higher barriers, and our model is therefore in agreement with their absence (Nolt and Sievers⁵ also found no evidence for such tunneling states). Furthermore, the large isotope shift of the KBr:Li $^+$ resonant mode frequency observed by Sievers and Takeno,¹² and their conclusion that the Br $^- \leftrightarrow$ Li $^+$ forces must be softened (relative to the Br $^- \leftrightarrow$ K $^+$ forces) to an extraordinary degree, are in agreement with the 3.26 Å curve of Fig. 2(a). For although the barriers are too low for off-centrism, the existence of shallow off-center wells in the potential illustrates the weakness of the restoring forces and permits the large amplitude oscillations necessary for

¹² A. J. Sievers and S. Takeno, Phys. Rev. **140**, A1030 (1965).

an explanation of the large isotope shift observed by Sievers and Takeno.

CNS found that a 0.8% decrease of the KBr LP (to 3.23 Å) reduced the frequency of the KBr:Li⁺ absorption peak by nearly half, whereas a 0.4% increase (to 3.27 Å) almost doubled the frequency. Fig. 2(a) illustrates our $\langle 111 \rangle$ KBr:Li⁺ results for these two values of the KBr lattice parameter (as well as for the room-temperature and 2°K values). For a precise calculation of the absorption frequencies, the potential energy of the impurity would have to be calculated for the entire neighborhood of the substitutional site. We have calculated the energy for only the $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ directions. Thus, a precise calculation of the motional state energies cannot be made. On the other hand, estimates of the frequencies (associated with the lattice parameters of Fig. 2(a) can be made on the basis of the $\langle 111 \rangle$ potential-energy curves; that is, we expect that the actual dependence on LP of the absorption frequency should be paralleled by the LP dependence of the absorption frequency for $\langle 111 \rangle$ motion. The $\langle 111 \rangle$ frequency trend can then be compared with the trend observed by CNS.

The 3.23 Å curve of Fig. 2(a) resembles a parabola (aside from a 0.0005-eV hump at the center) and can be fitted by a harmonic oscillator (HO) potential. The resulting HO frequency is 72 cm⁻¹. The 3.26 Å curve is not so simple, but attempts to fit it by a double-harmonic-oscillator (DHO) potential yield a "tunneling splitting" between 15 and 47 cm⁻¹, depending on the fitting procedure. The "tunneling splitting" here is simply the energy difference between the two lowest states and is found by using the formula¹⁸ for the DHO splitting. The 3.27 Å curve was also fitted to a DHO potential, and a splitting of about 11 cm⁻¹ was obtained. Thus, the ratios of the frequencies are about 0.35:1:2.3 (where the average value 31 cm⁻¹ of the two extremes is taken for the 3.26 Å LP frequency); the corresponding ratios of the frequencies observed by CNS are about 0.62:1:1.7. Thus the $\langle 111 \rangle$ frequency estimates agree qualitatively with the trend observed by CNS. They are also extremely sensitive to changes in lattice parameter, in fact somewhat more so than the CNS frequencies. We also note that the large stress-induced frequency shifts, observed by Nolt and Sievers,⁵ of the KBr:Li⁺ resonant mode again demonstrate how sensitive the potential energy must be to changes in lattice spacing, in agreement with our results.

CNS plotted the KBr:Li⁺ resonant absorption frequency that they observed as a function of lattice parameter and found that a fair fit to the data was obtained with a straight line. Extrapolation of this straight line to zero frequency is expected to give an estimate of the lattice parameter which marks the completion of the passage from an on-center configuration to one which

is off-center. This extrapolation gives a lattice parameter about equal to the room-temperature value (3.293 Å) used in QD. Although the CNS measurements were on alloy samples, the KBr:Li⁺ calculations of QD also indicate that the 3.293 Å LP KBr:Li⁺ configuration will be off-center, since the zero-point energy estimates for this case are only about half the barrier-height energies; therefore, tunneling will be necessary if the impurity is to move from one off-center well to another, and thus the system is off-center. According to our model, then, the transition (observed by CNS) of the KBr:Li⁺ mode from class I to class II behavior corresponds to the growth in barrier heights which accompanies an increase in lattice parameter.

IV. KCl:Li⁺ RESULTS AND DISCUSSION

The KCl:Li⁺ minimum-energy-configuration results are given in Table I. The lattice parameter of KCl at liquid-helium temperatures is 3.117 Å, and the room-temperature value is 3.147 Å. Plots of the KCl:Li⁺ configuration energy as a function of the impurity displacement ζ are shown in Fig. 2(b) for four KCl lattice-parameter values. The figure illustrates that the off-center well depth at 2°K is only a third of the room-temperature depth. The total dipole moment of the defect center is 5.15 D at 2°K, compared with 6.23 D at room temperature; the 2°K value is thus in better agreement with Lombardo and Pohl's experimental value⁴ of 2.54 D than the room-temperature value. Although the 2°K KCl:Li⁺ configuration is not as strongly off-center as the room-temperature configuration, the well depth is still great enough to give an off-center configuration, in qualitative agreement with experiment.

As shown in Table I, establishment of a strong on-center KCl:Li⁺ configuration requires that the lattice parameter be reduced to 3.070 Å (by "strong" we mean that the impurity displacement $\zeta=0$). Using available compressibility data, we have calculated the hydrostatic pressure necessary to achieve a 3.070 Å KCl lattice parameter and find that 7 kbar should be sufficient at 2°K. We expect that there will exist a smaller pressure at which off-center character will disappear, since the barriers will fall short of the heights necessary for off-centrism, in a manner similar to the 2°K KBr:Li⁺ case. The precise pressure will be sensitive to the repulsive parameters used. Thus an experiment to determine the pressure dependence of some off-center property, such as the tunneling splitting, could provide a means of deriving a better semi-empirical repulsive potential.

As seen from the KCl:Li⁺ results in Table I, expansion of the KCl lattice is expected to strengthen KCl:Li⁺ off-center character by producing deeper wells which are further off center. As a consequence, alloying KI with KCl:Li⁺ (to increase the average lattice spacing) should make possible a stronger electrocaloric

¹⁸ E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), p. 73.

TABLE II. $\langle 111 \rangle$ KCl:Li⁺ field gradients.

LP (Å)	$V_{z'z'}$ ^a	$V_{x'x'}$ ^a	$V_{y'y'}$ ^a
3.070	0.000	0.000	0.000
3.080	0.212	-0.106	-0.106
3.090	0.659	-0.329	-0.329
3.100	0.999	-0.499	-0.499
3.110	1.637	-0.818	-0.818
3.120	2.106	-1.053	-1.053
3.133	2.345	-1.173	-1.173
3.140	2.344	-1.172	-1.172
3.147	2.882	-1.441	-1.441
3.150	2.885	-1.443	-1.443
3.155	3.160	-1.580	-1.580
3.160	3.158	-1.579	-1.579
3.165	3.594	-1.797	-1.797
3.170	3.592	-1.796	-1.796
3.180	3.894	-1.947	-1.947
3.190	4.557	-2.278	-2.278
3.200	4.552	-2.276	-2.276

^a Units of e/a^3 , where a is the lattice parameter (LP).

effect, and off-centrism experiments should be possible at higher temperatures with these samples. The greater lattice spacing should also intensify the electric field gradient at the Li⁷ nucleus, thus facilitating experimental observation of the nuclear magnetic resonance (NMR) quadrupole splittings. We have calculated the field gradient components at the Li⁷ nucleus for the $\langle 111 \rangle$ KCl:Li⁺ configurations of Table I. The results are given in Table II. Assuming Vegard's law, a solid solution of KCl with 10 molar % KI should lead to an LP increase of about 1% (giving about the room temperature KCl LP of 3.147 Å). The field gradient is thereby increased by about 50%, and the central barrier height is seen from Table I to be more than doubled: From 0.012 to 0.031 eV (the barrier between adjacent $\langle 111 \rangle$ minima increases from 0.003 to 0.008 eV). These increased barrier heights will reduce tunneling and thus further facilitate experimental detection of the quadrupole splittings. Unfortunately, the I⁻ ions present will complicate the NMR spectra, since those Li⁺ ions with I⁻ neighbors will have their cubic environment destroyed even without any off-center displacement and will thus be subjected to additional electric field gradients. However, the dependence of the quadrupole splitting of the Li⁺Cl⁻₆ centers on the direction of the applied electric field should be quite different from that of the Li⁺I⁻_xCl⁻_{6-x} centers. Furthermore, since the magnitudes of the field gradients should differ for the two types of defect centers, distinct NMR spectra should result. A successful identification of the quadrupole splittings associated with Li⁷Cl⁻₆ should therefore be possible.

Alderman¹⁴ has recently measured the stress-induced KCl:Li⁷ quadrupole interaction at liquid-helium temperatures. His measured value is in good agreement with the value predicted by Table II, which for the liquid-helium-temperature lattice parameter yields

¹⁴ Donald W. Alderman (private communication).

e^2qQ/h equal to 85 kHz. This differs from Alderman's value by about 15%.

V. CONCLUDING REMARKS

The present work shows that KBr:Li⁺ is on-center according to the model of QD, if the liquid-helium-temperature value of the KBr lattice parameter is used for the calculations. No *ad hoc* changes in the model were necessary for this qualitative agreement with experiment, only recognition of the importance of using the precise lattice-parameter value was required. We find that the estimated dependence on lattice parameter of the $\langle 111 \rangle$ KBr:Li⁺ mode frequency is similar to that observed by CNS in their observations of the KBr:Li⁺ resonant mode frequencies; the potential yielded by the model thus displays the same strong dependence on lattice parameter which the results of CNS, and of Nolt and Sievers indicate must be a feature of the actual potential. Furthermore, extrapolation of the CNS results to a KBr lattice-parameter value expected to yield an off-center KBr:Li⁺ configuration, gives a value which our model also predicts to have off-center character. We conclude, then, that the model *does* give a satisfactory account of the observed features of the KBr:Li⁺ system.

Use of the liquid-helium-temperature value of the KCl parameter (3.117 Å) yields an electric dipole moment (5.15 D) in better agreement with Lombardo and Pohl's experimental value (2.54 D) than use of the room-temperature KCl lattice parameter gives. KCl:Li⁺ is still found to be off-center when the 2°K lattice parameter is used, so qualitative agreement with experiment is still obtained. We have estimated that 7 kbars hydrostatic pressure is necessary to force KCl:Li⁺ into a strong ($\xi=0$) on-center configuration. An experimental measurement of the pressure dependence of KCl:Li⁺ off-centrism would be interesting, for it would not only test the accuracy of our 7 kbar estimate, but it could also furnish the data necessary for a more appropriate Li⁺ ↔ Cl⁻ semiempirical repulsive potential.

From the results of the present work, we conclude that off-centrism is critically dependent on the lattice spacing: the equilibrium position is determined by a competition between the polarization and repulsive energies, in which the polarization forces promote off-centrism, and the repulsive forces oppose it; the polarization energy, however, falls off more slowly with interionic separation than the repulsive energy does; thus an increase in lattice spacing promotes off-centrism by weakening the repulsive forces relative to the polarization forces. The main reason that KBr:Li⁺ is on-center and KCl:Li⁺ is off-center appears to be that the Br⁻ ↔ Li⁺ repulsive potential is stronger than the Cl⁻ ↔ Li⁺ repulsive potential. Were it not for this disparity in repulsive potential, KBr:Li⁺ would be expected to be more strongly off-center than KCl:Li⁺, since Br⁻ is about 40% more polarizable than Cl⁻.

TABLE III. Constants used in the calculation of lattice distortion.

Crystal	293°K Nearest- neighbor distance (Å)	0°K Nearest- neighbor distance (Å)	Repulsive force ^a parameter A (10 ⁻⁹ erg)	Repulsive force ^a parameter ρ (Å)	Polarizability of cation ^b (Å ³)	Polarizability of anion ^b (Å ³)
KCl	3.147	3.117	3.63	0.324	1.33	2.96
LiCl	2.570	2.554	0.782	0.332	0.029	2.96
KBr	3.293	3.26	3.93	0.334	1.33	4.16
LiBr	2.751		0.821	0.348	0.029	4.16

^a The repulsive parameters are taken from M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 26.
^b The polarizabilities were taken from J. R. Tessman, A. H. Kahn, and W. Shockley [Phys. Rev. **92**, 890 (1953)].

Although the model still requires a quantum-mechanical treatment of the repulsive interaction if quantitative results are to be expected, the qualitative successes of the model in explaining features of KBr:Li⁺ and KCl:Li⁺ indicate that it can be usefully applied to problems of defects in ionic crystals.

APPENDIX

The values of the parameters used in the calculations are listed in Table III. The room-temperature value of the KCl lattice spacing is given by Schaefer¹⁵ and quoted by Tosi.¹⁶ The room-temperature value of the KBr spacing was taken from Born and Huang.¹⁷ The liquid-helium-temperature KCl lattice constant is quoted by Karo¹⁸ and is based on data and expressions given in Born and Huang. It is also obtained by a linear extrapolation of Schaefer's data (for 293 and 90°K). The liquid-helium-temperature KBr lattice constant is given by Clayman, Nolt, and Sievers.¹⁰ It is also given

¹⁵ G. Schaefer, J. Phys. Chem. Solids **12**, 233 (1960).

¹⁶ M. P. Tosi, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 1.

¹⁷ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 26.

¹⁸ A. M. Karo, J. Chem. Phys. **33**, 7 (1960); Ref. 17, pp. 54, 52.

by Born and Huang and is obtained as well if the linear coefficient of thermal expansion is determined from Schaefer's data and used to extrapolate down from Born and Huang's room-temperature value. Other room-temperature values are given in the literature, but it appears that the experimental values of the room-temperature KCl and KBr lattice constants vary by at most 0.3%. The temperature dependence of these quantities appears to be linear.

The repulsive parameters and polarizabilities used are room-temperature values. The polarizabilities are expected to be insensitive to temperature, since the difference in thermal energy between 0° and 293°K is very small compared to the electronic energies of the ions. The polarizabilities were taken from the least square fits of Tessman, Kahn, and Shockley.¹⁹ Uncertainties in the polarizability values are probably large, possibly larger than 25%. The temperature dependence of the repulsive parameters is not accurately known. This together with the uncertainty in the room-temperature repulsive potential, makes the calculation of the repulsive energy the weakest part of the model.

¹⁹ J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).