STRESS-INDUCED FREQUENCY SHIFT OF A LATTICE RESONANT MODE*

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Recent studies have shown that low-lying tunneling states are associated with a translational instability of the lithium impurity in the KCl lattice.[1] Some observed properties of this defect system are well described by a model in which the lithium ion moves in a multiwell potential formed by the neighboring ions with a repulsive barrier at the normal lattice site.[2] However, the far-infrared transmission of KCl:LiCl single crystals does not permit an identification of the impurity-induced energy-level scheme since no sharp absorption lines and only one broad band at 40 cm^{-1} have been observed in the spectral region from 3 to 100 cm^{-1}. Previously, we have reported[3] a sharp resonant-mode absorption in KBr:Li^6Br at 17.81 ± 0.1 cm^{-1} with a full width at one-half-maximum absorption of 0.7 cm^{-1}. In this note we wish to report the effect of uniaxial stress on the KBr:Li^6Br system. The application of stress produces a relative frequency shift of the resonant mode which is approximately 100 times larger than previously observed for either localized modes[4] or gap modes.[5] This large frequency shift allows us to probe the local symmetry of the lithium defect and to investigate the possibility of a translational instability of the lithium ion in the KBr lattice. The results discussed below imply that no low-lying tunneling states occur for Li^+ in KBr.

The transmission spectrum of a KBr:Li^6Br crystal was obtained at a series of stress levels with the *E* vector of the radiation polarized in various directions relative to the uniaxial stress. A lamellar-type interferometer[6] was employed to obtain the interferogram of the transmitted radiation in the range from 3 to 50 cm^{-1}. The transmission spectrum was calculated by performing a subsequent numerical Fourier transform of the interferogram. A resolution of 0.2 to 0.5 cm^{-1} was maintained over the above frequency range. Polarization of the radiation was produced by a 500-line-per-inch etched nickel grid located 5 mm from the sample.

The samples used in this study were single crystals cut from a boule which had been grown in a bromine atmosphere from a melt containing 0.05 mole% isotopically pure Li^6. The concentration was determined chemically to be approximately 4×10^{17} $\mathrm{Li}^+/\mathrm{cm}^3$. The samples were approximately 13×13 mm in a section normal to the beam and 2.5 mm thick. A sample temperature of 2°K was maintained during the experiment by exchange-gas coupling to the surrounding pumped liquid-helium bath. Static weights were used to produce uniaxial compressional stress in the sample up to about 2 $\mathrm{kg/mm}^2$. For stresses higher than 2 $\mathrm{kg/mm}^2$, a manually operated hydraulic pump and piston arrangement was used.

The experimentally determined absorption frequency as a function of applied uniaxial stress is shown in Fig. 1 for two crystallographic orientations. For stress applied along the [100] axis and also along the [111] axis, two absorption lines which shifted linearly with applied stress were measured. For stress along the [110] direction, three absorptions were observed. Frequency shifts as large as 2.5 cm^{-1}, equivalent to a relative shift of 14%, have been observed for the *E* vector polarized parallel to stress in the [100] direction. In all cases, the relative absorption strengths for different polarizations remain constant as a function of stress.

From the splitting produced by stresses in different crystallographic directions, we de-

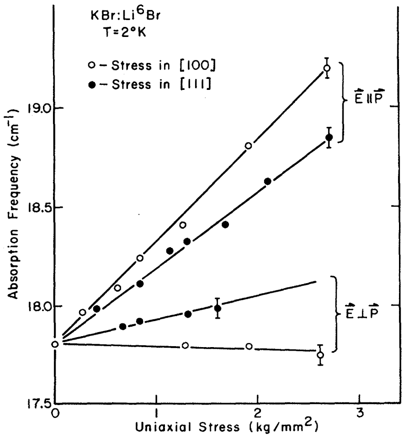

FIG. 1. Absorption-frequency centroid versus applied uniaxial stress. *E* represents the electric vector of the polarized radiation and *P* the applied uniaxial stress. The full width at half-maximum absorption of the resonant mode is about 0.7 cm^{-1}.

duce that the electric dipole transition is between the two vibrational states which transform as the A_{1g} and T_{1u} irreducible representations of the O_h point group. The absence of any stress-induced intensity dependence leads us to the conventional model of an A_{1g} ground and a three-fold degenerate T_{1u} excited state. Also since a single absorption line is observed over the entire temperature range[7] for no applied stress, low-lying "gerade" tunneling states from 0.2 to 10 cm^{-1} above the A_{1g} ground state are unlikely.[8]

From the slopes of the absorption frequency versus applied stress, it is possible to estimate the anharmonic coupling of the resonant mode to long-wavelength acoustic distortions of A_{1g} (spherical), E_g (tetragonal), and T_{2g} (trigonal) symmetry. If the direction cosines of the pressure P with respect to the crystal axes are labeled by α, β, and γ and the direction cosines of the polarization vector E relative to the crystal axes by α', β', and γ', then the slope of the frequency versus stress curve for a cubic crystal is given by[9]

$$\begin{aligned} d\omega/dP = {} & A(s_{11}+2s_{12}) + B(s_{11}-s_{12}) \\ & \times[(2\gamma'^2-\alpha'^2-\beta'^2)(2\gamma^2-\alpha^2-\beta^2) \\ & +3(\alpha'^2-\beta'^2)(\alpha^2-\beta^2)] \\ & +2Cs_{44}(\alpha'\beta'\alpha\beta+\beta'\gamma'\beta\gamma+\gamma'\alpha'\gamma\alpha), \end{aligned} \tag{1}$$

where A, B, and C are the coupling coefficients associated with strain components which transform like the representations A_{1g}, E_g, and T_{2g}, respectively, and s_{11}, s_{12}, and s_{44} are the compliances appropriate to the local region around the impurity. From our experiments we find the coefficients in Eq. (1) to be,[10] in units of $\text{cm}^{-1}\ \text{mm}^2\ \text{kg}^{-1}$,

$$A(s_{11}+2s_{12}) = 0.16 \pm 0.03,$$

$$B(s_{11}-s_{12}) = 0.10 \pm 0.02,$$

$$Cs_{44} = 0.26 \pm 0.08,$$

where the stress has been assumed positive for compression of the sample.

In general, one would anticipate that the compliances appropriate to the local region around the impurity would not be the same as for the unperturbed crystal. However, as the influence of the defect becomes spatially localized, the appropriate compliances should approach the values for the pure crystal. Both high-frequency localized modes and low-frequency resonant modes which are associated with nearest-neighbor force-constant changes satisfy this criterion. Assuming the lithium ion to be in this latter category, the coupling coefficients are found to be, in cm^{-1},

$$A = 880 \pm 160,$$

$$B = 360 \pm 70,$$

$$C = 140 \pm 45.$$

On this basis we deduce that the resonant mode in this system is most strongly coupled to long-wavelength, spherically symmetric, acoustic modes of the surrounding lattice.

In summary, the study of anomalously large frequency shifts produced by stress applied to the defect system of Li^+ in KBr has enabled us to conclude the following: (1) The local symmetry of the lithium impurity is cubic; (2) the resonant mode exhibits a strongly anharmonic character; (3) the excited state of the resonant mode couples most strongly to lattice distortions of spherical symmetry; and (4) no evidence of low-lying tunneling states has been found. This latter conclusion indicates that a large potential barrier does not occur at the normal lattice site for lithium in KBr as has been previously observed for lithium in KCl. Thus our results suggest that the dynamics of the lithium impurity differs considerably in these two alkali-halide host lattices.

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THEORY OF DISPLACEABLE POINT DEFECTS IN CRYSTALS*

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There has been considerable recent interest[1] in polarizable dipole ion molecules in alkali halides, particularly OH^-, NO_2^-, and CN^- However, the small ion Li^+ in KCl has also been found to behave as a highly polarizable system by Sack and Moriarty,[2] and by Lombardo and Pohl.[3] Pohl suggested that the small Li^+ ion might not be stable at the lattice site and Matthew[4] showed this to be possible on theoretical grounds; Dienes et al.[5] have supplied further evidence to support this view that the effective potential may have multiple well structure.

To interpret the many experiments on symmetry, thermal properties, optical properties, and behavior of the Li^+ impurity under applied stress or electric fields, a usable theoretical model is required. Such a model was developed by Devonshire[6] for orientable molecular defects; it is not applicable to the small point-ion defect. In the important limit where the small ion experiences almost a harmonic potential (weak multiwell terms in the potential), the Devonshire model naturally yields the free-rotor spectrum while, in fact, the three-dimensional harmonic oscillator (HO) spectrum is required; this difference becomes particularly apparent in the excited states where degeneracies of rotor (librator) and oscillator differ. The purpose of this Letter is to outline a theoretical model applicable to Li^+ and similar small point-ion defect systems.

First we assume that the host ions around a Li^+ impurity relax to a position of octahedral symmetry. Potentials with this symmetry may have 6 wells along ⟨100⟩ (denoted XY_6), 8 along ⟨111⟩ (XY_8), 12 along ⟨110⟩ (XY_{12}). The model potential is the appropriate three-dimensional multiwell analog of the one-dimensional double-well harmonic oscillator. Octahedral symmetry restricts the form of the potential; in XY_6 and XY_8 the most general potential has constant-energy surfaces which are ellipsoids of revolution with axes passing through the center of symmetry. In general, the potential will have four parameters: curvatures $m\omega_1{}^2$, $m\omega_2{}^2$, $m\omega_3{}^3$ (where m is the impurity mass) and the distance r_0 of the minima from the lattice site. When the wells are "deep" (i.e., high barriers between wells) the ground state of the system XY_n ($n=6, 8, 12$) is n-fold degenerate. For finite, but large, r_0 the levels are split by tunneling. In the other extreme of small r_0 and small barriers, the simple spherical oscillator levels develop.

The high-barrier case was treated as follows. The ground-state tunneling splittings were calculated by a method analogous to the linear-combination-of-atomic-orbitals approximation using HO ground-state basis wave functions localized in each well. The results depend upon the several different barriers between different wells, as well as on overlaps of the localized basis states. The behavior may be illustrated by the XY_8 model. Figure 1(a) shows the well locations and labeling of the localized basis states for XY_8. Group theory requires that the ground-state multiplet splits into 4