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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

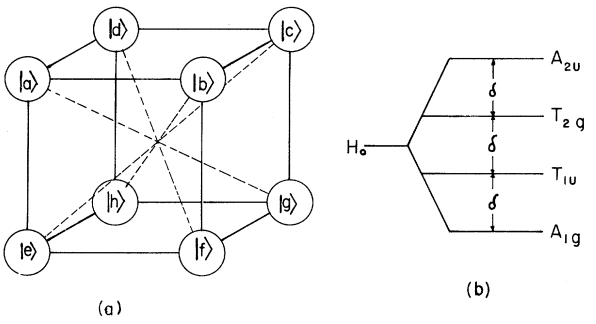

FIG. 1. (a) Location of well minima and labeling of the localized HO basis states for XY_8. (b) Ground-state tunnel splittings in high-barrier limit with α dominant. Here A_{1g} and A_{2u} are singly degenerate; T_{1u} and T_{2g} are triply degenerate. $\delta = 2(\alpha - \frac{1}{2}\hbar\omega S)$.

levels as tabulated in Table I. The overlap integrals S, S', S'', and tunneling matrix elements α, β, γ have the correspondence S and α between adjacent corners, S' and β between opposite corners on the same face, S'' and γ between diagionally opposite corners through the cube.

In this high-barrier limit, the integrals S depend on the basis orbital parameters through $\exp[-m\omega r^2/\hbar]$, where r is the distance between well minima. Because of this strong dependence on r, $S \gg S' \gg S''$. Similarly, the relative magnitudes of α, β, γ depend not only on the overlaps but also on the potential structure between the wells. We have studied both anisotropic

Table I. Energies of the ground-state tunnel splittings in XY_8.

$$E_{A1g} = (E_0 + 3\alpha + 3\beta + \gamma)/(1 + 3S + 3S' + S''),$$

$$E_{T1u} = (E_0 + \alpha - \beta - \gamma)/(1 + S - S' - S''),$$

$$E_{T2g} = (E_0 - \alpha - \beta + \gamma)/(1 - S - S' + S''),$$

$$E_{A2u} = (E_0 - 3\alpha + 3\beta - \gamma)/(1 - 3S + 3S' - S''),$$

where $S = \langle a|b\rangle = \langle b|c\rangle = \cdots$, etc.,

$S' = \langle a|f\rangle = \langle a|h\rangle = \cdots$,

$S'' = \langle a|g\rangle = \langle b|h\rangle = \cdots$,

$E_0 = \langle a|H|a\rangle = \langle b|H|b\rangle = \cdots$,

$\alpha = \langle a|H|b\rangle = \langle b|H|c\rangle = \cdots$,

$\beta = \langle a|H|c\rangle = \langle b|H|d\rangle = \cdots$,

$\gamma = \langle a|H|g\rangle = \langle b|H|h\rangle = \cdots$,

and H is the multiwell Hamiltonian.

$(\alpha_1 \neq \omega_2 \neq \omega_3)$ and spherically shaped HO wells. If the wells are not strongly anisotropic, α is dominant over β and γ with two consequences: First, the energy spectrum takes the particular form of equally spaced levels shown in Fig. 1(b); second, the orbitals have their maximum amplitude along the cube edges of Fig. 1(a). Thus the ion may be thought of semiclassically as shuttling around the surface of the cube, rather than tunneling through the middle as would be appropriate if γ dominated. In this sense the motion is quasirotational and the lowest level structure coincidentally resembles the Devonshire molecular-rotor model.

On the other hand, for small barriers and small r_0 the spherical HO limiting structure may be obtained. It is instructive to classify the symmetry representation in both this and the high-barrier limit, and then to join the two extremes in a compatible way using perturbation and group theory. Thus we examined the lower levels in some detail and the range of behavior for (XY_8) is illustrated in Fig. 2; details on this and other configurations will be presented elsewhere.

We relate our model to experimental observations as follows. Inelastic experiments in Li:KCl by Byer and Sack[7] support the (XY_8) configuration. This is not in conflict with the-

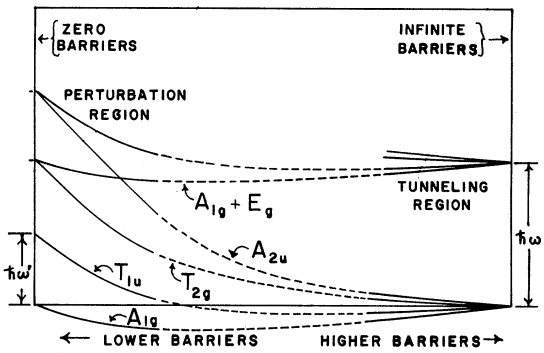

FIG. 2. The energy-level structure compatible with symmetry considerations is given for two extremes, corresponding to the single three-dimensional well HO on the extreme left, and to deep isolated XY_8 wells on the extreme right. When tunneling between deep wells is introduced, the levels are modified and may be classified according to symmetry types as shown by the solid lines near the right-hand side of the figure; the structure shown in Fig. 1(b) corresponds to the lowest set of levels A_{1g}, T_{1u}, T_{2g}, A_{2u}. In the other limit, the introduction of a weak multiwell perturbation splits the HO levels as shown near the left-hand side. Between these limits the levels connect as indicated by the dotted lines.

oretical calculations[4,5] of the potential; relative minima along ⟨100⟩ may accompany absolute minima along ⟨111⟩. Dielectric experiments[9] and thermal-conductivity experiments[8] establish a set of excitations having energy of order $\delta \simeq 1\ \mathrm{cm}^{-1}$. Optical-absorption experiments by Nolt and Sievers[10] find a broad line at approximately 40 cm^{-1} in Li:KCl. We may fit these and a number of other results by a "deep"-well model, as indicated on the right-hand side of Fig. 2. The eight-fold degenerate ground state of the uncoupled deep-well system is split into four levels equally spaced because α dominates; thus the Li^+ shuttles around the cube surface of Fig. 1, in a quasirotational motion. Appropriate parameters for Li:KCl are $\hbar\omega \simeq 50\ \mathrm{cm}^{-1}$, $r_0 \simeq 0.87$ Å. This leads to ground-state splittings of the order of $\delta \simeq 1\ \mathrm{cm}^{-1}$; these are presumed responsible for electrocaloric and related effects.

On the other hand, it appears that the low-barrier limit (r_0 small) applies to the Li:KBr system. No electrocaloric effect has been observed[11] for temperatures of a few degrees Kelvin; thus, the ground state may be assumed not to be a tunnel split-level system like Li:KCl. The optical data[12] show a sharp resonant mode at 17.8 cm^{-1} for Li^6:KBr. Additional theoretical studies which we have carried out on the stress-induced splittings[10] of this absorption line are in accord with the idea that in Li^6:KBr the system is described according to the left-hand side of Fig. 2, the A_{1g}-T_{1u} spacing being $\hbar\omega' \simeq 18\ \mathrm{cm}^{-1}$. In this limit the defect has essentially no rotational character in its spectrum of states.

The polarization and electrocaloric effect for all temperatures and fields have been calculated for Li:KCl from this model; those, together with the stress-field splitting calculation in Li:KBr, will be presented elsewhere.

In closing, we comment on the ingredients of a complete treatment of this problem. So far we have envisaged the motion of a defect only in a relaxed, but otherwise rigid, lattice.[13] The more general treatment of the coupled dynamic lattice-defect system will lead not only to line shifts and broadening in the weak-coupling limit, but also perhaps to Jahn-Teller-like dynamic states in the strong-coupling case.

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