terms in the equation for τ.)

Our conclusion regarding the inconsistency of $J\neq 0$ with $\tau = 0$ is presumably model independent so long as J is Coulombic in origin. In formula (1), the integration over ω also includes summation over bound states so that even in the case in which an impurity level lies well below the conduction band, one cannot treat the electrons in that level on a different footing than the conduction electrons. That is to say that the calculation of τ must include *all* the electrons, be they in the conduction band or in virtual or real bound states.[9]

The work in Ref. 4, since it is based on the persistence of the $(2S+1)$-fold degeneracy right through to $T=0$, does not suffer from the contradiction just outlined. On the other hand, it is evident that a complete off-shell solution for $\tau_{k,k'}$, made self-consistent with $J_{k,k'}$, is needed for a more detailed understanding of this problem.

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[9] The system might exhibit properties resembling those of a singlet state (with J finite) if $\tau(z)$ vanished only for selected energies, particularly at the Fermi energy, but it is hard to see why this should occur, except perhaps accidentally.

STRONG-COUPLING THEORY OF PARAELECTRIC IMPURITIES IN ALKALI HALIDES[*]

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The excitation energies of dipolar impurities such as OH^- or CN^- in alkali halides are calculated, using a modification of the Devonshire model in which it is assumed that the major contribution to the dipolar potential is due to the asymmetrical distortion of the lattice by the dipole.

Recent work on OH^- impurities in KCl[1,2] and CN^- impurities in KCl[3] has pointed out several similarities between the two systems. Both types of impurities are free to rotate between six equilibrium directions along the [100] directions of the crystal. In each case, the energy-level spectrum is characterized by low-lying "tunneling" states with energy separation Δ and higher energy "librational" states of energy ν_l.[2,4] For both systems an externally applied uniaxial stress along a [100] direction produces an energy splitting between the two directions parallel to the stress and the four perpendicular directions.[2,5] The constant of proportionality between the energy splitting and the stress has been measured for KCl:KOH[6,7] and KCl:KCN.[3] Table I contains a summary of the experimental values contained in the literature for the quantities described above.

The "Devonshire model" offers a simple explanation for the tunneling and librational energy splittings. However, this model is not trivially correct; it uses one parameter K, the strength of the octahedral potential, to calculate two independent energy differences. As emphasized in Refs. 1 and 3, the two systems differ in that the Devonshire model works for CN^- and fails for OH^-. For CN^- a Devonshire potential of approximately $K=20\ \mathrm{cm}^{-1}$ gives reasonable values for both the tunneling and librational energy differences. For OH^- a potential of $K=530\ \mathrm{cm}^{-1}$ is needed to explain the 293-cm^{-1} librational level, but the very small tunneling energy of $\Delta=0.21\ \mathrm{cm}^{-1}$ requires a potential of $K=1600\ \mathrm{cm}^{-1}$. Modification of the specific functional form of the Devonshire potential can bring the two calculated values of K closer together, but the magnitude of the discrepancy seems to preclude any explanation based on a free rotor moving in a fixed potential of octahedral symmetry.

The purpose of this Letter is to offer a modification of the Devonshire model that accounts for the level structure of OH^- in KCl and relates this structure to the strength of the strain parameter α. The model is based on the following argument: The ellipticity of the dipole distorts the lattice by pushing away the two nearest-neighbor K^+ ions along the O-H axis and pulling in the four nearest-neighbor ions perpendicular to this axis. As in the Jahn-Teller effect, the instantaneous crystal field as seen by the dipole is thus lowered in symmetry from octahedral to tetragonal. The six low-lying "tunneling states" are now linear combinations of the six many-body states in which both the dipole axis and the accompanying lattice distortion are directed along a particular [100] direction. In this model, the small value of Δ arises because the "tunneling" matrix element between states oriented along different [100] directions includes a factor representing the change in orientation of the lattice distortion. The importance of this effect is directly related to the nonspherical shape of the ion, a property that also results in the splitting of levels under an externally applied stress. A situation similar to the present one occurs in the dynamical Jahn-Teller effect,[8] where the coupling between the electron and the lattice displacements is weak enough to allow tunneling between different Jahn-Teller states. The "lattice overlap integrals" discussed here are analogous to the "orbital reduction factors" of Ref. 8.

We can relate the lattice strain to the motion of the ion by writing an approximate Hamiltonian for the entire system:

$$H=\sum_{\vec{k},\lambda}\omega_{\vec{k},\lambda}C_{\vec{k},\lambda}{}^{\dagger}C_{\vec{k},\lambda}-B\nabla_{\theta,\varphi}{}^{2}+V^{0}(\theta,\varphi)-\sum_{\alpha}\vec{f}_{\alpha}(\theta,\varphi)\cdot\vec{R}_{\alpha}. \tag{1}$$

Here the first term refers to the phonon spectrum of pure KCl, the second term is the kinetic energy of the rotating dipole with $\hbar^2/2I=B$, and the term $V^0(\theta,\varphi)$ is a rotational potential energy of octahedral symmetry (such as the Devonshire potential). The quantity $\vec{f}_\alpha(\theta,\varphi)$ is the force exerted by the dipole on the nearest-neighbor K^+ ion at the lattice site α. $\vec{R}_\alpha$ is the second-quantized expression for the displacement of this ion:

$$\vec{R}_{\alpha}=\sum_{\vec{k},\lambda}(2\Omega\rho\omega_{\vec{k}\lambda})^{-1/2}\times[C_{\vec{k}\lambda}\exp(i\vec{k}\cdot\vec{r}_{\alpha})+C_{\vec{k}\lambda}{}^{\dagger}\exp(-i\vec{k}\cdot\vec{r}_{\alpha})]\vec{e}_{\vec{k}\lambda}. \tag{2}$$

Here Ω is the volume, ρ is the mass density, $\vec{r}_\alpha$ is the position of the lattice site α with respect to the impurity site, and $\vec{e}_{\vec{k}\lambda}$ is the polarization vector of the phonon mode $\vec{k},\lambda$; the six nearest-neighbor lattice sites are identified by $\alpha=\pm x,\pm y,\pm z$. The difference in mass between the impurity dipole and the Cl^- ion it replaces is neglected, as is any change in the volume of the lattice cell occupied by the impurity. With these assumptions, a simple approximation for the angular dependence of $\vec{f}_\alpha(\theta,\varphi)$ is

$$\begin{aligned}\vec{f}_{\pm z}(\theta,\varphi)&=\pm A(\cos^2\theta-\tfrac{1}{3})\vec{k},\\ \vec{f}_{\pm x}(\theta,\varphi)&=\pm A(\sin^2\theta\cos^2\varphi-\tfrac{1}{3})\vec{i},\\ \vec{f}_{\pm y}(\theta,\varphi)&=\pm A(\sin^2\theta\sin^2\varphi-\tfrac{1}{3})\vec{j},\end{aligned} \tag{3}$$

where $\vec{i},\vec{j},\vec{k}$ are unit vectors in the x,y,z directions, respectively.

The solution of Eq. (1) is complicated by the coupling between the motion of the lattice and the impurity in the final term. However, in the "strong-coupling" limit, when the displace-

Table I. Summary of experimental data.

	B (cm^{-1})	Δ (cm^{-1})	ν_l (cm^{-1})	α (cm^3)
KCl:KOH	19^a	0.21^b	293^c	$3.7\times10^{-23\,d}$ $0.59\times10^{-23\,e}$
KCl:KCN	1.25^f	$0.8^{f,g}$	12^f	$0.13\times10^{-23\,f,g}$

[a] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill Book Company, New York, 1955), p. 639.

[b] Ref. 2.

[c] Ref. 1.

[d] Ref. 6.

[e] Ref. 7. The conclusions of the present work support this value.

[f] Ref. 3.

[g] Estimated from curves and other data given in Ref. 3.

ments of the nearest-neighbor ions due to the impurity are larger than the zero-point motion of these ions, an approximate self-consistent solution can be obtained by assuming that the lattice and the dipole move independently. Thus, the state in which the dipole is directed along the $+z$ direction is approximated by the product state

$$|+z\rangle = \psi_z(\theta, \varphi)\phi_z(Q). \tag{4}$$

The functions ψ and ϕ refer to the dipole and the lattice, respectively; Q represents all of the lattice coordinates. Taking the expectation value of (1) with $\psi_z(\theta, \varphi)$ results in the following Hamiltonian for the lattice, which can then be solved for $\phi_z(Q)$:

$$H^{\mathrm{lat}} = \sum_{\vec{\mathrm{k}}, \lambda} \omega_{\vec{\mathrm{k}}, \lambda} C_{\vec{\mathrm{k}}\lambda}{}^{\dagger} C_{\vec{\mathrm{k}}\lambda} - \sum_{\alpha} \langle \vec{\mathrm{f}}_{\alpha}{}^{z} \rangle \cdot \vec{\mathrm{R}}_{\alpha}; \tag{5}$$

here

$$\langle \vec{\mathrm{f}}_{\alpha}{}^{z} \rangle = \langle \psi_z(\theta, \varphi) | \vec{\mathrm{f}}_{\alpha}(\theta, \varphi) | \psi_z(\theta, \varphi) \rangle.$$

Approximately, $|\langle \vec{\mathrm{f}}_{\pm z}{}^{z} \rangle| \approx \frac{2}{3}A$ and $|\langle \vec{\mathrm{f}}_{\pm x}{}^{z} \rangle| = |\langle \vec{\mathrm{f}}_{\pm y}{}^{z} \rangle| \approx -\frac{1}{3}A$; these expressions are not exact equalities because of the zero-point libration of the dipole around the $+z$ axis. One now obtains the effective potential for the dipole by taking the expectation value of H with respect to $\phi_z(Q)$:

$$H^{\mathrm{dip}}(\theta, \varphi) = -B\nabla_{\theta, \varphi}{}^{2} + V^{0}(\theta, \varphi) - \sum_{\alpha} \vec{\mathrm{f}}_{\alpha}(\theta, \varphi) \cdot \langle \vec{\mathrm{R}}_{\alpha}{}^{z} \rangle, \tag{6}$$

where

$$\langle \vec{\mathrm{R}}_{\alpha}{}^{z} \rangle = \langle \phi_z(Q) | \vec{\mathrm{R}}_{\alpha} | \phi_z(Q) \rangle;$$

$$|\langle \vec{\mathrm{R}}_{x}{}^{z} \rangle| = |\langle \vec{\mathrm{R}}_{y}{}^{z} \rangle| = -\tfrac{1}{2}|\langle \vec{\mathrm{R}}_{z}{}^{z} \rangle|.$$

If we assume that the final term of (6) is the major contribution to the rotational potential and neglect $V^0(\theta, \varphi)$, the angular dependence of the potential is completely determined by (3):

$$H^{\mathrm{dip}}(\theta, \varphi) \approx -B\nabla_{\theta, \varphi}{}^{2} - A|\langle \vec{\mathrm{R}}_{z}{}^{z} \rangle|(3\cos^{2}\theta - 1). \tag{7}$$

The ground state of H^{dip} is $\psi_z(\theta, \varphi)$; the first excited state is a librational state.

The self-consistent procedure described above leads to expressions for the six directed states $|z\rangle$, $|-z\rangle$, $\cdots$, and to the energy of the librational state in terms of the parameters B, A, and the $\omega_{\vec{\mathrm{k}}, \lambda}$, $\vec{\mathrm{e}}_{\vec{\mathrm{k}}, \lambda}$. The stress parameter α is related to A by

$$\alpha = (2a/C_{11})(|\langle \vec{\mathrm{f}}_{\pm z} \rangle| - |\langle \vec{\mathrm{f}}_{\pm x} \rangle|) \approx (2a/C_{11})A, \tag{8}$$

where a is the lattice spacing and C_{11} is the elastic stiffness constant of KCl. The analysis of the tunneling splitting[2,4,5] becomes much simpler if the overlap between states rotated by 180°, $\langle z | -z \rangle$, is much smaller than the overlap between states rotated by 90°, $\langle z | x \rangle$. In the present theory this is guaranteed by Eq. (7) if $A|\langle \vec{\mathrm{R}}_{z}{}^{z} \rangle|/B \geqslant 6$, since $\langle \psi_z(\theta, \varphi) | \psi_{-z}(\theta, \varphi) \rangle \approx 0$ if this condition holds. Then the splitting Δ is given by

$$-\tfrac{1}{2}\Delta \approx \langle z | H | x \rangle - \langle z | x \rangle \langle z | H | z \rangle. \tag{9}$$

Use of Eqs. (1) and (4)-(6) allows a simplification to

$$\begin{aligned} \Delta &= 2\langle \phi_z(Q) | \phi_x(Q) \rangle \langle \psi_z(\theta, \varphi) | \psi_x(\theta, \varphi) \rangle \\ &\quad \times (|\langle \vec{\mathrm{R}}_{z}{}^{z} \rangle| - |\langle \vec{\mathrm{R}}_{x}{}^{z} \rangle|)(|\langle \vec{\mathrm{f}}_{z}{}^{z} \rangle| - |\langle \vec{\mathrm{f}}_{x}{}^{z} \rangle|) \\ &= \tfrac{9}{2}\langle \phi_z(Q) | \phi_x(Q) \rangle \langle \psi_z(\theta, \varphi) | \psi_x(\theta, \varphi) \rangle \\ &\quad \times |\langle \vec{\mathrm{R}}_{z}{}^{z} \rangle| \cdot |\langle \vec{\mathrm{f}}_{z}{}^{z} \rangle|. \end{aligned} \tag{10}$$

The quantities above have been evaluated with the aid of calculations of the phonon spectrum in KCl.[9] The lattice overlap integral, $S \equiv \langle \phi_z(Q) | \phi_x(Q) \rangle$, is given by

$$S = \exp\{-1.21 \times 10^{47}\alpha^{2}\}, \tag{11}$$

where α is the stress parameter in cm^3. Figure 1 shows the calculated value of Δ/BS as a function of α^2/B; B and Δ are both measured in units of cm^{-1}. In Fig. 2, the calculated librational energy ν_l/B is plotted as a function of α^2/B.

Because of the very strong dependence of S on α^2, the most practical way to check the theory is to calculate α from the experimental values of Δ and ν_l. The results are tabulated in Table II. For OH$^-$ the two values of α are in good agreement with each other and with the experimental value of Ref. 7. The lack of agreement for CN$^-$ implies that the effective potential acting on this impurity includes a major contribution from $V^0(\theta, \varphi)$, the part of the potential that is independent of the lattice distortion.

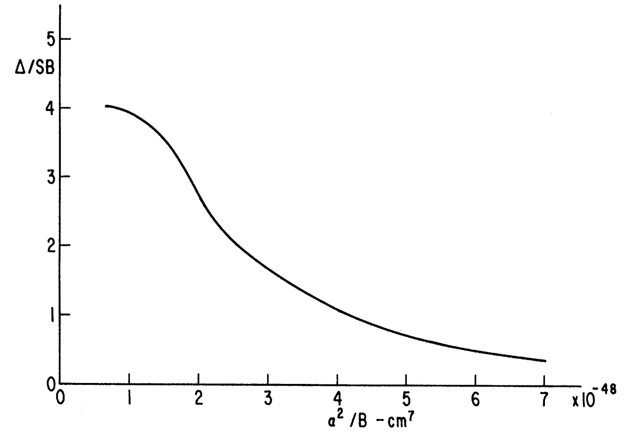

FIG. 1. Calculated value of Δ/SB as a function of α^2/B for the KCl lattice. The units of α are cm^3 and all energies have units cm^{-1}.

One consequence of the Hamiltonian (1) is a simple explanation of the fact that OH$^-$ orients along the [100] directions. A calculation of $V^0(\theta, \varphi)$ based on a point-charge model indicates that the potential minima are along the [111] directions unless a fairly large displacement of the OH$^-$ center of mass from the lattice site is assumed.[10] In the present theory, one can fix θ and φ and adjust the lattice distortion to minimize the expectation value of H. This gives an effective potential energy for rotations of the dipole that are slow enough for the lattice to follow and remain in equilibrium. Leaving out the unknown contribution of $V^0(\theta, \varphi)$, this potential has minima along the [100] directions.

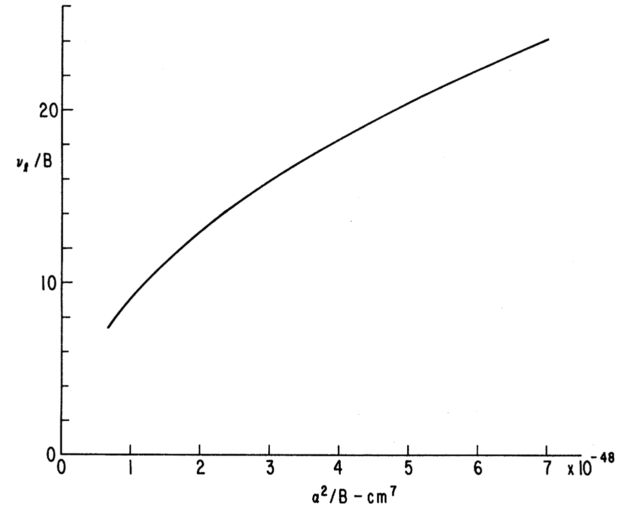

FIG. 2. Calculated value of ν_l/B as a function of α^2/B for a dipolar impurity in KCl.

Table II. Theoretical values of α, in 10^{-23} cm^3, calculated from the data of Table I.

	Calculated from Δ	Calculated from ν_l
KCl:KOH	0.65	0.69
KCl:KCN	0.21	0.12

A possibly serious defect of Eq. (1) is that it implicitly assumes that the OH$^-$ center of mass remains stationary at the lattice site. If the center of mass moves, the effective rotational constant B is decreased[10]; therefore, the integral $\langle\psi_z(\theta, \varphi)|\psi_x(\theta, \varphi)\rangle$ is not given correctly by the above calculation. However, the rapidly varying factor S will probably still allow a reasonably accurate determination of α from Δ. Neither the Devonshire model nor the present model account for an additional level of KCL:KOH at 32 cm^{-1} reported in Ref. 1. The details of this calculation, corrections to the strong-coupling approximation, and the effect of the Hamiltonian (1) on the lattice dynamics will be discussed in a future publication.

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