appears that the magnetization is polarized along $\vec{H}_e$, and one must require the density matrix to show this property. In the experiment of Walstedt,[3] where the nonsecular part of the dipolar Hamiltonian is relatively small, the assumption of separate Zeeman and dipolar spin temperatures seems much more straightforward and valid.

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†RCA Fellow, 1965-1966.

‡Alfred P. Sloan Research Fellow.

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PHOTON AND PHONON INTERACTIONS WITH OH$^-$ AND OD$^-$ IN KCl†

Cheuk K. Chau, Miles V. Klein, and Brent Wedding
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

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Infrared measurements reveal the existence of summation bands at 32 and 293 cm^{-1} above the main stretching band in KCl:KOH. The 32-cm^{-1} level correlates well with a 14°K depression in thermal conductivity curves which also suggest phonon scattering off tunneling levels. These results are inconsistent with the predictions of the Devonshire model.

The OH$^-$ ion has been shown by Lüty and coworkers to substitute for a Cl$^-$ ion in KCl and to align in an electric field in discrete $\langle 100\rangle$ directions.[1] The types of molecular energy levels to be expected of this ion in KCl are the following:

(1) The characteristic O-H infrared stretching level occurs near 3600 cm^{-1}; its frequency is only weakly modified by the surrounding lattice.[2]

(2) If the crystal potential were negligible, we would have a free symmetric rotor with energy levels given by

$$E_J = \hbar^2 J(J+1)/(2I) \equiv BJ(J+1), \tag{1}$$

where I is the moment of inertia, $B \approx 19$ cm^{-1} for OH$^-$, and $J = 0, 1, 2, \cdots$.

The simplest octahedral-crystal potential that can act on the OH$^-$ rotor to yield energy minima along $\langle 100\rangle$ can be written as

$$V = kB[\tfrac{3}{2} - \tfrac{5}{2}(x^4+y^4+z^4)/r^4], \tag{2}$$

in terms of the dimensionless strength parameter k. The energy levels of Eq. (1) then split and shift as a function of k as shown in Fig. 1.[3] This model seems to describe fairly well the thermal and optical properties of KCl:KCN and KBr:KCN.[4]

In the strong-barrier or large-k limit, two new classes of energy levels appear, which can be discussed using a basis of states localized near the six equivalent $\langle 100\rangle$ minima.

(3) The lowest three states are then very close together with a splitting as shown in the inset of Fig. 1 due to tunneling of the ions among these minima.[5] The splitting Δ is about 0.3 cm^{-1}.[5,6]

(4) The OH$^-$ ion should also execute two-dimensional harmonic oscillations or librations about each potential minimum. For a strong potential k in Fig. 1 this produces a transition between one of the levels in the lowest tunneling multiplet and one of the levels in the next higher multiplet (which is quite spread out). This transition should possess an electric dipole moment, as should the "pure" stretching (i.e., stretching + tunneling) and the stretching

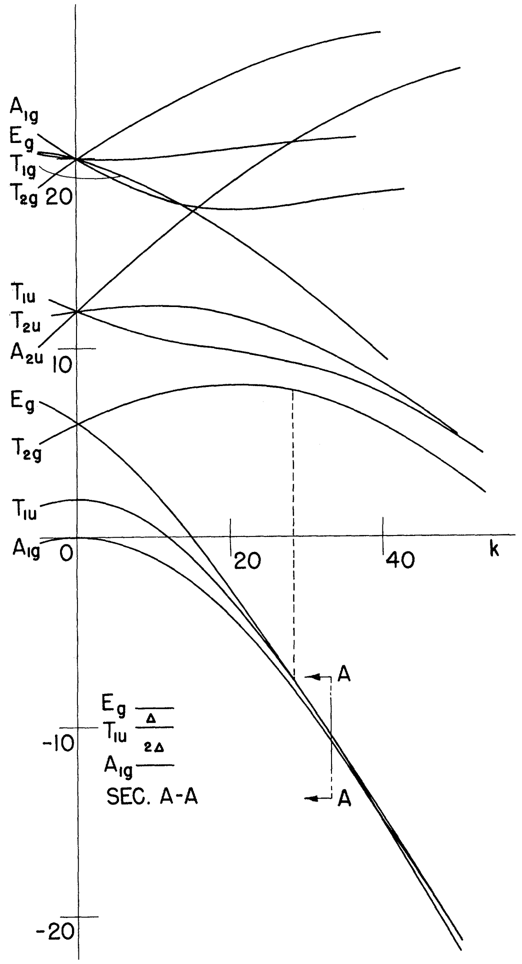

FIG. 1. Devonshire's quantum mechanical calculation (in units of B) of the energy levels of a symmetric rotor in the octahedral field of Eq. (2) as a function of the strength parameters k. The curves are labeled by their appropriate irreducible representation of the full octahedral point group. The dotted line corresponds to the transition that we assign to the librator, C-A, in Fig. 2, having a frequency of 293 cm^{-1}.

+ libration combination transitions.

We now present optical evidence for a librator level at 293 cm^{-1} and optical and thermal evidence for an energy level at 32 cm^{-1} that cannot be explained by the above "Devonshire model" of rotation in an octahedral field. The infrared absorption spectrum of KCl:KOH[7] is shown in Fig. 2, and our assignment of energy levels for this system and for KCl:KOD is shown in Table I. We assign the 293-cm^{-1} C-A level to the librator for the following reasons: (1) Its frequency is near that for OH^- librators in other systems (300-600 cm^{-1}),[8] (2) the frequency shifts approximately by the ratio $(I_{\mathrm{OH}}/I_{\mathrm{OD}})^{1/2} = 1.375$, and (3) we have seen a similar level in KBr:KOH, where C-$A = 304$ cm^{-1} and where a strong absorption has been observed directly at 312 cm^{-1}.[9,10]

Our thermal-conductivity data discussed below establish that line B is quite definitely a summation band on the high-energy side of line A. The 32-cm^{-1} level B-A does not fit the Devonshire model, if we assume that the tunneling levels and the librational levels are already accounted for. Some aspects of our librator data are also inconsistent with the model, for one can show that for large k all the $n=0$ to $n=1$ librational transitions that are allowed by symmetry (namely, $A_{1g} \to T_{1u}$, $E_g \to T_{1u}$, $E_g \to T_{2u}$, $T_{1u} \to T_{1g}$, and $T_{1u} \to T_{2g}$) should occur with about equal probability. We observe only the single broad band C in Fig. 2. On the other hand, for a nearly free rotor the $T_{1u} \to T_{2g}$ transition would be strongest, because it would arise from the lowest allowed $\Delta J = 1$ transition. We arbitrarily assign the 293-cm^{-1} energy level C-A to this transition as shown in Fig. 1 and obtain the result $k = 28.3$ for the potential constant k in Eq. (2). The tunneling barrier height $5Bk/4$ then becomes 670 cm^{-1}. It is clear that there is no place for a 32-cm^{-1} level in this model. It also seems clear that for such a large k value we should observe librational transitions other than $T_{1u} \to T_{2g}$, but we see only one main line, plus a weak line at 3984 cm^{-1}.

The OH to OD frequency ratio for the new level (Table I) is very close to $(I_{\mathrm{OH}}/I_{\mathrm{OD}})^{1/2}$, which strongly suggests that the new level is some sort of torsional harmonic oscillator. But the low frequency will make the zero-point angular excursions extremely large; one can easily show that in the ground state

$$\langle\theta\rangle^2 = B/\hbar\omega = 19/32, \text{ or } \theta_{\mathrm{rms}} = 0.8 \text{ rad.}$$

It is hard to imagine how such an oscillation can occur in a potential that also gives a ten times higher librational frequency. Line B possesses some structure; the sharp line quickly broadens with increasing temperature as shown in Fig. 2. This behavior is not concentration dependent in the range from 700 to 1500 ppm.

Another anomalous feature of the optical results is the extreme weakness of the infrared absorption lines. An oscillator strength f may be defined by the equation[11]

$$f = (A\mu c/ne^2\pi)9\eta/(\eta^2+2)^2. \tag{3}$$

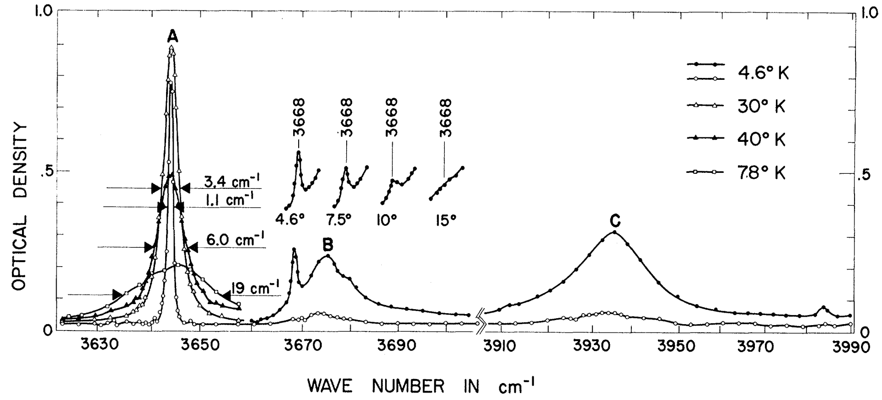

FIG. 2. Infrared absorption curves for two different OH^- concentrations in KCl. The data (solid circles) from the crystal of higher concentration, 1500 ppm,[7] are plotted to reveal the structure of the sidebands B and C. The other data show the temperature dependence of the main peak A as well as the sidebands for a crystal with 250 ppm [KOH]/[KCl]. The temperature dependence of the "spike" component of line B is shown above it.

[c is the velocity of light; $A = \int \alpha(\nu) d\nu$ is the area under absorption line.] For a classical or quantum mechanical harmonic oscillator with charge e and reduced mass μ imbedded in a medium of refractive index η, f would be unity. For a $(J=0) \rightarrow (J=1)$ rotation-vibration transition, angular matrix elements would reduce f to $\frac{1}{3}$. Table II shows the results that can be obtained from Fig. 1 and from additional data. These very low values for f seem to imply that an effective charge e^*, that is very much less than e, is oscillating. This conclusion has also been reached by Fritz, Lüty, and Anger.[7]

Low-temperature thermal-conductivity data are shown in Fig. 3. We associate the pronounced dip near 14°K in KCl:KOH and 10°K in KCl:KOD with strong scattering resonances for phonons interacting with the respective 32 and 23 cm^{-1} $B-A$ optical levels. At the lowest temperatures employed, the conductivity is also considerably reduced, probably because of interactions of phonons with the tunneling levels. Because the tunneling splitting is small, any resonance dip would occur considerably below 1°K. This is borne out by the set of data taken down to 0.3°K on sample "700-OH" by Radosevich. Note that the phonon scattering off OD^- is several times stronger than that off OH^- at low temperatures.

The data in Fig. 3 also contain some evidence for interactions among OH^- impurity ions, because the thermal resistance is not linear in OH concentration. In Table III we present values for the 2°K scattering cross section which have been calculated from $K(n)$, the conductivity at concentration n (OH^-/cm^3), using

$$\sigma(n) = K(0)/[nK(n)l(0)]. \tag{4}$$

Here $l(0)$ is the low-temperature phonon mean free path for the pure crystal, which we equate with the Casimir value $1.12w$. (w = width of the sample, assumed square.)

The observed increase of σ with n can be explained if we assume that the spectrum of tun-

Table I. Summary of 5°K optical data.

	Frequency in cm^{-1}			Librator	New level
	A	B	C	$=C-A$	$=B-A$
KCl:KOH	3643	3675	3936	293	32
KCl:KOD	2685	2708	2910	225	23
OH/OD	1.36	1.36	1.35	1.30	1.40

Table II. Oscillator strengths for OH^- in KCl.

Temperature (°K)	Line A[a] (10^{-3})	Line B[b]	Line C[b]
4.6	0.93	$\approx 0.4 \times 10^{-3}$	$\approx 0.9 \times 10^{-3}$
20	2.0		
30	3.2		
40	3.1		
50	3.2		
78	3.6		
300	4.5		

[a] Measured on a crystal with 250 ppm OH (open circles on Fig. 2).

[b] Measured on a crystal with 750 ppm OH.

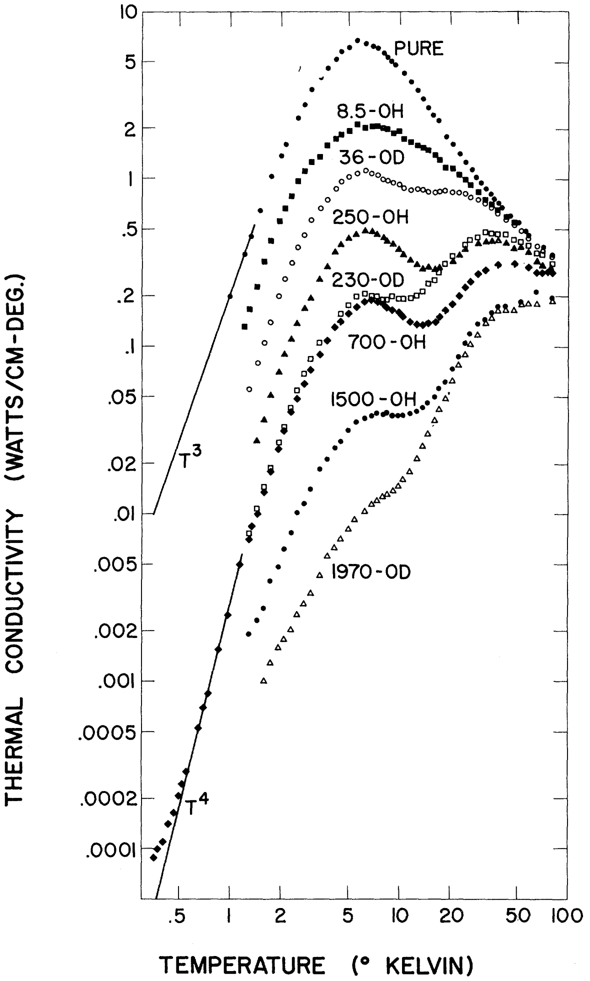

FIG. 3. Thermal conductivity of KCl:KOH and KCl:KOD. The curves are labeled with the concentrations in parts per million.[7] The crystals used for curves "250-OH" and "1500-OH" are the same used for the infrared data in Fig. 2. The data below 1.2°K on crystal "700-OH" were taken by L. G. Radosevich.

Table III. Phonon-scattering cross sections at 2°K.

KCl:KOH		KCl:KOD	
n (10^{18} cm^{-3})	σ (10^{-16} cm^2)	n (10^{18} cm^{-3})	σ (10^{-16} cm^2)
4.0	0.048	0.58	0.19
11.3	0.08	3.7	0.225
24.3	0.18	32	0.46

neling levels broadens with concentration. Then the resulting shift of some of the levels to higher energies would give a better energy match for resonance phonon scattering at the temperature of most of these measurements. This broadening, which may be indicative of dynamic interactions among the OH$^-$ dipoles,[12] was indicated first by dielectric constant measurements[13] and then by microwave absorption measurements.[5,6]

We intend to publish elsewhere a more complete report of these experiments plus additional results on other OH- and OD-doped alkali halides.[14] Measurements are also under way to study the effect of an electric field on the optical and thermal properties. We conclude by mentioning that in NaCl the very strong phonon scattering discovered earlier[15] now seems definitely to be due to OH impurity.[16] There is a depression in the conductivity curves near 5°K which shifts to 3°K with OD doping. The approximate 10-cm^{-1} energy level in NaCl:NaOH implied by this depression may be similar in origin to the 32-cm^{-1} level in KCl:KOH.

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