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Linewidths of Paraelectric-Resonance Transitions

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Calculations are given for the linewidths of the paraelectric resonance transitions of OH$^-$ ions introduced as impurities in KCl. The methods are applied to the transitions reported by Feher, Shephard, and Shore. The width of the narrow line of this experiment is caused both by the dipole-dipole interaction and by strains, presumably arising from dislocations. The broad line observed is primarily strain-broadened.

I. INTRODUCTION

The microwave spectroscopy of dipolar impurities in alkali-halide crystals has excited a great deal of recent interest.[1-5] The spectroscopy of these impurities shows a strong analogy to that of paramagnetic ions. The transitions observed between the energy states of the dipoles have become known as paraelectric resonance transitions.

An experiment by Feher, Shepherd, and Shore[2] shows this analogy in a striking way. A crystal of KCl was grown with a small number of OH$^-$ ions introduced substitutionally for Cl$^-$ ions. The crystal was placed in an ordinary electron-resonance spectrometer in an external static electric field. Two separate resonance transitions were observed and identified; one of them was fairly narrow, the other quite broad.

The calculation of linewidths of paramagnetic resonance lines is a highly developed field. In this paper, we extend some of its well-known techniques to the paraelectric case, with the aim of calculating from first principles the observed linewidths.[2]

In Sec. II we review the Hamiltonian and wave functions which have been proposed for the OH$^-$, following the work of FSS and Shore.[4] In Sec. III we apply the classic moment techniques of Van Vleck to the calculation of paraelectric-resonance linewidths arising from the dipole-dipole interaction. We first give a model calculation for a resonance line in zero external field, then apply the methods developed to the transitions of the FSS experiment. In Sec. IV we consider strains as a line-broadening mechanism.

II. HAMILTONIAN

Shore[4] gives a detailed discussion of the model Hamiltonian which we use. We briefly reproduce his major points. In the absence of an external electric field, an OH$^-$ ion in KCl finds itself in a strong octahedral crystal electric field. If the crystal field is very strong, the eigenstates of the ion are six strongly localized states, approximately degenerate, corresponding to the dipole pointing along the coordinate axes. The states can be written

$$|z\rangle,\ |-z\rangle,\ |x\rangle,\ |-x\rangle,\ |y\rangle,\ |-y\rangle. \qquad (1)$$

We will not specify these states further except to say that they are orthogonal and that

$$\langle z|ex|z\rangle = -\langle z|ez|-z\rangle = \mu, \qquad (2)$$

where μ is the dipole moment. Similar equations hold for x and y, and all matrix elements of the type $\langle z|x|x\rangle$, $\langle z|y|z\rangle$, $\cdots$, are taken to be zero because the states are assumed to be very strongly localized.

In the parts of the FSS experiment which we consider the external fields (both the dc field $\mathbf{E}_0$ and the ac field $\mathbf{E}_{\mathrm{ac}}$) were along a $\langle 100\rangle$ axis, which we designate as the z axis. Hence the parts of the Hamiltonian for interaction with the field

$$\mathcal{H}_E + \mathcal{H}_{\mathrm{ac}} = -\mathbf{p}\cdot(\mathbf{E}_0 + \mathbf{E}_{\mathrm{ac}}) \qquad (3)$$

have the following nonvanishing matrix elements:

$$\begin{aligned} \langle z|\mathcal{H}_E|z\rangle &= -\mu E_0, & \langle z|\mathcal{H}_{\mathrm{ac}}|z\rangle &= -\mu E_{\mathrm{ac}},\\ \langle -z|\mathcal{H}_E|-z\rangle &= \mu E_0, & \langle -z|\mathcal{H}_{\mathrm{ac}}|-z\rangle &= \mu E_{\mathrm{ac}}. \end{aligned} \qquad (4)$$

If the E fields are the external fields, then μ is the dipole moment uncorrected for local fields.

In a real crystal, for which the crystal field is not of infinite strength, there will be a finite probability of rotational tunneling among the states of Eq. (1). This probability will be largest for 90° rotations. We write the Hamiltonian describing the tunneling on the basis of Eq. (1);

$$\mathcal{H}_0 = -\tfrac{1}{2}\Delta \begin{pmatrix} 0 & 0 & 1 & 1 & 1 & 1\\ 0 & 0 & 1 & 1 & 1 & 1\\ 1 & 1 & 0 & 0 & 1 & 1\\ 1 & 1 & 0 & 0 & 1 & 1\\ 1 & 1 & 1 & 1 & 0 & 0\\ 1 & 1 & 1 & 1 & 0 & 0 \end{pmatrix}. \qquad (5)$$

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* Supported by the National Science Foundation.

[1] U. Kuhn and F. Lüty, Solid State Commun. **3**, 31 (1965); I. Shepherd and G. Feher, Bull. Am. Phys. Soc. **10**, 735 (1965); R. W. Dreyfus and W. E. Bron, *ibid.* **11**, 73 (1966); W. E. Bron and R. W. Dreyfus, Phys. Rev. Letters **16**, 165 (1966); L. A. Vredevoe, Phys. Rev. **153**, 312 (1967); G. D. Mahan, *ibid.* **153**, 983 (1967).

[2] G. Feher, I. W. Shepherd, and H. B. Shore, Phys. Rev. Letters **16**, 500 (1966), henceforth referred to as FSS.

[3] W. N. Lawless, Physik Kondensierten Materie **5**, 100 (1966); **5**, 403 (1966); Phys. Rev. Letters **17**, 1048 (1966); W. Zernik, Phys. Rev. **139**, A1010 (1965); M. W. Klein, *ibid.* **141**, 489 (1966).

[4] H. B. Shore, Phys. Rev. **151**, 570 (1966).

[5] I. Shepherd and G. Feher, Phys. Rev. Letters **15**, 195 (1965); H. Hartel and F. Luty, Phys. Status Solidi **12**, 347 (1965).

Table I. Wave functions for $E_0=0$ and for $E_0=7.3$ eV/cm.

State	Energy	Representation label
$E_0=0$; symmetry group O_h		
$\psi_0=(\frac{1}{6}\sqrt{6})\{\mid x\rangle+\mid -x\rangle+\mid y\rangle+\mid -y\rangle+\mid z\rangle+\mid -z\rangle\}$	-2Δ	A_{1g}
$\psi_1=(\frac{1}{2}\sqrt{2})\{\mid z\rangle-\mid -z\rangle\}$ $\psi_2=(\frac{1}{2}\sqrt{2})\{\mid x\rangle-\mid -x\rangle\}$ $\psi_3=(\frac{1}{2}\sqrt{2})\{\mid y\rangle-\mid -y\rangle\}$	0	T_{1u}
$\psi_4=\frac{1}{2}\{\mid x\rangle+\mid -x\rangle-\mid y\rangle-\mid -y\rangle\}$ $\psi_5=(\frac{1}{6}\sqrt{3})\{2\mid z\rangle+2\mid -z\rangle-\mid x\rangle-\mid -x\rangle-\mid y\rangle-\mid -y\rangle\}$	Δ	E_g
$E_0=7.3$ kV/cm; symmetry group C_{4V}		
$\varphi_0=(1.575)^{-1/2}(\psi_0+0.681\psi_1+0.333\psi_5)$	$-2.925\ \Delta$	$1A_1$
$\varphi_1=(2.99)^{-1/2}(\psi_0+0.936\psi_1-1.06\psi_5)$	$-0.728\ \Delta$	$2A_1$
$\varphi_2=\psi_2$ $\varphi_3=\psi_3$	0	E
$\varphi_4=\psi_4$	Δ	B_1
$\varphi_5=(1.794)^{1/2}(0.25\psi_0-0.855\psi_1+\psi_5)$	$2.644\ \Delta$	$3A_1$

The parameter Δ measures the tunneling probability. This form of Hamiltonian is also suitable to the translational states proposed by Bron and Dreyfus.[1]

The effect of strains must now be taken into account. We neglect the effect of shear strains, and we also neglect the dilation or breathing mode

$$S_3=e_{xx}+e_{yy}+e_{zz}. \tag{6}$$

The dilation gives an unimportant over-all shift in energy levels.

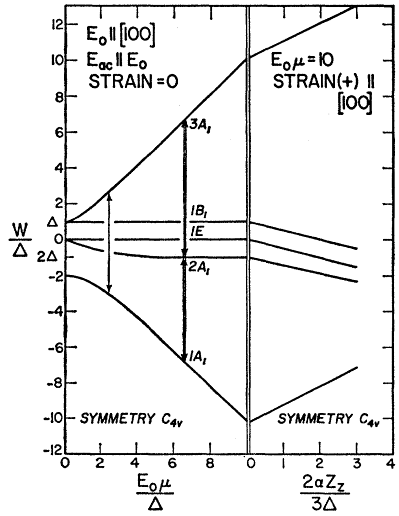

Fig. 1. Energy level diagram of an OH^- dipole in a crystal field of octahedral symmetry with an electric field along a ⟨100⟩ axis. The double lines indicate an allowed transition, the single line a forbidden transition. The effect of a uniaxial strain in the [100] direction is indicated in the right half of the figure. (After FSS.)

We may then write, following Shore, the effect of crystal distortions on the OH^- ions. In terms of the stresses, the Hamiltonian is given by

$$\begin{aligned}\langle z\mid \mathcal{H}_S\mid z\rangle&=\langle -z\mid \mathcal{H}_S\mid -z\rangle=\tfrac{2}{3}\alpha(Z_z-\tfrac{1}{2}X_x-\tfrac{1}{2}Y_y),\\ \langle x\mid \mathcal{H}_S\mid x\rangle&=\langle -x\mid \mathcal{H}_S\mid -x\rangle=\tfrac{2}{3}\alpha(X_x-\tfrac{1}{2}Y_y-\tfrac{1}{2}Z_z),\\ \langle y\mid \mathcal{H}_S\mid y\rangle&=\langle -y\mid \mathcal{H}_S\mid -y\rangle=\tfrac{2}{3}\alpha(Y_y-\tfrac{1}{2}X_x-\tfrac{1}{2}Z_z).\end{aligned} \tag{7}$$

All the other matrix elements vanish. Here α is an experimentally measured parameter.[5]

The dipole-dipole interaction between OH^- ions is

$$\mathcal{H}_{\rm dd}=(e^2/\epsilon R_{ij}^3)[\mathbf{r}_i\cdot\mathbf{r}_j-(\mathbf{r}_i\cdot\mathbf{R}_{ij})(\mathbf{r}_j\cdot\mathbf{R}_{ij})/R_{ij}^2]. \tag{8}$$

Here ϵ is the static dielectric constant, $e\mathbf{r}_i$ is the dipole operator for the site i, and $\mathbf{R}_{ij}$ is the vector between the site i and the site j.

The parameters μ, Δ, α, and ϵ have been measured.[2,6] Their values are

$$\mu=(4.0\pm0.2)\times10^{-18}\ \text{esu},$$

$$\Delta/k_B=0.30\text{°K},$$

$$\epsilon=4.85.$$

Two different values of α have been given in the literature[5]

$$\alpha=3.7\times10^{-23}\ \text{cm}^3,$$

$$\alpha=0.59\times10^{-23}\ \text{cm}^3.$$

A calculation by Shore seems to support the second

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[6] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed., p. 156.

value.[7] The full Hamiltonian for the OH^- ions is, from (3), (5), (7), and (8),

$$\mathcal{H}_T=\sum_i(\mathcal{H}_{0i}+\mathcal{H}_{Ei}+\mathcal{H}_{\mathrm{ac}i}+\mathcal{H}_{Si})+\sum_{i>j}\mathcal{H}_{\mathrm{dd}}(ij). \quad (9)$$

The sum is over all the occupied OH^- sites. The terms $\mathcal{H}_{Si}$ and $\mathcal{H}_{\mathrm{dd}}$ give rise to the broadening of the resonance lines.

The Hamiltonian $\mathcal{H}_0+\mathcal{H}_E$ appropriate to noninteracting ions in an unstrained crystal was diagonalized by FSS. In Fig. 1 we give their results for the energy levels as a function of applied field. The representation labels refer to the group C_{4V} appropriate to the KCl crystal with an electric field along the z axis.

Shore has given the wave functions of $\mathcal{H}_0+\mathcal{H}_E$ in terms of the states $|z\rangle$, $|-z\rangle$, etc., for very strong and very weak electric fields. (That is, for $\mu E_0\gg\Delta$ and $\mu E\ll\Delta$, respectively.) In Table I we give the wave functions for $E_0=0$ and for $E_0=7.3$ kV/cm, which corresponds to the narrow line. The narrow line was identified as the forbidden transition $1A_1\leftrightarrow 3A_1$. The two transitions $1A_1\leftrightarrow 2A_1$, $2A_1\leftrightarrow 3A_1$ were identified with the broad line of the experiment. These allowed transitions are not resolved because of their breadth. The calculation of the widths of these resonance lines is the concern of this paper.

As FSS have shown, when $\mathcal{H}_S$ of Eq. (7) is taken into account we obtain at once a qualitative understanding of the relative linewidths of the two transitions. We can see this from the right half of Fig. 1, where we plot the energy of the various levels versus the stress, for a uniaxial stress Z_z. The levels $1A_1$, $3A_1$ move nearly parallel under the influence of the stress; hence the forbidden transition is not appreciably strain-broadened. However, the stress has a large effect on the two allowed transitions.

We need another broadening mechanism for the forbidden transition. We turn to the dipole-dipole interaction, as treated in Sec. III. The allowed transitions seem to be strain-broadened. We attempt to make the FSS argument more quantitative in Sec. IV.

III. DIPOLAR BROADENING

In a classic exposition, Van Vleck[8] calculated the moments of paramagnetic resonance lines broadened by the dipole–dipole interaction. In this section we apply his techniques to the paraelectric case.

We do not use the full treatment of Van Vleck, which is fairly complicated even for paramagnetic resonance, but we take advantage of the following fact: In experiments of the type performed by FSS we always consider crystals with small fractional concentrations of OH^- ions. Kittel and Abrahams[9] have treated analogous paramagnetic systems. They show that for sufficiently small fractional concentrations of paramagnetic (in our case, paraelectric) impurities all of Van Vleck's equations reduce to expressions involving sums only over pairs of ions. Hence the moments are given by expressions of identical form if we treat a single pair or if we treat a large number of ions. We can treat each pair of OH^- ions separately, and sum over all such pairs. We use this procedure in all the calculations in this section.

In order to illustrate our techniques, we now present a model calculation in which we take $E_0=0$. The time-independent part of the Hamiltonian for a pair of ions at points i and j is just

$$\mathcal{H}=\mathcal{H}_{0i}+\mathcal{H}_{0j}+\mathcal{H}_{\mathrm{dd}}. \quad (9')$$

The time-dependent part is

$$\mathcal{H}_{\mathrm{ac}}=\mathcal{H}_{\mathrm{ac}\,i}+\mathcal{H}_{\mathrm{ac}\,j}. \quad (9'')$$

If we examine Fig. 1 we see that at zero external field two transitions at a single site are possible: one of energy Δ, the other of energy 2Δ. We now calculate the broadening of the latter transition due to $\mathcal{H}_{\mathrm{dd}}$.[10]

The relevant wave functions are given in Table I. Using these, we construct a 36-dimensional direct-product space with the basis vectors $\psi_\alpha(i)\psi_\beta(j)$. Here α and β run from 0 to 5, and i and j are site labels. Using this basis, we can find the matrices of the operators in (9).

The calculations of the matrix elements are straightforward with the relations given in Sec. II. One point should be noted: We must insure that we are calculating the moments only of the transition of energy 2Δ. This corresponds to Van Vleck's "truncation" procedure. To this end we neglect for the purposes of this calculation all matrix elements of $\mathcal{H}_{\mathrm{ac}\,i}$ other than

$$\langle\psi_0(i)\,|\,\mathcal{H}_{\mathrm{ac}\,i}\,|\,\psi_1(i)\rangle=\langle\psi_1(i)\,|\,\mathcal{H}_{\mathrm{ac}\,i}\,|\,\psi_0(i)\rangle=-\mu E_{\mathrm{ac}}/\sqrt{3}. \quad (10)$$

We now apply Van Vleck's equation[8]:

$$\hbar^2\langle(\Delta\omega)^2\rangle=-\mathrm{Tr}[\mathcal{H},\mathcal{H}_{\mathrm{ac}}]^2/\mathrm{Tr}(\mathcal{H}_{\mathrm{ac}})^2-(\hbar\omega_0)^2. \quad (11)$$

In our case, $\hbar\omega_0=2\Delta$. The actual calculation using (8)–(11) is tedious.

After the commutator is squared out, the traces taken, the final average over all pairs performed, we have the result

$$\hbar^2\langle(\Delta\omega)^2\rangle=(f\mu^4/6\epsilon^2)\sum_j{}'(1/R_{ij}^6)(1.22+1.67\cos^2\theta_{ij}). \quad (12)$$

Here f is the fractional concentration of OH^- ions, and θ_{ij} is the angle between the vector $\mathbf{R}_{ij}$ and the z axis.

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[7] H. B. Shore, Phys. Rev. Letters **17**, 1142 (1966).

[8] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[9] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

[10] The much weaker transition of energy 2Δ corresponding to two transitions each of energy Δ, at two different sites, will be ignored.

The sum is over all sites $j \neq i$ whether or not occupied by an OH^- ion. We have used the relation (see Ref. 9)

$$\sum_{ij}{}' \text{ (occupied sites)} = Nf \sum_{j}{}' \text{ (all sites)}, \qquad (13)$$

where N is the total number of impurity ions. For a fcc lattice like the one formed by the Cl^- sites of KCl, the sum in (12) has the value $205.5/a^6$, where a is the lattice parameter.

All the odd moments of the transition at 2Δ are zero, as one may show by explicit examination of the relevant matrices. The next even moment, the fourth, is calculated in a similar way using the relations[8]

$$\langle(\Delta\omega)^4\rangle = \langle\omega^4\rangle - 6\omega_0^2\langle(\Delta\omega)^2\rangle - \omega_0^4,$$
$$\langle\omega^4\rangle = (1/\hbar^4) \operatorname{Tr}[\mathcal{H}, [\mathcal{H}, \mathcal{H}_{ac}]]^2 / \operatorname{Tr}(\mathcal{H}_{ac})^2. \qquad (14)$$

Once more the explicitly known matrices are commuted, squared, and their trace taken in the 36-dimensional direct-product basis. The calculations are fairly long, but lead to the relatively simple result

$$\hbar^4\langle(\Delta\omega)^4\rangle = (f\mu^8/6\epsilon^4) \sum_{j}{}' (1/R_{ij}^{12})(0.43 + 18\cos^8\theta_{ij}$$
$$-28\cos^6\theta_{ij} + 12.67\cos^4\theta_{ij} + 0.48\cos^2\theta_{ij} - 2\cos^2\theta_{ij}\sin^4\theta_{ij}$$
$$\times \cos^2\phi_{ij}\sin^2\phi_{ij} - 18\cos^4\theta_{ij}\sin^4\theta_{ij}\sin^2\phi_{ij}\cos^2\phi_{ij}). \qquad (15)$$

Here ϕ_{ij} and θ_{ij} are the azimuthal and polar angles of $\mathbf{R}_{ij}$ with respect to the crystalline axes. For a fcc lattice the entire sum in (15) has the value $871.62/a^{12}$.

This equation is quite a bit more complicated than Van Vleck's corresponding expressions. This is due to the complicated and rather low symmetry of the electric dipole states. For instance, the appearance of the azimuthal angle ϕ_{ij} in the expressions arises from the fact that the dipoles can be localized about any of the six coordinate directions, so that the dipole-dipole interaction depends on the exact orientation of $\mathbf{R}_{ij}$.

The low symmetry of the electric dipoles should be contrasted with the cylindrical symmetry of the more familiar magnetic dipole states. In a strong electric field E_0, the wave function changes form corresponding to the alignment of the electric dipoles along the z axis. In this case the ϕ_{ij} dependence will drop out.

The Van Vleck techniques that we have used up till now are limited in validity to the high-temperature region. Because the FSS experiment was performed at 1.3°K, the high-temperature approximation (i.e., all the states are equally populated) may not be valid. We must extend our calculations to finite temperatures. An extension of this type has been carried for the analogous paramagnetic case by several authors.[11] We may compactly reexpress their results for the paraelectric case by using the autocorrelation functions.

Table II. Temperature dependence of the second and fourth moments of the transition with energy 2Δ in the absence of an applied electric field or strain field. The parameter η is defined by $\eta = \hbar\mu/\epsilon a^3$.

T(°K)	$\langle(\Delta\omega)^2\rangle/f\eta^2$	$\langle(\Delta\omega)^4\rangle/f\eta^4$
1	31.73	119.39
2.5	33.23	134.76
5	33.75	140
7.5	33.92	141.76
10	34	142.63
∞	34.26	145.27

We now give, without proof,[12] an expression for the autocorrelation function $\Gamma(t)$ from which all the moments may be derived.

$$\Gamma(t) = C\exp(-i\omega_0 t)$$
$$\times \sum_{ij}{}' \operatorname{Tr}(\exp(-\mathcal{H}/kT)[\mathcal{H}_{ac}^-(t), \mathcal{H}_{ac}^+]),$$
$$C = \{\sum_{ij}{}' \operatorname{Tr}\exp(-\mathcal{H}/kT)[\mathcal{H}_{ac}^-, \mathcal{H}_{ac}^+]\}^{-1}. \qquad (16a)$$

Here ω_0 is the resonance frequency of the noninteracting system of dipoles, and the sum is over all pairs of sites occupied by OH^- ions.

The operators appearing inside the traces are defined as follows:

$$\begin{aligned} \langle n|\mathcal{H}_{ac}^+|m\rangle &= 0 && \text{for} \quad E_m > E_n, \\ &= \langle n|\mathcal{H}_{ac}|m\rangle && \text{for} \quad E_m < E_n; \\ \langle n|\mathcal{H}_{ac}^-|m\rangle &= \langle n|\mathcal{H}_{ac}|m\rangle && \text{for} \quad E_m > E_n, \\ & \quad 0 && \text{for} \quad E_m < E_n. \end{aligned} \qquad (16b)$$

Here $|m\rangle$ and $|n\rangle$ are eigenstates of the pair of ions at sites i and j. Also,

$$\mathcal{H}_{ac}^+(t) = \exp(i\mathcal{H}t/\hbar)\mathcal{H}_{ac}^+\exp(-i\mathcal{H}t/\hbar). \qquad (16c)$$

The relation

$$\langle(\Delta\omega)^2\rangle = -d^2\Gamma(t)/dt^2|_{t=0} \qquad (17)$$

gives us an expression for the second moment of the transition (for finite temperatures) in terms of traces. A typical term is the following:

$$\operatorname{Tr}(\exp(-\mathcal{H}/kT)\mathcal{H}_{ac}^-\mathcal{H}\mathcal{H}_{ac}^+\mathcal{H}).$$

We handle the exponential factor by using the approximation

$$\exp(-\mathcal{H}/kT) \cong \exp(-\mathcal{H}_0/kT). \qquad (18)$$

Here $\mathcal{H}_0 = \mathcal{H}_{0i} + \mathcal{H}_{0j}$. The eigenvalues of $\mathcal{H}_0$ are known (Table I) along with the matrices of $\mathcal{H}$ and $\mathcal{H}_{ac}$. We

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[11] M. H. L. Pryce and K. W. H. Stevens, Proc. Phys. Soc. (London) **A63**, 36 (1950); K. Kambe and T. Usui, Progr. Theoret. Phys. (Kyoto) **8**, 302 (1952); M. McMillan and W. Opechowski, Can. J. Phys. **38**, 1168 (1960); **39**, 1369 (1961).

[12] The proof is easy and follows closely the one given by G. E. Pake *Paramagnetic Resonance* [(W. A. Benjamin, Inc., New York, 1962), Sec. 7–1] except that Pake uses the high-temperature approximation.

TABLE III. Linewidths of the forbidden transition. (Column 3 is for the dipole-dipole interaction.)

Concentration of OH^-, in cm^{-3}	$\hbar\beta$ (exptl), (erg)[a]	$\hbar\beta$ (theoret), (erg)
1.3×10^{18}	0.7×10^{-16}	0.16×10^{-16}
4×10^{17}	0.3×10^{-16}	0.05×10^{-16}
3×10^{16}	0.1×10^{-16}	0.37×10^{-18}

[a] G. Feher (private communication).

proceed as before with explicit and somewhat lengthy matrix calculations to find the results which are given in Table II.

We turn to the calculation of the linewidth of the forbidden transition of the FSS experiment. We replace Eq. (9a) by

$$\mathcal{H}=\mathcal{H}_{0i}+\mathcal{H}_{0j}+\mathcal{H}_{Ei}+\mathcal{H}_{Ej}+\mathcal{H}_{\mathrm{dd}}. \tag{19}$$

The steps leading to the calculations of the moments are identical to those above: We choose a product basis which diagonalizes the first four operators in Eq. (19). This is the basis $\phi_\alpha(i)\phi_\beta(j)$ where α and β run from 0 to 5, and the functions ϕ_α are given in Table I. We then calculate the matrices of the operators appearing in the correlation function (16).

We make a simplifying approximation in carrying out the work. The eigenstates ϕ correspond to "aligned" dipoles under the influence of a strong external electric field. So we replace Eq. (8) by

$$\mathcal{H}_{\mathrm{dd}}\cong(e^2/\epsilon R_{ij}^3)(1-3Z_{ij})z_iz_j. \tag{20}$$

Here Z_{ij} is the z component of the vector $\mathbf{R}_{ij}$.

The truncation of Eq. (10) is performed to pick out the correct transition $\phi_0(i)\leftrightarrow\phi_5(i)$. Because of the net alignment of dipoles, we expect the resonance line to be asymmetrically shifted. This is indeed the case, but the shift turns out to be small, about 0.02 of the unshifted resonance frequency.

The even moments of the line are calculated to be

$$\hbar^2\langle(\Delta\omega)^2\rangle=0.27(f\mu^4/\epsilon^2)\sum_j{}'(1/R_{ij}^6)(1-3\cos^2\theta_{ij})^2, \tag{21}$$

$$\hbar^4\langle(\Delta\omega)^4\rangle=0.28(f\mu^8/\epsilon^4)\sum_j{}'(1/R_{ij}^{12})(1-3\cos^2\theta_{ij})^4. \tag{22}$$

The sums in (21) and (22) have been calculated numerically to be $68.9/a^6$ and $325.2/a^{12}$, respectively.

To compare with the FSS experiment we use the moments (21) and (22) to fit a CO Lorentzian line with CO at $\omega_0\pm\alpha$ and half-width β at half-maximum intensity.

The value of β and α are found from the well-known relations

$$\langle(\Delta\omega)^2\rangle=2\beta\alpha/\pi, \tag{23a}$$

$$\langle(\Delta\omega)^4\rangle=2\beta\alpha^3/3\pi. \tag{23b}$$

The values of β found from (21)–(23) are compared with the measured values in Table III.

For the two higher concentrations of OH^- listed in the table the agreement to within one order of magnitude may be considered satisfactory. Certainly the simplicity of our treatment should lead us to expect no better. We have used observed values of the dipole moment uncorrected for the polarizability of the medium. The calculation by Mahan (Ref. 1) suggests that this procedure is a good approximation.

In fact our use of the experimental dipole moment takes into account a possible charge-dipole effect which may arise if the OH^- is displaced along one of six equivalent $\langle100\rangle$ axes. As pointed out by Bron and Dreyfus,[1] the permanent dipole moment of the OH^- ion is oriented so that the proton always falls on the $\langle100\rangle$ axis away from the nearest K^+ after the ion is displaced. Suppose we consider a positive and a negative charge of equal magnitude to be present at the lattice point from which the OH^- is displaced. The negative charges preserve the crystal arrangement so that its effect on the other OH^- ions has been accounted for in the crystal field approximation. The positive charge at the lattice point and the negative charge on the displaced OH^- form a dipole moment. This dipole moment has the same direction as the permanent dipole moment of the OH^-, namely, along the [100] axis. The resultant dipole moment is what is measured experimentally.

The disagreement of two orders of magnitude of the last line of Table II suggests that we have neglected a line-broadening mechanism which is independent of concentration of OH^-. We should expect such a mechanism in any case, because the measured linewidths are not linear in f, as they are expected to be from the discussion in Ref. 9.

We can apply the techniques developed here to estimate the dipolar width of the allowed transition of FSS. As we might expect, the predicted width turns out to be much too small (by a factor of $\sim10^{-2}$) to explain the experimental values.

To rectify both of these discrepancies we now turn to a discussion of static strain broadening.

IV. STRAIN BROADENING

The Hamiltonian $\mathcal{H}_S$ given in Eq. (7) will describe a line broadening provided there exists an inhomogeneous stress field in the crystal. We now inquire into the possible sources of such a stress field. First, there may be dislocations present in the crystal. This would give rise to a broadening independent of the concentration of OH^-. Also, strains may be introduced when the OH^- ions are substituted for the Cl^-, due to differences in ionic radius. This is a concentration-dependent effect.

The stresses at a point i in an isotropic, elastic medium due to an edge dislocation at the point j are given by.[13]

$$\begin{aligned} X_x &= -Yb\sin\phi_{ij}(2+\cos 2\phi_{ij})/2\pi(1-\sigma)R_{ij}, \\ Y_y &= Yb\sin\phi_{ij}\cos 2\phi_{ij}/2\pi(1-\sigma)R_{ij}, \\ Z_z &= -2\sigma Yb\sin\phi_{ij}/2\pi(1-\sigma)R_{ij}. \end{aligned} \tag{24}$$

Here R_{ij} and ϕ_{ij} are cylindrical coordinates, with the end of the dislocation as center, the dislocation line as the z axis, and the Burger vector along the x axis. Further, Y is the shear modulus, σ is the Poisson's ratio, and b is the magnitude of the Burger vector, $b \cong 10^{-8}$ cm. For simplicity we adopt a model in which the dislocations are all parallel and occur randomly with probability f_d at lattice points in a plane perpendicular to their common direction. To find the total stress field at i we sum (24) over all dislocations j. Then we calculate the various combinations of stresses appearing in $\mathcal{H}_S$.

Our total Hamiltonian now is $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_E+\mathcal{H}_S$. We use the first two operators as a zero-order Hamiltonian, and $\mathcal{H}_S$ as a perturbation. Using the zero-order eigenfunctions ϕ_α of Table I we find

$$\begin{aligned} \langle\phi_0|\mathcal{H}_S|\phi_0\rangle &= \Delta E(1A_1) = 0.61\sum_j L_{ij}, \\ \langle\phi_5|\mathcal{H}_S|\phi_5\rangle &= \Delta E(3A_1) = 0.71\sum_j L_{ij}. \end{aligned} \tag{25}$$

Here

$$\begin{aligned} L_{ij} &= \tfrac{2}{3}\alpha(Z_{zij}-\tfrac{1}{2}X_{xij}-\tfrac{1}{2}Y_{yij}) \\ &= Yb\alpha(1-2\sigma)\sin\phi_{ij}/3\pi(1-\sigma)R_{ij}. \end{aligned} \tag{26}$$

The sums in (25) are over all dislocations j. The shift in the resonance frequency is given by

$$\hbar\Delta\omega_i = \Delta E(3A_1)-\Delta E(1A_1) = 0.10\sum_j L_{ij}. \tag{27}$$

The observed moments of the strain broadened line are the averages over the independent sites i of the powers of $\hbar\Delta\omega_i$. If $f_d \ll 1$, we can see by the methods of Ref. 9 that

$$\hbar^2\langle(\Delta\omega)^2\rangle = f_d(0.10)^2 {\sum_j}' L_{ij}^2, \tag{28}$$

$$\hbar^4\langle(\Delta\omega)^4\rangle = f_d(0.10)^4 {\sum_j}' L_{ij}^4. \tag{29}$$

These sums are over all lattice points in the plane intersecting the dislocations. They have been performed numerically.

We now use these expressions to fit the anomalous low-concentration datum point in the FSS experiment by finding the half-width from (23), (28), and (29). We find that f_d must be about 10^{-4} if we use the value of α given by Shepherd and Feher, whereas the value reported by Hartel and Lüty requires f_d to be about 6×10^{-4}. These probabilities correspond to densities of dislocation lines $\rho_d \sim 4\times10^{10}$ cm^{-2} or $\rho_d \sim 27\times10^{10}$ cm^{-2}. These values are perhaps not much higher than what one would expect, so that the proposed broadening mechanism is possibly correct.

We now discuss the allowed (broad) transition of the FSS experiment. This transition takes place at a large electric field (i.e., $E_0\mu/\Delta \gg 1$; here $E_0=19.4$ eV/cm), so that we can use the high-field wave functions given by Shore[14] to diagonalize the zero-order Hamiltonian $\mathcal{H}_0+\mathcal{H}_E$. To consider the effect of the dislocations on the allowed transition we once more use $\mathcal{H}_S$ as a perturbation to find

$$\begin{aligned} \Delta E(1A_1) &= 1.14\sum_j L_{ij}, \\ \Delta E(2A_1) &= -0.54\sum_j L_{ij}, \\ \Delta E(3A_1) &= 0.80\sum_j L_{ij}. \end{aligned} \tag{30}$$

The moments for the transitions $1A_1 \leftrightarrow 2A_1$ are

$$\begin{aligned} \hbar^2(\Delta\omega)^2 &= (1.68)^2 f_d \sum_j L_{ij}^2, \\ \hbar^4(\Delta\omega)^4 &= (1.68)^4 f_d \sum_j L_{ij}^4. \end{aligned} \tag{31}$$

For $2A_1 \leftrightarrow 3A_1$, the factor 1.68 becomes 1.33. The sums in (31) are over all lattice points in the plane intersecting the dislocations.

If we use the values found for f_d for the forbidden transition along with Eq. (23) we find a value for the half-width of the allowed transition

$$\hbar\beta = 2.5\times10^{-16}\text{ erg}.$$

Because the half-width is proportional to the product of f_d and α, both values for α give the same result. The experimentally measured half-width [from Fig. 1(a) of Ref. 2] is about 1.25×10^{-16} erg. Our dislocation hypothesis seems to give reasonably consistent results.

To estimate the broadening due to the crystal strains arising from the introduction of the OH^- ions we adopt a simple model: We consider the OH^- ions to be spherical occlusions in elastic and isotropic KCl. The stress field arises from the different ionic radii of Cl^- and

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[13] J. Friedel, *Dislocations* (Pergamon Press, Inc., New York, 1964), p. 21.

[14] Reference 4, Eqs. (5) and (6).

OH^-. The ionic radius of OH^- is about equal to $\mu/e = 0.8\times10^{-8}$ cm. Pauling[15] gives for the ionic radius of Cl^- 1.8×10^{-8} cm. The fractional change of radius, which we denote by δ, is 0.55.

The displacement field in an elastic isotropic medium induced at a point i by a spherical occlusion at a point j has been found by Mott and Nabarro.[16]

$$\begin{aligned} u_r &= \kappa R_{ij}, & R_{ij} &< R_0, \\ u_r &= \kappa R_0^3/R_{ij}^2, & R_{ij} &> R_0. \end{aligned} \tag{32}$$

Here u_r is the radial component of the displacement field, and R_0 = original radius of the occlusion. Also κ is defined, so that $\delta-\kappa$ is the fractional change in "lattice parameter" of the occlusion. We set $\delta \approx \kappa$.

The corresponding stresses are found using the standard methods of elasticity theory. In particular, we can write the combinations appearing in $\mathcal{H}_S$.

$$\begin{aligned} L_{ij} &= (2\alpha/3)\left(Z_z - \tfrac{1}{2}X_x - \tfrac{1}{2}Y_y\right) \\ &= [G\alpha R_0^3\delta/(1+\sigma)R_{ij}^3](1-3\cos^2\theta_{ij}), \\ M_{ij} &= (2\alpha/3)\left(X_x - \tfrac{1}{2}Y_y - \tfrac{1}{2}Z_z\right) \\ &= [G\alpha R_0^3\delta/(1+\sigma)R_{ij}^3](1-3\sin^2\theta_{ij}\cos^2\phi_{ij}), \\ N_{ij} &= (2\alpha/3)\left(Y_y - \tfrac{1}{2}X_x - \tfrac{1}{2}Z_z\right) \\ &= [G\alpha R_0^3\delta/(1+\sigma)R_{ij}^3](1-3\sin^2\theta_{ij}\sin^2\phi_{ij}). \end{aligned} \tag{33}$$

Here G is Young's modulus. Again the total stress at site i due to the occlusions alone is the sum of (33) over all the other occlusions j. We now repeat the derivation leading to (31) to find, for $1A_1 \leftrightarrow 2A_1$,

$$\begin{aligned} \hbar^2\langle(\Delta\omega)^2\rangle &= (1.45)^2 f \sum_j{}' L_{ij}^2, \\ \hbar^2\langle(\Delta\omega)^4\rangle &= (1.45)^4 f \sum_j{}' L_{ij}^4. \end{aligned} \tag{34}$$

For the transition $2A_1 \leftrightarrow 3A_1$, the factor 1.45 is replaced by 1.43. The sums in (34) are over all lattice points and L_{ij} is given by (33). The OH^- concentration is 3×10^{16} cm^{-3}.

To compare with the FSS experiment we compute the half-width of the allowed transition leaving δ as a parameter. Using the experimental value $\hbar\beta = 1.26\times10^{-16}$ erg gives $\delta \simeq 2$, instead of 0.55 estimated above from atomic radii. Here we have used the Shepherd and Feher value of α. If we use that of Hartel and Lüty we get $\delta \simeq 12$. In either case, if occlusions were the only stress-producing mechanism, we would probably be able to understand the width of the allowed transition with reasonable accuracy. The remaining discrepancy could arise from the anisotropy of the crystal, and from nonlinear terms.

If both occlusions and dislocations are considered at once, the situation is somewhat different. For it is the stresses that add, not the half-widths. With the density of dislocations found above, the stress field of the occlusions is completely negligible compared with that of the dislocations. If the dislocations we have postulated do indeed exist, the occlusion stresses have no appreciable effect on either transition.

V. SUMMARY

Our very simple models appear to give a good semiquantitative account of the linewidths of the FSS experiment. The situation is particularly clear for the forbidden transition for the higher concentration levels reported. We obtain fair agreement with experiment by considering dipolar broadening alone.

For the lowest concentration of OH^- we are led to postulate dislocations as a broadening mechanism. The datum point is fitted to find the concentration of dislocations. This concentration has a fairly reasonable value.

Turning to allowed transitions, we find that the dipolar broadening is negligible. Using the density of dislocations found from the forbidden transition, the calculated width of the allowed transition due to the dislocations agrees with the experimental value within a factor of 2.

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[15] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N. Y., 1960), 3rd ed., p. 451.

[16] N. F. Mott and F. R. N. Nabarro, Proc. Phys. Soc. (London) **52**, 86 (1940).