erties, have similar phonon-focusing characteristics. The latter are directly relatable to the similarity in the ratios of their elastic constants, as mentioned above. This fact constitutes particularly strong evidence, in addition to the experimental evidence from the other alkali halides, for the validity of the focusing theory presented.

In view of these considerations, it is concluded that the correlation between the intensities of the pulses observed experimentally and those predicted theoretically from the elastic constants of the materials studied is sufficiently high to confirm the basic correctness of the theory used and the validity of the various assumptions made.

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Theory of Paraelectric Resonance and Relaxation

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The theory of paraelectric resonance (PER) and relaxation is reformulated to allow a consistent treatment of dynamic lattice processes, even in the case when coupling to the lattice is strong. A simple model Hamiltonian is used and certain response functions are calculated without using perturbation theory. It is shown that the main effect of the strong lattice coupling at low temperatures is to induce a renormalization of the tunneling parameter of the paraelectric dipoles. The structure of phonon sidebands in PER is discussed. The theory predicts a strong transfer of intensity from the PER lines to the sidebands above a certain characteristic temperature. A treatment is given of paraelectric relaxation using the same techniques. A calculation of the temperature dependence of dipole-lattice relaxation time agrees well with experiment with adjustment of two parameters.

I. INTRODUCTION

There has been a good deal of recent interest in "paraelectric" impurities in solids; that is, impurities which have electric dipole moments and rotational degrees of freedom.[1,2] The microwave spectroscopy of such impurities has come to be known as "paraelectric resonance" (PER).[3] In a PER experiment, an external electric field is applied to a sample containing paraelectric impurities, and the absorption of microwave radiation of fixed frequency is observed as a function of applied electric field. The analogy with paramagnetic resonance is obvious.

The best-known examples of PER are the experiments performed on substitutional OH^- impurities in a KCl host lattice. In this case, the OH^- aligns preferentially along the $\langle 100 \rangle$ axes of the host. Microwave-induced 90° tunneling transitions have been observed by several groups.[3]

In previous treatments of this phenomenon, the host lattice has been assumed to provide a static potential with minima in the proper directions; the dipole rotates by tunneling between these minima.[4] Such an approach ignores the possibility of dynamic lattice processes such as phonon emission and absorption. The present study attempts to go beyond the static approach. We will be primarily concerned with calculating resonance linewidths and relaxation times arising from the impurity-phonon interaction.

That such a treatment is desirable is shown experimentally by the strikingly large linewidths of the observed resonances, much larger than those of typical magnetic resonances. It seems clear that these broadenings arise either from inhomogeneities (strains) in the host, or relaxation due to phonons. In either case the lattice-impurity coupling is a large effect.

It is also clear on physical grounds that impurities such as OH^- are strongly affected by lattice deformations. The OH^- impurity is somewhat different in size and quite different in shape (it is not spherical, of course) from the Cl^- it replaces. The lattice must deform to accommodate its substitution, and this deformation depends on the orientation of the OH^-.

This situation is quite different from that of paramagnetic impurities which are usually weakly coupled to lattices. The main point of the theory we give is to treat the impurity-phonon interaction *without* assuming it to be weak. This contrasts with the treatment of some authors who have used perturbation theory, as in the paramagnetic case, to calculate linewidths and relaxation times for paraelectric defects.[5,6] We will comment more on the work of these authors below.

It is important not to misjudge the results of the strong coupling. We will show that, at low temperatures, the major effect of the phonons is not to enormously broaden resonance lines, but to renormalize certain coupling constants. We attribute the broad lines found in PER to inhomogeneous strain broadening, as has been previously suggested.[7]

It might be maintained that large random perturbations of OH^- energy levels are inconsistent with the successes of the static theory in predicting thermodynamic functions such as specific heat. For example, the calculations of Shepherd and Feher of Schottky anomalies due to OH^- in KCl agree very well with experiment, even though sharp levels of a single energy are assumed.[2] Might we not expect that random strains would "wash out" the specific-heat peaks of the simple calculation? We deal with this objection in Appendix A. The result is that, as usual, specific heat is a poor indicator of the details of the energy-level distribution.[7]

It is most likely that low-temperature PER linewidths do not arise from dynamic processes. However, as we shall see (Secs. III and IV), there is a characteristic temperature T_0 such that for $T > T_0$, PER lines do begin to broaden and decrease in intensity as a result of the lattice coupling. Also, dipole-lattice relaxation times can be directly measured. For these reasons a careful treatment of the dipole-phonon interaction is necessary.

Some of the results we will derive here have been extensively studied in quite different contexts; there is a strong resemblance between our treatment and many results in the theory of F centers and other optical analogs of the Mössbauer effect.[8] The fact that phonon coupling does not necessarily lead to broadening has long been realized in those fields: The unbroadened spectral transitions give rise to so-called "zero-phonon" lines. Below we will show that PER lines can be identified as zero-phonon transitions.

In Secs. II–V we will treat dipole-phonon interaction in terms of a simple model. The model, which we believe to contain the essential physics of the problem, is explained in Sec. II, and certain response functions important for the interpretation of PER are defined. In Sec. III two of the response functions are calculated in the approximation that lifetime effects may be neglected. No assumption is made about the weakness of the lattice coupling. In Sec. IV lifetimes of excited states of the dipoles are calculated, and comparison is made with relaxation experiments. In Sec. V we discuss the applicability of our results.

A recent paper by Pirc and Gosar[9] on paraelastic relaxation bears great similarity to our treatment. Their approach is more formal than the present one, but a number of the results are identical. Our emphasis is quite different, however; in Sec. II–V we will point out several similarities and differences between the two treatments.

II. MODEL HAMILTONIAN AND RESPONSE FUNCTIONS

The low-lying (rotational-tunneling) levels of a paraelectric impurity are relatively complicated.[4] We simplify the problem by considering a two-level system interacting with lattice vibrations. Our Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I \ , \tag{1a}$$

$$\mathcal{H}_0 = \epsilon s_z - \Delta_0 s_x + \sum_{\vec{k}} \omega_{\vec{k}} a_{\vec{k}}^\dagger a_{\vec{k}} \ , \tag{1b}$$

$$\mathcal{H}_I = i s_z \sum_{\vec{k}} W_{\vec{k}} (a_{\vec{k}} - a_{\vec{k}}^\dagger) \ . \tag{1c}$$

Here and elsewhere $\hbar = 1$, and s_x, s_y, and s_z are spin-$\frac{1}{2}$ matrices. The first term in $\mathcal{H}_0$ represents the two states ("up" or "down") of a paraelectric impurity located at the origin. The tunneling between up and down orientations is represented by the second term; Δ_0 is the tunneling matrix element. Estle and others have previously used this model.[10] The third term is the Hamiltonian for the lattice vibrations: $a_{\vec{k}}$ and $a^\dagger_{\vec{k}}$ are phonon annihilation and creation operators. The interaction between the dipole and the strain of the lattice is given by $\mathcal{H}_I$; the $W_{\vec{k}}$ are coupling constants. The sign of the interaction depends on the orientation of the dipole; i.e., the dipole pulls or pushes on its neighbors depending on its orientation.

Many of the results in Secs. III and IV are independent of the exact form of the coupling. For numerical work we need a model for $W_{\vec{k}}$ and also for the lattice spectrum. In Appendix B we derive an expression for $W_{\vec{k}}$ in the Debye model, using a method similar to one used previously by one of the present authors.[11] The result is

$$W_{\vec{k}} = (2W_0\omega_{\vec{k}}\omega_D/3N)^{1/2} \ . \tag{2}$$

Here ω_D is the Debye cutoff frequency, N is the number of unit cells in the crystal, and W_0 is a dimensionless parameter related to the response of the lattice to external strain. We regard W_0 as an adjustable parameter.

In a PER experiment we apply microwave radiation to a sample containing paraelectric impurities. This adds to the Hamiltonian of Eq. (1) a term of the form

$$-V(t)s_\alpha \ . \tag{3}$$

The effects of the time-dependent external field $V(t)$ are described by the generalized susceptibility

$$\chi_{\beta\alpha}(t) = i\theta(t)\langle[s_\beta(t),\ s_\alpha(0)]\rangle \ . \tag{4}$$

Here θ is the step function, the brackets denote a thermal expectation value, and $s_\beta(t)$ is a Heisenberg operator. The frequency-dependent susceptibility $\chi_{\beta\alpha}(\omega)$ is the Fourier transform of $\chi_{\beta\alpha}(t)$:

$$\chi_{\beta\alpha}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\, \chi_{\beta\alpha}(t) \ . \tag{5}$$

The imaginary part of $\chi_{\beta\alpha}(\omega)$ is proportional to the power absorbed from an external field. From Eq. (4) we can derive standard results relating power dissipation to the fluctuations of the system[12]:

$$\mathrm{Im}\,\chi_{\beta\alpha}(\omega) \equiv \chi''_{\beta\alpha}(\omega) = \tfrac{1}{2}(1 - e^{-\omega/k_BT}) \times \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle s_\beta(t)s_\alpha(0)\rangle \ . \tag{6}$$

Here k_B is Boltzmann's constant and T is the temperature.

In paraelectric resonance the quantity that is measured is χ_{zz}, since an external field in the z direction couples to the dipole through $V(t)s_z$. In PER, the operators s_x and s_y do *not* correspond to components of the dipole along the x and y directions in space. We can think of the z axis as the "physical" axis and the x axis as the "tunneling" axis.

III. CALCULATION OF χ_{-+} AND χ_{zz}

The response of the system described by Eq. (1) to an external field could be studied in at least two ways. If the dipole-lattice coupling were small, we could treat $\mathcal{H}_0$ as a zero-order Hamiltonian and $\mathcal{H}_I$ as a perturbation. This is the approach of Vredevoe and of Dick.[5] The eigenstates of $\mathcal{H}_0$ are the zeroth-order states in this method; they are linear combinations of the up and down states with energies $\pm\frac{1}{2}(\epsilon^2+\Delta_0^2)^{1/2}$.

In this paper we want to treat $\mathcal{H}_I$ exactly. We are forced to regard the tunneling term as a perturbation. In our zeroth-order solution, the dipole points either up or down with energies $\pm\frac{1}{2}\epsilon$. Our results are valid only when $(\Delta/\epsilon) \ll 1$, where Δ is the observed tunneling parameter. (As we shall see, $\Delta < \Delta_0$.)

If we neglect terms of order Δ_0, the Hamiltonian can be exactly diagonalized by a unitary transformation. We put

$$H = e^{-is_zS}\,\mathcal{H}\,e^{is_zS} \ , \tag{7a}$$

$$S = \textstyle\sum_{\vec{k}}(W_{\vec{k}}/\omega_{\vec{k}})\,(a_{\vec{k}} + a^\dagger_{\vec{k}}) \ . \tag{7b}$$

A simple calculation gives

$$H = H_0 + H_1 + C \ , \tag{8a}$$

$$H_0 = \epsilon s_z + \textstyle\sum_{\vec{k}}\omega_{\vec{k}}\, a^\dagger_{\vec{k}}a_{\vec{k}} \ , \tag{8b}$$

$$H_1 = -\tfrac{1}{2}\Delta_0(s_-e^{iS} + s_+e^{-iS}) \ . \tag{8c}$$

Here C is a constant which we discard. The off-diagonal part of the new Hamiltonian H_1 is proportional to the small parameter Δ_0. (Note that we regard Δ_0 as small only as a formal device. In particular we do not require $\Delta_0/\epsilon < 1$.) The "large" off-diagonal terms have been removed by redefining the phonons to be vibrations around the equilibrium positions of the distorted lattice. The distortion of the crystal depends on the orientation of the dipole, as does the nature of the "new" phonons.

When radiation is applied to a system described by H_0, the susceptibilities will exhibit a sharp line at $\omega = \epsilon$ (from "flipping the spin") and a continuum of phonon sidebands. The off-diagonal operator H_1 will induce relaxation processes. Thus for appreciable Δ_0 the sharp line will be broadened.

It is useful to illustrate the behavior of the system by calculating χ''_{-+}. This function does not have a direct physical interpretation in PER, although in spin-resonance work χ_{-+} is the response to a transverse magnetic field. From Eq. (6) we note that χ_{-+} is determined by the quantity

$$\rho(t) = \langle s_-(t)s_+(0)\rangle \ . \tag{9}$$

We cannot calculate $\rho(t)$ exactly; however it is well known that the value of ρ for $\Delta_0 = 0$ [which we denote by $\rho_0(t)$] can be evaluated.[8,13] We put

$$\rho_0(t) = \langle e^{iH_0 t} s'_- e^{-iH_0 t} s'_+ \rangle \ . \tag{10}$$

Here $s'_\mp$ are the transformed operators

$$s'_\mp = e^{-is_z S} s_\mp e^{is_z S} \tag{11}$$

[cf. Eq. (7a)]. The spin matrices appearing in the exponents in Eqs. (10) and (11) can be untangled by standard techniques. If we then perform the thermal average over dipole orientations, we find

$$\rho_0(t) = n_- e^{-i\epsilon t} \langle e^{iS(t)} e^{-iS(0)} \rangle_{\text{ph}} \ , \tag{12a}$$

$$n_- = e^{\beta\epsilon/2} / (e^{\beta\epsilon/2} + e^{-\beta\epsilon/2}) \ . \tag{12b}$$

The brackets $\langle \rangle_{\text{ph}}$ indicate the remaining thermal average with respect to the phonons and $\beta = (k_B T)^{-1}$. The operator $S(t)$ is given by

$$S(t) = \textstyle\sum_{\vec{k}} V_{\vec{k}} (a_{\vec{k}} e^{-i\omega_k t} + a^\dagger_{\vec{k}} e^{i\omega_{\vec{k}} t}) \ , \tag{13}$$

where $V_{\vec{k}} = W_{\vec{k}} / \omega_{\vec{k}}$. The factor to be thermally averaged in Eq. (12a) can be thought of as a kind of overlap integral between the distortions of the lattice corresponding to the up and down states.

By applying a standard identity[14] we can put Eq. (12a) in the form

$$\rho_0(t) = n_- e^{-i\epsilon t} \exp[-\textstyle\sum_{\vec{k}} V_{\vec{k}}^2 i \sin(\omega_{\vec{k}} t)]$$
$$\times \langle \exp\{\textstyle\sum_{\vec{k}} V_{\vec{k}} i [a_{\vec{k}} (e^{-i\omega_{\vec{k}} t} - 1) + a^\dagger_{\vec{k}} (e^{i\omega_{\vec{k}} t} - 1)]\} \rangle_{\text{ph}} \ . \tag{14}$$

The last factor in Eq. (14) may be evaluated using Bloch's theorem[15]:

$$\langle e^{i(\gamma a_{\vec{k}} + \gamma^* a^\dagger_{\vec{k}})} \rangle = \exp[-|\gamma|^2 (n_{\vec{k}} + \tfrac{1}{2})] \ . \tag{15}$$

Here $n_{\vec{k}} = (e^{\beta\omega_{\vec{k}}} - 1)^{-1}$ is the Bose distribution function. Combining Eqs. (14) and (15) we find

$$\rho_0(t) = n_- e^{-i\epsilon t} R(t) \ , \tag{16a}$$

$$R(t) = \exp\{\textstyle\sum_{\vec{k}} V_{\vec{k}}^2 [(n_{\vec{k}} + 1)(e^{-i\omega_{\vec{k}} t} - 1) + n_{\vec{k}} (e^{i\omega_{\vec{k}} t} - 1)]\} \ . \tag{16b}$$

The single function $R(t)$ contains information about absorption and emission of any number of phonons; the term involving $(n_{\vec{k}} + 1)$ describes emission and the term in $n_{\vec{k}}$ absorption. We can see this by writing the response function χ''_{-+}:

$$\chi''_{-+}(\omega) = \tfrac{1}{2}(1 - e^{-\beta\omega}) n_- R(\omega - \epsilon) \quad , \tag{17a}$$

where $R(\omega)$ is the Fourier transform of $R(t)$. The function $R(\omega)$ has a useful symmetry property,

$$R(-\omega) = e^{-\beta\omega} R(\omega) \ . \tag{17b}$$

This can be proved most easily using Eq. (12a). We sort out the contribution from phonon processes of various orders by expanding the exponential in Eq. (16b):

$$R(\omega - \epsilon) = \exp[-\textstyle\sum_{\vec{k}} V_{\vec{k}}^2 (2n_{\vec{k}} + 1)]$$
$$\times \{\delta(\omega - \epsilon) + \textstyle\sum_{\vec{k}} V_{\vec{k}}^2 [n_{\vec{k}} \delta(\omega - \epsilon + \omega_{\vec{k}})$$
$$+ (n_{\vec{k}} + 1)\delta(\omega - \epsilon - \omega_{\vec{k}})] + \cdots\} \ . \tag{18}$$

The first term in braces is the unbroadened "zero-phonon" (resonance) line; the second describes single-phonon emission and absorption, and so on. The terms with phonon assistance are not "relaxation" processes. They are simply sidebands. Relaxation is described by H_1, which we have neglected so far (see Sec. IV).

This division between diagonal phonon terms (which lead to sidebands) and off-diagonal terms (which give rise to relaxation) is exactly the point of view taken in treating zero-phonon lines in optical spectroscopy.[8] The origin of our off-diagonal term is quite different from the relaxation terms in optical problems; there is no optical analog to tunneling. Nevertheless, in the absence of relaxation it should not be surprising to find many features of Eq. (18) which are familiar from previous work. For instance, each term in Eq. (18) is reduced by an exponential factor in front which has the form of a Debye-Waller factor; it indicates how much oscillator strength has been transferred from the zero-phonon line to the sidebands.

In the Debye model we use Eq. (2) to find the standard result, for $k_B T \ll \omega_D$:

$$\exp[-\textstyle\sum_{\vec{k}} V_{\vec{k}}^2 (2n_{\vec{k}} + 1)] = e^{-W_0 - W_1} \ , \tag{19}$$

$$W_1 = (\tfrac{2}{3}\pi)(k_B T / \omega_D)^2 W_0 \equiv T^2 / T_0^2 \ . \tag{20}$$

The characteristic temperature T_0 was introduced by Gosar and Pirc[16] in a context similar to this one. It is a useful parameter: For temperatures above T_0-induced multiphonon absorption and emission becomes important. As the sidebands grow with temperature, the zero-phonon line decreases in intensity. Well below T_0 the zero-phonon line is reduced only by the constant factor e^{-W_0}.

The strong temperature dependence e^{-T^2/T_0^2} of the intensity of the zero-phonon line is a well-known effect. It seems not to have been previously noticed that this effect is probably the reason for one of the striking features of PER. It is found that PER lines of OH$^-$ in KCl are relatively insensitive to temperature until $T \approx 10$ °K. Then the resonance rapidly disappears into the background.[3] If we assume that the lines are inhomogeneously broadened, and that $T_0 \approx 10$ °K, we have a simple explanation for the phenomenon.

The expansion in Eq. (18) is not useful for the actual evaluation of $R(\omega)$. We will calculate $R(\omega)$ somewhat differently in order to see in detail the structure of the sidebands. In the Debye approximation, the sum appearing in Eq. (16b) can be written

$$\textstyle\sum_{\vec{k}} V_{\vec{k}}^2 [(n_{\vec{k}} + 1)(e^{-i\omega_{\vec{k}} t} - 1) + n_{\vec{k}} (e^{i\omega_{\vec{k}} t} - 1)]$$

$$= - W_0 - W_1 + \frac{2W_0}{\omega_D^2} \int_0^{\omega_D} dx\, x \left\{ \frac{2\cos xt}{e^{\beta x} - 1} + e^{-ixt} \right\} . \tag{21}$$

First, suppose $T = 0$. Then only the second term in brackets survives. This term describes emission of zero-point phonons. Then,

$$R(\omega - \epsilon) = e^{-W_0}\,\delta(\omega - \epsilon) + e^{-W_0} \int_{-\infty}^{\infty} e^{i(\omega-\epsilon)t} \left[\exp\left(\frac{2W_0}{\omega_D^2} \int_0^{\omega_D} dx\, x e^{-ixt} \right) - 1 \right] dt . \tag{22}$$

The integral in this equation can be approximated by the method of steepest descents if $W_0 \gg 1$,

$$R(\omega - \epsilon) \approx e^{-W_0}\,\delta(\omega - \epsilon) + (\pi W_0 \omega_D^2)^{-1/2} \times \exp[-(\omega - \epsilon - \tfrac{2}{3} W_0 \omega_D)^2 / W_0 \omega_D^2] . \tag{23}$$

The zero-phonon line (the first term) is accompanied by a Gaussian sideband resulting from phonon emission. What makes this case appear different from former work on zero-phonon transitions are the orders of magnitude involved: The sideband is centered at $\omega = \frac{2}{3} W_0 \omega_D + \epsilon$. This frequency is *very* much larger than ϵ for any PER experiment. For very low temperatures ($T \ll T_0$), the resonance line will stand alone, isolated from the sideband. The only effect of the lattice coupling on the resonance line at this stage is to introduce a Debye-Waller factor. This simple result goes a long way toward explaining the success of the static-lattice theory of PER.

For finite temperatures, the high-frequency part of the susceptibility is essentially unchanged as long as $k_B T \ll \omega_D$. However, for smaller frequencies $\omega \approx k_B T$ the effects of thermal phonons become important. In this case we let the upper limit of the integral in Eq. (21) become infinite and introduce a convergence factor $e^{-\alpha x}$ in the second term of the integrand. These approximations lead to a power-series expansion for $R(\omega)$, valid for $k_B T,\ \omega \ll \omega_D$:

$$R(\omega) = e^{-W_0 - W_1}\,\delta(\omega) + e^{-W_0 - W_1} \frac{3W_1 \beta}{\pi^2} \frac{\beta\omega}{[1 - e^{-\beta\omega}]} \times \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} D_j^k W_1^{j+k} \left(\frac{\beta\omega}{2\pi} \right)^{2k} . \tag{24a}$$

This expansion is derived, and a table of the first few coefficients D_j^k is given, in Appendix C. Each value of $j + k$ in the summation corresponds to a term in Eq. (18); the term in $(W_1)^{j+k}$ is a $(j + k + 1)$-phonon process. We will find it useful below to have a series in ascending powers of temperature. The sum in Eq. (24a) can be rewritten:

$$\sum_{j=0}^{\infty} \left(\frac{T}{T_0} \right)^{2j} \sum_{k=0}^{\infty} D_j^k \left(\frac{\omega}{2\pi k_B T_0} \right)^{2k} . \tag{24b}$$

The sideband portion of $R(\omega)$ is continuous and does not vanish as ω passes through zero; thus the sideband intensity due to thermal phonons is not necessarily negligible in the vicinity of the resonance line. Since $W_0 + W_1$ can be quite large in paraelectrics, the intensity of the sideband integrated over the width of the zero-phonon line (cf. Sec. IV) could exceed the intensity of the zero-phonon line, and the resonance could be "swamped" by the featureless sideband. It is not clear whether this effect would be observable in PER.

We now turn to the calculation of χ''_{zz} which is the quantity of physical interest in PER. It is easy to see that neglecting terms of order Δ_0 (as above) will give $\chi''_{zz}(\omega) = 0$ for $\omega \neq 0$. This is because the only term in the original Hamiltonian [Eq. (1)] which connects up and down spins is the tunneling term, which involves Δ_0. We must use the full Hamiltonian $H = H_0 + H_1$.

From Eq. (6) we note once more that we need only calculate

$$\mu(t) = \langle s_z(t) s_z(0) \rangle = \langle e^{i(H_0 + H_1)t} s_z e^{-i(H_0 + H_1)t} s_z \rangle . \tag{25}$$

We calculate μ to the lowest nonvanishing order in Δ_0.

In what follows we take the thermal average using a partition function $\mathrm{tr}(e^{-\beta H_0})$, and a corresponding density matrix. This is somewhat inconsistent because the correction factors are of the same order (Δ_0^2) as the term we will calculate. However, these corrections are not important for finite frequency components of μ.

We proceed by performing another unitary transformation on the Hamiltonian to eliminate terms linear in Δ_0:

$$e^{i\Delta_0 X} H e^{-i\Delta_0 X} = H_0 + O(\Delta_0^2) . \tag{26}$$

Here X is a Hermitian operator to be determined below. Now Eq. (25) can be rewritten, to the lowest order in Δ_0, as

$$\mu(t) = \langle e^{iH_0 t} \tilde{s}_z e^{-iH_0 t} \tilde{s}_z \rangle , \tag{27}$$

$$\tilde{s}_z = e^{i\Delta_0 X} s_z e^{-i\Delta_0 X} \tag{28}$$

[cf. Eqs. (10) and (11)]. Expanding Eq. (28) yields

$$\tilde{s}_z = s_z + i\Delta_0 [X, s_z] + \cdots , \quad = s_z - i\Delta_0 (x s_+ - x^\dagger s_-) + \cdots . \tag{29}$$

Here we have written $X = (x s_+ + x^\dagger s_-)$. The new operator x involves only phonon operators. If we insert Eq. (29) into Eq. (27) and perform the trace over spin variables we find

$$\mu(t) = \tfrac{1}{4} + \Delta_0^2 [n_+ e^{i\epsilon t} \langle x(t) x^\dagger \rangle_{\mathrm{ph}} + n_- e^{-i\epsilon t} \langle x^\dagger(t) x \rangle_{\mathrm{ph}}] , \tag{30a}$$

$$n_\pm = e^{\mp\beta\epsilon/2} / (e^{\beta\epsilon/2} + e^{-\beta\epsilon/2}) \,. \tag{30b}$$

Here, as in Eq. (12), $\langle\,\rangle_{\text{ph}}$ indicates the remaining thermal average with respect to phonon variables.

The Fourier transform of Eq. (30a) can be written

$$\begin{aligned}\mu(\omega) = \tfrac{1}{4}\,\delta(\omega) + \Delta_0^2\, Z^{-1} \sum_{a\,b} e^{-\beta E_a} \\ \times [n_+ \delta(\omega + E_a - E_b + \epsilon)\, |\langle a|x|b\rangle|^2 \\ + n_- \delta(\omega + E_a - E_b - \epsilon)\, |\langle b|x|a\rangle|^2]\,.\end{aligned} \tag{31}$$

In this equation Z is the partition function for the phonons, and $|a\rangle$ and $|b\rangle$ are complete sets of states of the phonons.

The matrix elements of the operator x are found from Eq. (26). We proceed in a standard way,[17] expanding the left-hand side and comparing coefficients to find

$$\epsilon x + [\textstyle\sum \omega_k a_k^\dagger a_k, x] = \tfrac{1}{2} i\, e^{-iS} \,. \tag{32}$$

Taking matrix elements between $|a\rangle$ and $|b\rangle$ gives

$$\langle a|x|b\rangle = \tfrac{1}{2} i \langle a|e^{-iS}|b\rangle / E_a - E_b + \epsilon. \tag{33}$$

Finally, Eq. (33) and Eq. (31) together imply

$$\begin{aligned}\mu(\omega) = \tfrac{1}{4}\{\, \delta(\omega) + (\Delta_0^2/\omega^2) \\ \times [\, n_- R(\omega - \epsilon) + n_+ R(\omega + \epsilon)]\}\,.\end{aligned} \tag{34}$$

Now from Eq. (6) we find the susceptibility

$$\begin{aligned}\chi''_{zz}(\omega) = (\Delta_0^2/8\omega^2)(1 - e^{-\beta\omega}) \\ \times [n_- R(\omega - \epsilon) + n_+ R(\omega + \epsilon)]\,.\end{aligned} \tag{35}$$

The two terms in brackets correspond to raising or lowering the spin.

The physical susceptibility χ_{zz} has a very similar form to χ_{-+} [Eq. (17)]. Our former discussion applies here as well: We now have two symmetrically placed resonance lines, two sidebands, etc. The Debye-Waller factors which we discussed above have a very interesting consequence in Eq. (35); since each $R(\omega)$ is multiplied by an exponential factor, the net effect is to *renormalize* the tunneling parameter Δ_0. In fact, we can put

$$\Delta^2 = \Delta_0^2\, e^{-W_0 - W_1} \,.$$

In this equation Δ is the "observed" tunneling parameter; note that we can easily have $\Delta \ll \Delta_0$. Renormalization of this type has previously been discussed by one of the authors.[11]

Equation (35) is similar to the final result given by Pirc and Gosar[9] for paraelastic systems. Pirc and Gosar have included relaxation in their treatment, while we have not yet done so. Thus near $\omega = \pm\epsilon$, we find sharp zero-phonon lines, while Pirc and Gosar find Lorentzians. Near $\omega = 0$, our phonon sidebands reduce to the low-frequency Debye relaxation term of Eq. (62) in Ref. 9. We can obtain a term of precisely the Debye form from Eq. (35) by taking the limit $\omega/\epsilon \to 0$ in the argument of the R's, and replacing ω^2 by $\omega^2 + (1/T_1)^2$ in the denominator (see Sec. IV). The high-frequency ($\omega \approx \omega_D$) behavior of our expression is not reproduced in Pirc and Gosar. This may be traced to the fact that they evaluated their Green's functions only near the poles $\omega = 0, \pm\epsilon$. Our treatment, on the other hand, is valid for all frequencies.

The susceptibility $\chi''_{zz}(\omega)$ as given by Eq. (35) is "second order" in Δ_0; thus H_1 is regarded as a small perturbation even though Δ_0 can be much larger than Δ, ϵ, or $k_B T$. This can be clarified by noting that the expansion of Eq. (29) is terminated at first order in Δ_0, implying that $\tilde{s}_z$ is not very different from s_z, i.e., that the eigenstates of the system are closely approximated by the dipole-up-dipole-down states, rather than symmetric and antisymmetric combinations of those states. To see what limit this places on the magnitude of Δ_0, we can write down the f sum rule for χ''_{zz}

$$\int_0^\infty d\omega\, \omega\, \chi''_{zz}(\omega) = -\tfrac{1}{4}\langle[[\mathcal{H}, s_z], s_z]\rangle = \tfrac{1}{4}\Delta_0 \langle s_x\rangle \tag{36a}$$

and require that $\langle s_x\rangle \ll 1$. Using Eqs. (35) and (23) for $\chi''_{zz}(\omega)$ in the above integral leads to $\Delta_0\langle s_x\rangle \approx \tfrac{1}{2}\Delta_0^2/(\tfrac{2}{3} W_0 \omega_D)$, from which we obtain the condition

$$\Delta_0 \ll W_0 \omega_D \,. \tag{36b}$$

The theory presented here is thus a "strong-coupling theory" in the sense that W_0 must be greater than a minimum value in order for Eq. (35) to be valid. However, the condition Eq. (36b) is not at all restrictive, and will always be satisfied if $W_0 > 1$, since Δ_0 must be considerably smaller than the constant $\hbar^2/2I$ which describes the splitting between rotational energy levels of the dipole in free space (≈ 27 °K for OH).

IV. RELAXATION

The off-diagonal part of the Hamiltonian H_1 is proportional to the parameter Δ_0. In this section we will consider its effects by using perturbation theory.

Our relaxation Hamiltonian H_1 is quite different from that used in optical problems. It is usual to include relaxation effects by adding an off-diagonal phonon-coupling term to the Hamiltonian. We expect such terms to be negligible in paraelectrics. Instead, all of the "spin-flip" terms here arise from a combination of tunneling and phonon emission or absorption. A formal similarity to the usual treatments may be seen by expanding the exponentials in Eq. (8c) to first order in S. In this section, as above, we will avoid making such expansions so that our expressions will be valid for strong coupling.

The operator H_1 gives rise to two effects: a shift in resonance frequency away from $\omega = \epsilon$, and relaxation effects such as the broadening of the zero-phonon lines. The first phenomenon is most simply treated by taking the thermal expectation value of H_1:

$$\begin{aligned}\langle H_1\rangle &= -\tfrac{1}{2}\Delta_0\left(s_-\langle e^{iS}\rangle + s_+\langle e^{-iS}\rangle\right)\\ &= -\tfrac{1}{2}\Delta_0\left(s_- e^{-(W_0+W_1)/2} + s_+ e^{-(W_0+W_1)/2}\right)\\ &= -\Delta s_x \,. \end{aligned} \tag{37}$$

In deriving this equation we have used Eqs. (15), (19), and the definition of the renormalized tunneling parameter Δ_0. If we add this part of H_1 to H_0 [Eq. (8b)], we find a (temperature-dependent) shift of the resonance frequency from ϵ to $(\epsilon^2+\Delta^2)^{1/2}$. If we were to attempt to find the shift of the resonance by using the first two terms of the original Hamiltonian, [Eq. (1b)], we would find $(\epsilon^2+\Delta_0^2)^{1/2}$. Since $\Delta \ll \Delta_0$ for strong coupling, the latter answer is entirely incorrect; it arises from the neglect of large terms in $\mathcal{H}_I$.

If our assumption $\Delta \ll \epsilon$ holds, then the shift of the resonance frequency is a small correction; henceforth we will neglect it. Lifetime broadening induced by H_1 is much more interesting.

With an off-diagonal term present in the Hamiltonian, a dipole can spontaneously change its state, e.g., from up to down, while emitting phonons. The rate for this process is given to order Δ_0^2 by the Golden Rule

$$\begin{aligned}1/\tau_{+-} &= 2\pi Z^{-1}\sum \left|\langle a,+|H_1|b,-\rangle\right|^2\\ &\quad\times e^{-\beta E_a}\,\delta(E_a-E_b+\epsilon)\\ &= \tfrac{1}{4}\Delta_0^2\int_{-\infty}^{\infty} dt\; e^{iEt}\,\langle e^{iS(t)}\,e^{-iS}\rangle_{\mathrm{ph}}\\ &= \tfrac{1}{2}\pi\,\Delta_0^2\,R(\epsilon)\,. \end{aligned} \tag{38}$$

The notation here is similar to that of Eq. (31). We have again neglected corrections to the density matrix, which in this case give rise to terms of order Δ_0^4. In the same way, the down-to-up transition rate can be shown to be

$$1/\tau_{-+} = \tfrac{1}{2}\pi\Delta_0^2 R(-\epsilon). \tag{39}$$

Thus the relaxation time T_1 for the dipole to reach thermal equilibrium is given by

$$1/T_1 = 1/\tau_{+-} + 1/\tau_{-+} = \tfrac{1}{2}\pi\Delta_0^2[R(\epsilon)+R(-\epsilon)]. \tag{40}$$

This result gives the dipole-lattice relaxation time of a paraelectric impurity to arbitrarily high orders in the phonon coupling. The same function $R(\omega)$ which described the phonon sidebands occurs again in this quite different context. Once again, the renormalized tunneling parameter Δ appears, since each term in brackets in Eq. (40) contains a factor of $e^{-W_0-W_1}$.

The expressions for $R(\omega)$ given in Sec. III can be used, together with Eq. (40), to evaluate the lifetime. From Eq. (24) we can find the "one-phonon" contribution

$$\begin{aligned}(1/T_1)^{(1)} &= 3W_1\beta^2\epsilon\Delta^2/2\pi)\coth(\tfrac{1}{2}\beta\epsilon)\\ &\approx (3\Delta^2/k_B T_0^2\pi)T\,. \end{aligned} \tag{41}$$

In the second line we have assumed $\beta\epsilon \ll 1$. In the temperature region $\epsilon \ll k_B T \ll k_B T_0$, the relaxation time is proportional to T and independent of ϵ. Results of this type have been derived by several authors using simple perturbation theory.[5,6,10] The only difference we have introduced by our more sophisticated treatment is to replace Δ_0 by $\Delta(T=0) = \Delta_0\, e^{-W_0}$.

When the temperature is raised until $T \approx T_0$, multiphonon processes become important. Dick and Strauch[6] and Vredevoe[5] have treated this situation by using second- and higher-order perturbation theory. They find in the Debye model terms in T^3 (from two-phonon processes), T^5, etc.

Our treatment gives similar results with an important exception: We have a temperature-dependent tunneling parameter Δ. When $T \approx T_0$, Δ starts to vary appreciably with temperature. We can illustrate the situation by using Eqs. (24), (40), and (41) to write

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)^{(1)} e^{-T^2/T_0^2}\sum_{j=0}^{\infty} D_j^0\left(\frac{T}{T_0}\right)^{2j}. \tag{42}$$

For convenience, we have supposed that $\epsilon \ll k_B T_0$ (this is usually true for paraelectric impurities) so that only the term with $k=0$ is important in the sum in Eq. (24b).

The term of order j in Eq. (42) corresponds to a $(j+1)$ phonon process. If we use the results of Appendix C to write out the first few terms in Eq. (42), we find

$$\begin{aligned}1/T_1 &= (1/T_1)^{(1)}(1-T^2/T_0^2+\cdots)(1+T^2/T_0^2+\cdots)\\ &= (1/T_1)^{(1)}[1+O(T^4/T_0^4)]\,. \end{aligned} \tag{43}$$

The two-phonon terms have been *exactly* cancelled by the decrease of Δ with temperature. The relaxation time contains terms of order T, T^5, etc., but T^3 is missing.

Paraelectric relaxation has been measured over a wide range of temperature by Kapphan and Lüty.[18] In Fig. 1 we give the results for the relaxation of OH$^-$ impurities in RbBr, along with theoretical curves derived from Eq. (42). We have adjusted two parameters in making the fit: They are the coefficient of T in $(1/T_1)^{(1)}$, or, in effect, $\Delta_0 e^{-W_0}$ and T_0. The one-phonon rate is taken as $(0.77\times 10^3)T$ sec^{-1}. (The effect of changing this parameter would be a uniform vertical shift of the theoretical curves.) As we see in Fig. 1, the best fit is obtained for $T_0 = (6.8 \pm 0.5)$ °K.

At temperatures higher than those shown in the figure, our predictions begin to deviate seriously from the data (we predict too rapid a relaxation rate). We believe this is due to our neglect of the

Debye cutoff in deriving Eq. (24), or possibly to a failure of the Debye approximation itself when the temperature is high enough for phonons far from the center of the Brillouin zone to participate in relaxation.

The multiphonon terms we have been discussing are all derived from the linear coupling in the original Hamiltonian. Nonlinear coupling would alter the picture considerably. However, the work by Dick and Strauch[6] seems to indicate that nonlinear terms give negligible contributions to the lifetime.

The effect of relaxation on paraelectric resonance should be to broaden the zero-phonon resonance lines into Lorentzians of width

$$1/T_2 = 1/2T_1 \; . \tag{44}$$

We would not expect to be able to directly observe the temperature-dependent width of a PER line because of inhomogeneous broadening. However, the *intensity* of the line will be proportional to e^{-T^2/T_0^2} as we remarked above.

V. DISCUSSION

A major conclusion of this paper is that many of the results of the static lattice theory of paraelectric resonance are correct if properly interpreted. For example, the resonance transition between the two dipole states is properly regarded as the zero-phonon line of the coupled dipole-lattice system. The coupling to phonons does not broaden the line out of existence; in fact very strong coupling decreases the relaxation rate, because of the decreased Δ. The usual formulas for the position and transition probabilities of resonance lines[10] are valid, provided that the correct temperature dependent Δ is used in these formulas. For the two-level system with $\epsilon \gg \Delta$, the intensity of the resonance line is given by Eq. (35) as $(\Delta^2/8\epsilon^2) \times \tanh(\frac{1}{2}\beta\epsilon)$. As the dipole-lattice coupling increases, Δ gets smaller and the intensity goes down. This reduction in intensity of the zero-phonon line by the Debye-Waller factor is well known in the theory of *F* centers and of shallow impurities in semiconductors.

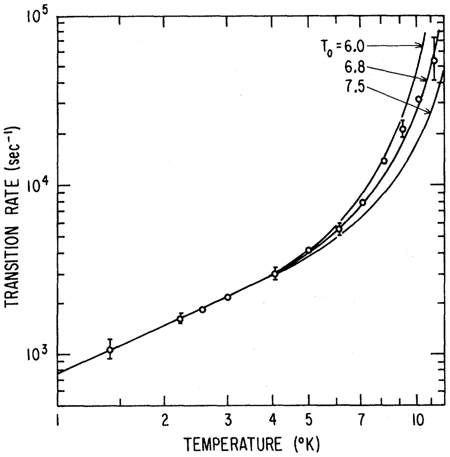

FIG. 1. Relaxation rate of OH^- impurities in RbBr as a function of temperature. The open circles are the data of Kapphan and Lüty (Ref. 18). The solid lines are theoretical curves for several values of T_0. The best fit is obtained with $T_0 = 6.8$ °K.

The values of $(1/T_1)^{(1)}$ and T_0 obtained by fitting the data of Kapphan and Lüty should in principle give information about the nature of the dipole-lattice coupling in RbBr : OH. However, the assumption of a two-level system in this paper and use of the Debye phonon spectrum in the calculations preclude the determination of more than rough estimates for the parameters of the real system. In order to determine Δ from Eq. (41) we must note that Kapphan and Lüty measured the relaxation rate of the optical absorption in a six-level system. The analysis of Dick[5] can be used to show that this is related to the relaxation between two levels by $(\tau^{-1})_{\mathrm{opt}} = 3(1/T_1)$; we therefore use the value $(1/T_1)^{(1)} = (0.26\times 10^3)T\ \mathrm{sec}^{-1}$ in Eq. (41). The result is $\Delta/k_B = (2.8\times 10^{-4})$ °K. The estimate of Dick and Strauch[6] for Δ is (5.2×10^{-4}) °K, in reasonably good agreement. These are very small values for Δ which make RbBr : OH an unlikely candidate for the observation of paraelectric resonance.

It is tempting to try to estimate W_0 by using Eq. (21) to write

$$W_0 = (3/2\pi^2)(\omega_D/k_B T_0)^2 \; . \tag{45}$$

However, W_0 and T_0 are determined by two very different sums over phonon modes, so that Eq. (45) is only valid within the Debye model. One possible way to proceed is to regard ω_D as an adjustable parameter and choose it to give a reasonable value of Δ_0, using Eq. (36). An estimate of Δ_0 can be obtained[11] from the observed infrared "librational frequency" of the dipole which is of the order of 300 cm^{-1} for OH^- in any alkali halide. The resulting value of Δ_0/k_B is 5 °K, which is probably a correct order of magnitude for all the alkali halides. This, along with the value of Δ already determined, requires that $W_0 \approx 20$. From Eq. (45) we then find $\omega_D/k_B \approx 80$ °K, a somewhat low but not unreasonable value. (The Debye temperature of RbBr is actually about 120 °K.) The condition (36b) for the validity of the theory is extremely well satisfied. A more detailed calculation, using realistic values for the $\omega_{\vec{k}}$ and $W_{\vec{k}}$, is clearly necessary if one is to improve on the present rough estimates.

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APPENDIX A

As we mentioned in Sec. I, there is an apparent contradiction between the success of the specific-heat calculation of Shepherd and Feher[2] which assumes that sharp tunneling levels exist, and the suggestion that the tunneling levels are subject to to large inhomogeneous broadening. A possible resolution of this difficulty would be to assume that PER lines are lifetime broadened. Since the conclusion of our work is that lifetime broadening is small for PER at low temperatures (i. e., $T \ll T_0$), we considered it worthwhile to make sure that the contradiction mentioned above does not, in fact, exist.

We have calculated the low-temperature specific heat of an OH^- dipole subject to random strains whose strength obeys a Gaussian distribution. The width of the Gaussian was varied until strain energies were appreciable fractions of the energy splittings. In Fig. 2 we give the specific heat as a function of the electric field for several values of the width, measured in terms of a dimensionless parameter $G = \alpha S / k_B T$ where S is the half-width of the distribution assumed,

$$\exp[-(e_{xx}^2 + e_{yy}^2 + e_{zz}^2)/S^2] . \tag{A1}$$

Here e_{xx}, etc., are the strains, and α is a strain coefficient.

As we can see, the specific heat is not a very reliable indicator of inhomogeneous broadening. Nonetheless, if all the broadening in the experiment of Feher, Shepherd, and Shore[3] is to be attributed to the strains, we would need $G \approx 0.6$. A distortion of the specific-heat curves could perhaps be detected if G were this large.[8]

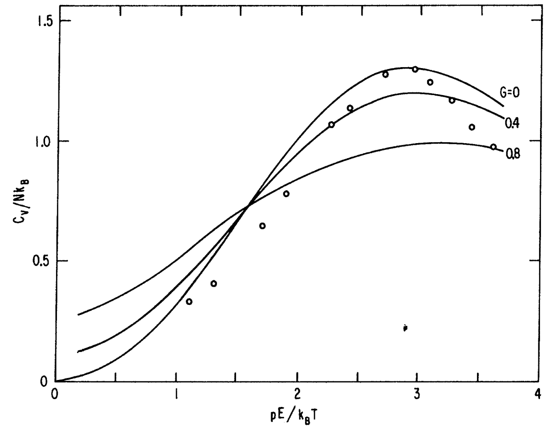

FIG. 2. Specific heat due to paraelectric impurities as a function of external electric field E, measured in units of k_BT/p, where p is the dipole moment. The field is along a ⟨100⟩ axis. It is assumed that $pE \gg \Delta$. The open circles are the data of Shepherd and Feher (Ref. 2), using the values of p and N given in that paper. The solid curves are theoretical predictions in the presence of random strains whose strength is characterized by the parameter G (defined in the text).

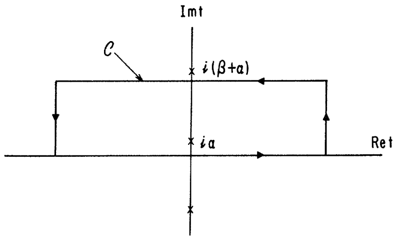

FIG. 3. Contour used to evaluate $J_n(\omega)$.

APPENDIX B

The form of the coupling constants $W_{\vec{k}}$ may be derived by a phenomonological treatment valid for long-wavelength phonons. We write an interaction term

$$A s_z (R_+^z - R_-^z) . \tag{B1}$$

Here A has the dimensions of a force and $R_\pm^z$ are the z components of the displacements of the nearest neighbors above and below the impurity. Expanding in phonon operators we get

$$2 i s_z A \sum_{\vec{k}} (2\Omega \rho \omega_{\vec{k}})^{-1/2} (a_{\vec{k}} - a_{\vec{k}}^\dagger) e_{\vec{k}}^z \sin(a k_z) . \tag{B2}$$

Here Ω is the volume, ρ is the mass density, a is the lattice spacing, and $e_{\vec{k}}^z$ is the z component of the polarization vector of the mode labeled by k. Note that Eq. (B2) has the same form as Eq. (1c).

In addition to the wave vector $\vec{k}$ we should affix another index specifying the branch of the spectrum and polarization for the phonon in question. We restrict ourselves from the outset to acoustic phonons because optical-phonon energies are very much larger than the tunneling splittings of paraelectric impurities. We may further restrict the summation in Eq. (B2) to longitudinal modes only because the factor $e_{\vec{k}}^z \sin(a k_z)$ tends to pick out modes for which the polarization is parallel to k.

Assuming $e_{\vec{k}}$ parallel to $\vec{k}$, and expanding

$$\sin(a k_z) \approx a k_z , \tag{B3}$$

we average over the directions of $\vec{k}$ to find

$$W_{\vec{k}} = (\tfrac{2}{3} A)(2\Omega \rho \omega_{\vec{k}})^{-1/2} a k . \tag{B4}$$

If we use a Debye approximation for the spectrum, we can express $W_{\vec{k}}$ in terms of the cutoff frequency ω_D:

$$W_{\vec{k}} = (2 W_0 \omega_{\vec{k}} \omega_D / 3N)^{1/2} . \tag{B5}$$

Here W_0 is a dimensionless parameter describing the strength of the dipole-phonon interaction. Using Eqs. (B4) and (B5) we have

TABLE I. Coefficients D_j^k

$k \diagdown j$	0	1	2	3	4	5
0	1.000	1.000	0.800	0.514	0.274	0.125
1	1.000	1.000	0.700	0.390	0.183	0.074
2	0.200	0.200	0.130	0.066	0.028	0.010
3	0.014	0.014	0.009	0.004	0.002	6×10^{-4}
4	5×10^{-4}	5×10^{-4}	2×10^{-4}	1×10^{-4}	5×10^{-5}	2×10^{-5}
5	8×10^{-6}	8×10^{-6}	5×10^{-6}	2×10^{-6}	8×10^{-7}	3×10^{-7}

$$W_0=A^2/3(6\pi^2)^{1/3}v^3\rho\ , \tag{B6}$$

where v is the velocity of sound.

The constant A can be related to the response of the dipole to an external strain. Because of the sequence of approximations made in arriving at Eq. (B5) it seems unlikely that reliable answers could be found from such an approach. We regard W_0 as an adjustable parameter.

APPENDIX C

We derive here the power-series expansion for $R(\omega)$. We must first evaluate the integral in Eq. (21), which we denote $I(t)$, using the approximations stated just before Eq. (24a). We have, after a few manipulations,

$$I(t)=\frac{2W_0}{\omega_D^2}\int_{-\infty}^{\infty}\frac{xe^{(it+\alpha)x}dx}{e^{\beta x}-1}\ , \tag{C1}$$

where α is a positive infinitesimal. This may be expressed in terms of a standard integral[19] with the result

$$I(t)=-3W_1\operatorname{csch}^2[(\pi/\beta)(t-i\alpha)]\ . \tag{C2}$$

From Eqs. (16b) and (19) we have

$$\begin{aligned}R(\omega)&=e^{-W_0-W_1}\delta(\omega)\\&\quad+e^{-W_0-W_1}(1/2\pi)\textstyle\int_{-\infty}^{\infty}dt\,e^{i\omega t}[e^{I(t)}-1]\ .\end{aligned} \tag{C3}$$

Expanding the exponential in the second term gives

$$\begin{aligned}&e^{-W_0-W_1}\sum_{n=1}^{\infty}\frac{1}{n!}\int_{-\infty}^{\infty}[I(t)]^n e^{i\omega t}\,dt/2\pi\\&\equiv e^{-W_0-W_1}\sum_{n=1}^{\infty}\frac{1}{n!}\,J_n(\omega)\ .\end{aligned} \tag{C4}$$

The integrals $J_n(\omega)$ can be evaluated by using the contour C shown in Fig. 3. We find

$$J_n(\omega)=(1-e^{-\beta\omega})^{-1}\oint_C[I(t)]^n e^{i\omega t}dt/2\pi\ . \tag{C5}$$

With a change of variables, $e^{2\pi t/\beta}=w$, the last factor becomes

$$(-3W_1)^n(2^{2n-1}\beta/\pi)\oint_{C'}w^{n-1+i\beta\omega/2\pi}(w-1)^{-2n}dw, \tag{C6}$$

where the transformed contour C' contains the singular point $w=1$. It is now straightforward to evaluate the integral in Eq. (C6), and arrive at the formula first given by Pirc and Gosar[9,16]

$$\begin{aligned}R(\omega)&=e^{-W_0-W_1}\delta(\omega)+e^{-W_0-W_1}(3W_1\beta^2\omega/\pi^2)\\&\quad\times(1-e^{-\beta\omega})^{-1}\left[1+\sum_{n=1}^{\infty}\frac{12^n(n!)^2W_1^n}{(n+1)!\,(2n+1)!}\right.\\&\quad\left.\times\prod_{k=1}^{n}\left\{1+\left(\frac{\beta\omega}{2\pi k}\right)^2\right\}\right]\ .\end{aligned} \tag{C7}$$

We expand the repeated product within the summation

$$\prod_{k=1}^{n}\left[1+\left(\frac{\beta\omega}{2\pi k}\right)^2\right]=\sum_{k=0}^{n}\alpha_k^n\left(\frac{\beta\omega}{2\pi}\right)^{2k}\ . \tag{C8}$$

Using Eq. (C7) we can rewrite the factor in square brackets in Eq. (C8),

$$\sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\frac{12^{j+k}[(j+k)!]^2\alpha_k^{j+k}}{(j+k+1)!\,(2j+2k+1)!}\ W_1^{j+k}\left(\frac{\beta\omega}{2\pi}\right)^{2k}\ . \tag{C9}$$

This specifies the coefficients D_j^k. The α_k^{j+k} are determined from the recursion relations

$$\alpha_0^l=1, \tag{C10a}$$

$$\alpha_m^l=\sum_{r=m}^{l}\frac{\alpha_{m-1}^{r-1}}{r^2}\ . \tag{C10b}$$

In Table I we give a number of the D_j^n. For use with connection with Eq. (42) it is useful to note that Eq. (C10a) implies

$$D_j^0=12^j(j!)/(2j+1)!\,(j+1)\ . \tag{C11}$$

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Some Aspects of Covalent Bonding in NaCl Structure Crystals: Application to the Lattice Dynamics of MgO[†]

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The lattice vibrational properties of heteropolar crystals of the NaCl structure are examined within the context of recent dielectric-screening theories of insulating crystals. Phillips's bond-charge approximation for the dielectric response of semiconductors with tetrahedral coordination is adapted to the treatment of partially covalent NaCl structure crystals. Application is made to MgO, where the gross violation of the Cauchy relation among the elastic constants points to the importance of noncentral forces arising from covalent effects. The bond-charge model in conjunction with a valence-force-field approximation for the short-range interactions is shown to provide an adequate description of the lattice spectrum in MgO.

I. INTRODUCTION

The character of the chemical bond which exists between the component atoms of a metallic or nonmetallic crystal is reflected in those properties of the crystal which depend directly on the electronic spectrum. These properties are, in turn, reflected in the linear dielectric-screening properties of the many-particle system consisting of the valence electrons alone. It is only natural, then, that recent advances in the understanding of the chemical bond[1-4] have been based on a dielectric-screening theory of the valence electrons of the crystal. Application of these ideas has met with considerable success in the understanding of the over-all trends of many of the physical properties of a large class of covalent and partially ionic diatomic crystals[5,6] with the formula $A_N B_{8-N}$. Of particular note is the successful correlation of a dielectric definition of electronegativity or ionicity[7] with the structure of the static electronic dielectric constant. This has led to the prediction, with good results, of ionization potentials and band structures of 68 binary compounds[6] of the form $A_N B_{8-N}$. Furthermore, a correlation has been shown to exist between the effective ionicity defined by Phillips and some of the regularities exhibited by the experimental elastic constants of ZnS structure semiconductors.[8]

The basic ideas which underlie the dielectric definition of electronegativity can be used to develop a model of lattice vibration spectra in covalent and partially ionic crystals. Such an extension was proposed by Phillips[4] and subsequently put on a more rigorous basis by Martin[9] in a dielectric-screening treatment of the lattice vibrations of silicon. It will be recalled that there have appeared recently several general formulations of the lattice vibration problem[10,11] which encompass in a unified manner the lattice dynamical description of both metallic and nonmetallic crystals. In his work on