WEAK COUPLING THEORY OF PARAELECTRIC ABSORPTION SPECTRA

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Abstract

Phonon effects in paraelectric impurity resonance and relaxation spectra are investigated for the weak coupling case by means of the Green's function decoupling method. Numerical results for the spectra in a wide frequency range are shown to be in agreement with the phenomenological theory based on dipole-lattice relaxation rates involving one-phonon induced tunneling processes. In the presence of an external bias field the spectrum contains a low frequency maximum associated with a Debye-type longitudinal relaxation. In the weakly coupled limit the resonance occurs near a frequency $f = \sqrt{\Delta^2 + \epsilon^2}$, where Δ is the bare tunneling frequency and ϵ the static field splitting, and is shifted from f due to the

effects of the dipole-lattice coupling. The phonon induced tunneling mechanism is also responsible for the broadening of the resonance line in the absence of inhomogeneous strains and electric fields in the crystal.

I. Introduction

It is well known from experiments that dipolar impurities in insulating crystals are responsible for two types of dynamic dielectric phenomena at low temperatures: In the case of OH^- in KBr, for example, one observes a Debye-type dielectric loss with a distribution of relaxation times near 10^{-5} sec. at temperatures of a few degrees.¹ Experiments in the microwave range usually reveal one or more resonance lines known as the paraelectric resonance.² For OH^- ^{2,3} and Li^+ ⁴ in KCl several such resonances have been found in the 10 - 65 GHz range, their exact positions depending on the strength and orientation of the static electric field. Although separated by a large frequency interval, these phenomena have a common physical origin, namely the phonon induced tunneling of the dipolar impurity between its crystal potential minima. This mechanism has been suggested by Sussman.⁵

From the theoretical point of view there are several interesting problems these systems offer to study. Calculations of the structure of the tunneling levels have been carried out using group theory arguments to predict the positions and relative strengths of the resonance lines.⁶ Another problem is the determination of the resonance line widths or, in a broader sense, of the shape of the entire paraelectric absorption spectrum.⁷ Experimental data indicate that paraelectric resonance lines are

broadened inhomogeneously due to the random strains and electric fields in the crystal. However, they are also expected to have a natural linewidth due to the interaction of the tunneling modes with phonons. In many cases this interaction is strong, thus necessitating the study of the dynamics of strongly coupled dipole-lattice systems. The qualitative aspects of this problem are well understood now. Two further steps have to be taken in order to develop a quantitative theory of paraelectric absorption for a given system: First, one has to develop a microscopic model for the interaction of the dipole with the lattice. For OH^- in RbBr this was done in connection with the calculation of the reorientation rates of the dipole using both the weak⁸ and strong⁹ coupling approach together with the application of shell model phonon spectra. Due to the large number of parameters involved in these calculations there is still some controversy regarding the strength of the dipole-lattice coupling. Indeed, agreement with experiments can be obtained by using either the strong or the weak coupling theory.⁹ The second step then involves the selection of a suitable theoretical method which will enable the calculation of dynamic dielectric properties using the microscopic model. In this work we make a step in the second direction by studying the application of the Green's function decoupling method¹⁰ to the problem of paraelectric resonance and relaxation. This method in its standard form is suitable for weakly coupled systems only.

Our aim is to perform an actual calculation of the paraelectric absorption spectrum using a simplified few-parameter model rather than a specific microscopic model for the dipole-lattice interaction. By choosing the weak coupling case we are able to examine in greater detail the general features of the dynamic susceptibility of paraelectric systems (including both Debye-type and resonance absorption in a single treatment) and to find the limitations of the theory in terms of the range of the various parameters involved in the calculation. No such calculation has been reported so far, although a general theory of the dynamics of paraelectric impurities for the weak coupling case has been outlined by Bowen.^{11,12} His treatment is based on the functional derivative technique which can in principle be extended to systems with any number of equilibrium orientations.

Our model is presented in Sec. II and a phenomenological approach is described which may be helpful for the understanding of the subsequent rather mathematical treatment. Sec. III contains the Green's function formalism and the details of the calculation. Numerical results, their interpretation, and a discussion follow in Sec. IV.

II. The Model and the Phenomenological Approach

It is usually possible and advantageous in experiments on paraelectric systems at low temperature to separate energetically two low lying tunneling states of the dipole from the rest of the tunneling multiplet. This is accomplished by applying a strong bias electric field or a uniaxial strain in a selected direction. Following an early idea of Sussman⁵, we can thus discuss the dynamical features of the system by using a two-level model of the paraelectric impurity. The model Hamiltonian is conveniently expressed in terms of Pauli spin matrices $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, etc.,^{11,12}

$$H = -(\Delta/2)\sigma_x + (\epsilon/2)\sigma_z + (1/2)\sum_k V_k Q_k \sigma_z + (1/2)\sum_k \{a_k^2 Q_k Q_{-k} + P_k P_{-k}\}. \quad (1)$$

The first term contains the off-diagonal tunneling matrix element Δ and the level splitting ϵ due to a bias electric field or strain. The dipole-phonon coupling constant is V_k , and $Q_k = i(a_k - a_{-k}^+)/\sqrt{2\omega_k}$ is the phonon normal coordinate as given in terms of the usual annihilation and creation operators a_k , a_{-k}^+ and frequency ω_k . The conjugate momentum is P_{-k} , hence $[Q_k, P_{-k}] = i\delta_{k,k'}$. Throughout this paper $\hbar = 1$.

The application of an oscillating probe field $E(t) = E e^{-i\omega t}$ causes a modulation of ϵ and the corresponding term to be added to H is

$$H_{\text{ext}} = -\mu\sigma_z E(t), \quad (2)$$

μ being the electric dipole moment of the impurity. According to the linear response theory the measured isothermal dynamic susceptibility of an ergodic system is the same as its isolated susceptibility,¹³

$$\chi(\omega) = \lim_{\eta \rightarrow 0} \frac{1}{V} \int_0^{\infty} dt e^{i\omega t - \eta t} \langle [M_z(t), M_z(0)] \rangle, \quad (3)$$

where $M_z = \sum \mu \sigma_z / V$ is the polarization operator. $\sum$ implies the sum over all impurities, and V is the volume. The remaining notation in (3) is standard, including the thermodynamic average with respect to (1) and the Heisenberg operators $M_z(t)$.

The calculation of $\chi(\omega)$ for our model is non-trivial even under the assumption of negligible interaction between the impurities, and the results will undoubtedly depend on the choice of the approximations to be used. However, we can to some extent anticipate the outcome of such a calculation by using the analogy with magnetic systems for which the Bloch equations give a good phenomenological description. Therefore, we shall interpret $\frac{1}{2}\Delta$ and $\frac{1}{2}\epsilon$ as two static fields, transverse and longitudinal, acting on the pseudo-spin $\underline{g}$ of the dipole. The macroscopic polarization vector $\underline{M}$ will then precess around the total instantaneous field $\frac{1}{2}\underline{F}(t)$ which is the vector sum of the external field $\mu \underline{E}(t)$ and a static field $\frac{1}{2}\underline{f}$ of magnitude $\frac{1}{2}\sqrt{\Delta^2 + \epsilon^2}$. See Fig. 1. To facilitate further discussion we introduce a new coordinate system X, Y, Z by a coordinate transformation which reverses the y -axis and makes the new Z -axis parallel to the static field $\frac{1}{2}\underline{f}$. According to Fig. 1

the unitary transformation relating the spin matrices $\sigma_x, \sigma_y, \sigma_z$ in the old, and $X = \sigma_x, Y = \sigma_y, Z = \sigma_z$ in the new system is:

$$\begin{aligned}\sigma_x &= X \sin \varphi + Z \cos \varphi \\ \sigma_y &= -Y \\ \sigma_z &= X \cos \varphi - Z \sin \varphi\end{aligned}\tag{4}$$

Obviously, $\cos \varphi = \Delta/f$ and $\sin \varphi = \epsilon/f$.

The total microscopic Hamiltonian (1) and (2) in the new frame is

$$\begin{aligned}H + H_{\text{ext}} &= -(f/2)Z + (1/2) \sum_k V_k Q_k \left(\frac{\Delta}{f} X - \frac{\epsilon}{f} Z \right) + H_{\text{lattice}} \\ &- \mu E \left(\frac{\Delta}{f} X - \frac{\epsilon}{f} Z \right) e^{-i\omega t}.\end{aligned}\tag{5}$$

Notice that there are now two components of the external r.f. electric field $\underline{E}$, a longitudinal field of magnitude $E_Z = -\frac{\epsilon}{f}E$, and a transverse field, $E_X = \frac{\Delta}{f}E$.

In a phenomenological theory the phonon part of the Hamiltonian is first ignored and its effects are included later ad hoc into the equations of motion for the spin polarization vector via the longitudinal and transverse relaxation times, T_1 and T_2 , respectively. The macroscopic pseudo-polarization vector can be thought of as a time-dependent statistical average of the operator $\underline{M} = C \underline{\sigma}(t)$, C being the concentration of paraelectric impurities. The only physical component of $\underline{M}$ is $M_Z = \frac{\Delta}{f} M_X - \frac{\epsilon}{f} M_Z$. Following the usual ideas involved in the derivation of the modified Bloch equations,¹⁴ we assume that $\underline{M}$ precesses around the total field $\underline{F}(t)$ according to the equation $\dot{\underline{M}} = \underline{M} \wedge \underline{F}(t)$ and relaxes towards

its instantaneous thermodynamic average value $\underline{M} = C \tanh(\beta F/2) \underline{F}/F$ where $\beta = 1/(k_B T)$. The equations of motion for $\underline{M}(t)$, linearized with respect to $\underline{E}(t)$, thus are:

$$\begin{aligned}\dot{M}_X &= f M_Y - [M_X - \frac{\Delta}{f^2} C \mu^2 \tanh(\beta f/2) E(t)]/T_2; \\ \dot{M}_Y &= -f M_X + \frac{\Delta}{f} C \mu^2 \tanh(\beta f/2) E(t) - M_Y/T_2; \\ \dot{M}_Z &= -[M_Z + \frac{\epsilon}{f} C \mu^2 (\beta/2) \operatorname{sech}^2(\beta f/2) E(t)]/T_1;\end{aligned}\quad (6)$$

Assuming a harmonic time dependence $M(t) = M(0) e^{-i\omega t}$ we can easily solve Eqs. (6) for $M_X(t)$ and $M_Z(t)$ and thus find the physical component $M_Z(t)$. The complex frequency dependent susceptibility then follows from $\chi(\omega) = M_Z(t)/E(t)$,

$$\chi(\omega) = \chi_L \frac{1}{1 - i\omega T_1} + \chi_T \frac{1}{2} \left\{ \frac{1 + ifT_2}{1 - i(\omega - f)T_2} + \frac{1 - ifT_2}{1 - i(\omega + f)T_2} \right\}. \quad (7)$$

The constants $\chi_L = C \mu^2 \beta (\epsilon/f)^2 \operatorname{sech}^2(\beta f/2)$ and $\chi_T = 2 C \mu^2 (\Delta/f)^2 \tanh(\beta f/2)/f$ are the equivalent of the longitudinal and transverse static susceptibility in the original frame as one would define them for a magnetic system. The actual static susceptibility of the paraelectric system is $\chi_0 = \chi_L + \chi_T$.

Eq. (7) is a superposition of a Debye-type longitudinal relaxation term and a transverse resonance term. The two relaxation times T_1 and T_2 can be estimated from the Hamiltonian (5) if the coupling constant V_k is known. Assuming for simplicity that the dominant coupling mechanism is through the lattice strains, we will write

$$V_k = \lambda \omega_k \sqrt{\pi Q/(rN)}, \quad (8)$$

where λ is a dimensionless coupling parameter, Ω the phonon cut-off frequency, N the number of unit cells, and r the number of phonon branches. For the phonon spectrum we will use a modified Debye form which correctly includes a Van Hove-type singularity at the zone boundary,¹⁵

$$\rho(\omega_k) = \gamma(\omega_k/\Omega)^2 \sqrt{1 - (\omega_k/\Omega)^2} \quad , \quad (9)$$

where the constant γ is fixed by the requirement that the total number of phonon modes is rN . By standard golden rule-type arguments we can now calculate the relaxation rate $1/T_1$. The result is

$$1/T_1 = 3\pi\lambda^2 (\Delta/\Omega)^2 \sqrt{1 - (f/\Omega)^2} f \coth(\beta f/2). \quad (10)$$

The transverse rate is $1/T_2 = 1/(2T_1)$. Notice that only the first, transverse term of the dipole-lattice coupling in (5) contributes to the rate (10).

The magnitude of the parameter λ determines whether we deal with a weakly or strongly coupled system. A crude, but useful criterion can be obtained from the strong coupling theory of dipole reorientation.¹⁶ It is shown there that under the influence of the strong dipole-lattice interaction the tunneling matrix element Δ is reduced by a polaron-like factor $\Delta \rightarrow \Delta'' = \Delta \exp[-\frac{1}{4} \sum_k |V_k|^2 \coth(\beta\omega_k/2)/\omega_k^3]$, usually referred to as the "dressing" factor. Using (8) and (9) this gives at low temperature $\Delta'' = \Delta e^{-\lambda^2}$. Thus, if $\lambda \gg 1$, we have a large dressing effect which is characteristic of a strong coupling. Conversely, $\lambda \ll 1$ means weak coupling,

which is the case we will discuss in the following.

To establish the connection with earlier work¹¹ we give the relationship between λ and the characteristic temperature T_0 which can be used as a measure for the coupling strength: $\lambda = \Omega / (\sqrt{2} \pi T_0)$. The rate (10) with $\Delta = \Delta''$ and $f \ll \Omega$ then becomes the one-phonon part of the relaxation rate in the strong coupling theory. There are some obvious limitations to the validity of the result (7). By writing down Eqs. (6) we have tacitly assumed that the kinetics of the system is governed by constant decay rates at all times. It is known, however, from the study of simpler related systems that the time (or frequency) dependence of the relaxation rates may become important already at moderate values of the coupling parameter λ .¹⁷ This affects the frequency dependence of $\chi(\omega)$ for ω not too close to the poles of the expression (7). Furthermore, in deriving Eq. (7) we have ignored the second term of the dipole-lattice interaction in (5) which does not contribute to the relaxation rate (10). We expect that this term will be responsible for the phase interruption effects as opposed to real transitions caused by the first term. Such effects can change the frequency dependence of $\chi(\omega)$ in the region between the two absorption maxima, and also cause a shift of the resonance frequency. To study these effects we now turn to the general expression (3) and apply the Green's function method for an approximate evaluation of $\chi(\omega)$.

III. Green's Function Method

We use the usual definitions of the commutator Green's functions for two operators A, B:¹⁰

$$G_{AB}(t) = \langle\langle A(t); B \rangle\rangle = \mp i \Theta(\pm t) \langle[A(t), B]\rangle, \quad (11)$$

where the upper sign refers to the retarded and the lower sign to the advanced Green's function, respectively. The corresponding Fourier transforms of $G_{AB}(t)$ are then written

$$G_{AB}(\omega) = \langle\langle A; B \rangle\rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} G_{AB}(t). \quad (12)$$

Here the frequency ω is complex with $\text{Im } \omega > 0$ for the retarded and $\text{Im } \omega < 0$ for the advanced Green's function. Integrating (12) by parts yields an equation of motion which is formally the same for both versions of $G_{AB}(\omega)$,

$$\omega \langle\langle A; B \rangle\rangle = \frac{1}{2\pi} \langle[A, B]\rangle + i \langle\langle \dot{A}; B \rangle\rangle; \quad i \dot{A} = [A, H], \quad (13)$$

which will be used repeatedly in what follows.

The dynamic susceptibility (3) is now expressed in terms of the Green's functions for the operators X and Z of Eq. (4) in the new frame as follows:

$$\chi(\omega) = -2\pi C\mu^2 \langle\langle \sigma_z; \sigma_z \rangle\rangle = -2\pi C\mu^2 \left\{ (\Delta/f)^2 G_{XX}(\omega+i\eta) - (\Delta\epsilon/f^2) [G_{XZ}(\omega+i\eta) + G_{ZX}(\omega+i\eta)] + (\epsilon/f)^2 G_{ZZ}(\omega+i\eta) \right\}. \quad (14)$$

To calculate the Green's functions in (14) we start with the equation of motion for $G_{XX}(\omega)$,

$$\omega \langle\langle X; X \rangle\rangle = -i f \langle\langle Y; X \rangle\rangle - i(\epsilon/f) \sum_k V_k \langle\langle Q_k Y; X \rangle\rangle, \quad (15)$$

and continue with the last function on the right hand side,

$$\omega \langle\langle Q_k Y; X \rangle\rangle = \frac{1}{\pi} \langle Q_k Z \rangle + i \langle\langle P_k Y; X \rangle\rangle + if \langle\langle Q_k X; X \rangle\rangle + i(\epsilon/f) \sum_{k'} V_{k'} \langle\langle Q_k Q_{k'} X; X \rangle\rangle + i(\Delta/f) \sum_{k'} V_{k'} \langle\langle Q_k Q_{k'} Z; X \rangle\rangle. \quad (16)$$

In similar fashion we derive other equations for the remaining of the 27 functions $\langle\langle A, B \rangle\rangle$, $\langle\langle Q_k A; B \rangle\rangle$, and $\langle\langle P_k A; B \rangle\rangle$, where A and B are X, Y, or Z. At that stage we decouple the chain of equations by approximating $\langle\langle Q_k Q_{k'} A; B \rangle\rangle \approx \langle |Q_k|^2 \rangle \delta_{k, -k'} \langle\langle A; B \rangle\rangle$ and neglecting $\langle\langle (Q_k P_{k'} + P_k Q_{k'}) A; B \rangle\rangle$, strictly keeping only terms up to the order $|V_k|^2$ in the coefficients before the functions $\langle\langle A; B \rangle\rangle$. Next we eliminate all functions $\langle\langle P_k A; B \rangle\rangle$ from the equations for $\langle\langle Q_k A; B \rangle\rangle$, and finally all $\langle\langle Q_k A; B \rangle\rangle$ from the equations for $\langle\langle A; B \rangle\rangle$. The latter can be written in compact form as a matrix equation:

$$\begin{pmatrix} \omega - (\epsilon/f)^2 L_{11}, & f + (\frac{\epsilon}{f})^2 L_{12}, & -\frac{\Delta \epsilon}{f^2} L_{11} \\ f + (\frac{\epsilon}{f})^2 L_{12}, & \omega - (\epsilon/f)^2 L_{11}, & \frac{\Delta \epsilon}{f^2} L_{12} \\ -\frac{\Delta \epsilon}{f^2} L_{11}, & \frac{\Delta \epsilon}{f^2} L_{12}, & \omega - (\Delta/f)^2 L_{11} \end{pmatrix} \begin{pmatrix} G_{XX}, G_{XY}, G_{XZ} \\ iG_{YX}, iG_{YY}, iG_{YZ} \\ G_{ZX}, G_{ZY}, G_{ZZ} \end{pmatrix} = \begin{pmatrix} I_{XX}, I_{XY}, I_{XZ} \\ I_{YX}, I_{YY}, I_{YZ} \\ I_{ZX}, I_{ZY}, I_{ZZ} \end{pmatrix} \quad (17)$$

The functions $L_{11}(\omega)$, $L_{12}(\omega)$, $L_{22}(\omega)$ are here given by

$$L_{11}(\omega) = \omega \sum_k |V_k|^2 \langle |Q_k|^2 \rangle (\omega^2 - f^2 - \omega_k^2) D_k^{-1}; \quad (18)$$

$$L_{12}(\omega) = f \sum_k |V_k|^2 \langle |Q_k|^2 \rangle (\omega^2 - f^2 + \omega_k^2) D_k^{-1}; \quad (19)$$

$$L_{22}(\omega) = L_{11}(\omega)_{f=0} \quad (20)$$

$$\text{with } D_k = \pi [(\omega - f)^2 - \omega_k^2] [(\omega + f)^2 - \omega_k^2]. \quad (21)$$

The inhomogeneous terms in (17) are (we give only the ones relevant to the calculation of $\chi(\omega)$):

$$I_{XX}(\omega) = (\epsilon/f) \omega \sum_k V_k \langle Q_k Z \rangle (\omega^2 - f^2 - \omega_k^2)^{-1} D_k^{-1}; \quad (22)$$

$$I_{YX}(\omega) = -\epsilon \sum_k V_k \langle Q_k Z \rangle (\omega^2 - f^2 + \omega_k^2)^{-1} D_k^{-1} - \langle Z \rangle / \pi$$

$$- (\Delta/f) \sum_k V_k \langle P_k Y \rangle / [\pi(\omega^2 - \omega_k^2)]; \quad (23)$$

$$I_{XZ}(\omega) = -(\epsilon/f) \omega \sum_k V_k \langle Q_k X \rangle (\omega^2 - f^2 - \omega_k^2)^{-1} D_k^{-1}$$

$$- 2 \epsilon \omega \sum_k V_k \langle P_k Y \rangle D_k^{-1}; \quad (24)$$

$$I_{YZ}(\omega) = (\epsilon/f) \sum_k V_k \langle P_k Y \rangle (\omega^2 + f^2 - \omega_k^2)^{-1} D_k^{-1}$$

$$+ \epsilon \sum_k V_k \langle Q_k X \rangle (\omega^2 + f^2 - \omega_k^2)^{-1} D_k^{-1} + \langle X \rangle / \pi; \quad (25)$$

$$I_{ZX}(\omega) = (\Delta/\epsilon) I_{XX}(\omega); \quad I_{ZZ}(\omega) = (\Delta/\epsilon) I_{XZ}(\omega). \quad (26)$$

The averages $\langle Q_k X \rangle$, $\langle Q_k Z \rangle$, and $\langle P_k Y \rangle$ can be calculated with the help of the identities $(d/dt) \langle Q_k A \rangle = 0$, $(d/dt) \langle P_k B \rangle = 0$, etc. In this way we obtain to the order V_k :

$$\langle Q_k Z \rangle = \frac{1}{2} (\epsilon/f) V_{-k} / \omega_k^2; \quad (27)$$

$$\langle Q_k X \rangle = V_{-k} \langle |Q_k|^2 \rangle \langle Z \rangle / (\omega_k^2 - f^2) - \frac{1}{2} (\Delta/f) V_{-k} / (\omega_k^2 - f^2); \quad (28)$$

$$\langle P_k Y \rangle = -(\Delta/f) \langle Z \rangle V_{-k} \langle |Q_k|^2 \rangle \omega_k^2 / (\omega_k^2 - f^2) + \frac{1}{2} V_{-k} / (\omega_k^2 - f^2). \quad (29)$$

All other averages are either zero or of an order higher than V_k .

The average $\langle Z \rangle$ will be approximated by its unperturbed value

$\langle Z \rangle_0 = \tanh(\beta f/2)$, and $\langle X \rangle$ which is of the order $|V_k|^2$ will be

neglected. This may not seem consistent with the above approx-

imations, however, it turns out that calculating $\langle Z \rangle$ and $\langle X \rangle$ in

$|V_k|^2$ order gives only the first terms of a poorly convergent series.

Strictly speaking, one should calculate the averages $\langle Z \rangle$ and $\langle X \rangle$ self-consistently using the spectral representation for the Green's functions $\langle\langle X; Y \rangle\rangle$ and $\langle\langle Z; Y \rangle\rangle$.¹⁸ The same argument applies to all other averages, including $\langle |Q_k|^2 \rangle$, which in zeroth order is simply $\coth(\beta\omega_k/2)/(2\omega_k)$. This immediately leads to a very difficult computational problem. Unlike the theory of ferromagnetism,¹⁹ however, the effective field acting on each pseudo-spin is here not strongly dependent upon the polarization of the other spins. Thus the self-consistency is a not too serious problem in our case and the approximations outlined above can be expected to be reasonably accurate, at least in the weak coupling limit.

There are more problems related to the self-consistency of the decoupling method. Since the method is applied to the frequency dependent Green's functions, one has little idea whether the approximate Green's functions would have the correct analytic behavior when transformed back into the time picture. As an indication of these problems we mention that $\langle\langle X; Z \rangle\rangle$ and $\langle\langle Z; X \rangle\rangle$ do not satisfy the exact formal relationship $G_{XZ}(\omega) = G_{ZX}(-\omega)$, and for this reason had to be calculated independently. Had we chosen to determine $\chi(\omega)$ from the anticommutator rather than commutator Green's functions using the same approximation scheme, the result would have been different. We have recently investigated this problem for a similar system²⁰ and found that the commutator functions gave results which were closer to the phenomenological

theory than the anticommutator version.

We need the solution of Eqs. (17) at $\omega + i\eta$ in a wide range of ω . For a given frequency ω we first split each element of the matrices into its real and imaginary part, for example,

$L_{11}(\omega + i\eta) = L'_{11}(\omega) + iL''_{11}(\omega)$, where

$$L'_{11}(\omega) = \frac{3}{2} (\lambda/\Omega)^2 \int_{-\Omega}^{+\Omega} \frac{dw w^3 \sqrt{1 - (w/\Omega)^2}}{w - f + w} \coth(\beta w/2) + (f - -f); \quad (30)$$

$$L''_{11}(\omega) = \frac{3}{2} \pi (\lambda/\Omega)^2 (f - \omega)^3 \coth[\beta(\omega - f)/2] \sqrt{1 - (\omega/\Omega)^2} \Theta[1 - (\frac{\omega - f}{\Omega})^2] + (f - -f). \quad (31)$$

In deriving these results we have used Eqs. (8) and (9) and the identity $(\omega - x + i\eta)^{-1} = \text{P.V.}(\omega - x)^{-1} - i\pi\delta(\omega - x)$. Notice that $-(\Delta/f)^2 L''_{11}(0)$ is equal to the longitudinal relaxation rate (10).

The resulting complex set of equations is then solved numerically for the real and imaginary parts of the functions G_{XX} , G_{XZ} , G_{ZX} , and G_{ZZ} , which are substituted into Eq. (14).

IV. Numerical Results and Discussion

The paraelectric absorption spectrum is given by the imaginary component of Eq. (14), $\chi''(\omega)$. The results of our calculation are shown in Figs. 2 - 4 for different values of the parameter λ and for various ranges of frequency ω . In Fig. 2 we have plotted $\chi''(\omega)$ versus $\log(\omega/\Omega)$ for $\lambda = 0.27$ over a broad frequency range. As anticipated from the phenomenological approach, the spectrum has a low frequency maximum at $\omega \approx 1/T_1$, where T_1 is given by the expression (10). The paraelectric resonance line lies slightly below $\omega = f$ and appears very narrow on a logarithmic scale, although its width is close to $2/(\Omega T_2)$ as shown later. We have not investigated in any detail the intensities of both peaks, however, it appears that the intensity of the lower peak is roughly proportional to $(\epsilon/f)^2$ and of the resonance line to $(\Delta/f)^2$ in accordance with the phenomenological result (7). The low frequency maximum disappears for $\epsilon \rightarrow 0$ which corresponds to zero bias field in which case the r.f. field in (5) becomes purely transverse. The real part of the susceptibility has no additional features and is not shown here. We have verified that $\chi'(0)$ is very close to the isothermal static susceptibility $\chi_0 = \chi_L + \chi_T$ as obtained in connection with Eq. (7).

In order to look more closely at the relaxation maximum we have plotted in Fig. 3 $\chi''(\omega)$ in the low frequency range for

three values of λ . For $\lambda = 0.1$, the weakest coupling studied, the maximum indeed lies very near $\omega = 1/T_1$ as expected. There is an apparent tendency of shifting the maximum towards lower values of ω with increasing λ . This may be due to the occurrence of frequency dependent rates like $L_{11}''(\omega)$, etc. in our general equation (17). Multi-phonon relaxation processes must be excluded as the cause of the shifts since the decoupling approximation carried out to the order $|V_k|^2$ is essentially limited to one-phonon transitions.

The paraelectric resonance line for $\lambda = 0.1$ is compared in Fig. 4 with the phenomenological result (7). The shapes of the two curves are obviously the same, however, the position of the line calculated by the Green's function method is lower by roughly 1%. For larger values of λ one finds still larger shifts towards lower frequencies. The width of the line is accurately given by $2/T_2$ ($=1/T_1$) as expected on the basis of Eq. (7). Notice that the resonance line here corresponds to an allowed transition. In experiments on multilevel systems one also observes lines which are forbidden by symmetry considerations, and appear as a result of symmetry breaking by local random strains and electric fields. The same effect is responsible for the shape of the line, which appears Gaussian⁴ rather than Lorentzian which would be the case if phonons were the main broadening mechanism. Phonon effects can be seen, however, in allowed transitions whose lines appear broader than those of forbidden transitions, and have a temperature

dependent width.²¹ Saturation measurements have been used to obtain an estimate of T_1 from resonance experiments.^{4,21}

It seems that the shifts of the resonance maxima have their origin in the real parts of the functions $L_{11}(w)$ etc. in Eq. (17). Numerical calculations indicate that $L'_{12}(w)$ is important at low frequencies and $L'_{11}(w)$ and $L'_{22}(w)$ for w near resonance. The terms proportional to $(\epsilon/f)^2 L_{11}(w)$ in Eq. (17) are due to the longitudinal part of the dipole-lattice interaction in the Hamiltonian(5), whose effect is a phase interruption²² of the up and down states of the dipole. The terms proportional to $(\Delta\epsilon/f^2)$ result from an interference between the longitudinal and transverse couplings. The existence of large real off-diagonal elements in the first matrix of Eq. (17) suggests an interpretation in terms of an additional field acting on the dipole whose strength is proportional to λ^2 and to a factor (ϵ/f) or $(\epsilon/f)^2$, that is, to the asymmetry of the potential energy for the up and down states. For large ϵ we can thus expect a breakdown of the decoupling approximation since the phonon field may become comparable to f in some frequency range. This indeed happens in our calculations. If we increase ϵ to values larger than Δ , we obtain negative values of $\chi''(w)$ in the region between the two maxima. Improvements of the method may be sought in changing the angle ϕ in Eqs. (4) in such a way that the static component of the phonon-induced field is eliminated from the transformed Hamiltonian.

We have mentioned earlier that the strong coupling theory of paraelectric resonance predicts a renormalization of the tunneling frequency which becomes a temperature dependent quantity decreasing with rising temperature.^{11,12} The resonance thus occurs near $\omega = f'' = \sqrt{\Delta''^2 + \epsilon^2}$, and is weighed by a factor $\sim (\Delta''/f'')^2$, which for $\epsilon \gg \Delta''$ may decrease with the temperature, an effect discussed in Ref. 12. It has further been shown¹¹ that the absorption spectrum for ω and $f'' > kT$ roughly follows the phenomenological expression (7) with $\bar{\Delta}$ and f renormalized as mentioned above.

An interesting point which is not well understood yet is the question whether the paraelectric resonance line could be interpreted as a zero-phonon line rather than a Lorentzian line obtained from the present weak coupling treatment. Experiments cannot give a definite answer here because, as we know, the lines appear inhomogeneously broadened. The existence of a zero-phonon line has been predicted in a strong coupling theory¹² on the basis of a lowest order perturbation expansion of $\chi(\omega)$ with respect to Δ'' . It remains to be shown, however, that higher-order terms in the expansion are not divergent at $\omega = f$ and that they do not cause a broadening of the delta-like line. The present weak coupling treatment does not support this possibility. A zero-phonon line can exist if the Green's function $G_{XX}(t)$ oscillates freely with a frequency f for long times.¹⁷ Clearly, this problem requires a more detailed study.

Our Eq. (17) is formally similar to the general result derived by Bowen⁷ for a two-level case. Because of the complexity of his functional derivative method we did not attempt here a detailed comparison between the two treatments. We should mention, however, that his theory predicts the same general structure for the dynamic susceptibility, that is, the existence of a low frequency relaxation maximum and a phonon-broadened paraelectric resonance line. It would be instructive to apply Bowen's formalism to the model for the dipole-lattice coupling used here in order to investigate the behavior of the susceptibility for large ϵ which, as mentioned earlier, led to difficulties in the present calculations.

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Figure Captions:

Fig. 1. Schematic presentation of the various terms in the Hamiltonian as fields acting on the pseudo-spin.

Fig. 2. Absorptive part of the paraelectric susceptibility vs. $\log(\omega/\Omega)$ in units of the static susceptibility χ_0 . The values of the parameters are: $\Delta/\Omega = 0.03$, $\epsilon/\Omega = 0.015$, $\beta\Omega = 12.5$.

Fig. 3. Low frequency absorption maximum for three values of the coupling strength λ . The arrows indicate the positions of the corresponding relaxation rates $1/(\Omega T_1)$, Eq. (10). Other parameters are the same as in Fig. 2.

Fig. 4. Comparison between the Green's function calculation (solid line) of paraelectric resonance line shape and the phenomenological result (7) (dashed line).

Fig. 1.

Fig. 2.

Fig. 2.

Fig. 3.

Fig. 4.