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Theory for the Interaction of Phonons with Nonharmonic Impurities and Their Effect on the Polarizability

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A new formalism is used to describe the interaction of localized nonharmonic impurities with a field. The impurity is described in terms of anticommuting Fermi operators, thus permitting the use of diagrammatic techniques. The formalism is used to study the impurity-phonon interaction in general, and to study, in particular, the effect of the phonon field on the impurity's polarizability. Using linear-response theory and thermodynamic Green's functions, the polarizability is obtained. It is found to contain a resonance term and a dipole relaxation term which is found to be present even when the impurity has no diagonal dipole matrix elements. The effect of the four-vertex part on the polarizability is to renormalize the impurity's dipole matrix elements and make them temperature dependent. The formalism is particularly suited to the study of highly polarizable impurities such as the proton in hydrogen-bonded ferroelectrics, off-center impurities, and permanent-dipole impurities.

I. INTRODUCTION

The interaction of the phonon field with a localized nonharmonic impurity having a finite number of physically relevant quantum-mechanical (QM) levels

and the interaction of these two systems with the electromagnetic field form an important class of problems occurring in solid-state physics. It will prove particularly useful to calculate physical properties such as the polarizability of the impu-

rity, thermal conductivity, optical line shapes, and energy transfer of electromagnetic radiation into phonons or acoustic energy. (Transfer of energy from a pulsed microwave field into acoustic radiation by the off-center lithium impurity in KCl has been observed.[1])

Of the many systems that fall within the general category of nonharmonic localized impurities, there are three types that are particularly suited to the new representation to be discussed below: (i) the proton in ferroelectric crystals containing hydrogen bonds such as potassium dihydrogen phosphate (KDP) and triglycine sulphate, where the ferroelectric ion (proton) has been described as being in a double-well potential[2]; (ii) impurities with an induced dipole moment such as the off-center Li in KCl[3] and Ag in RbCl[4]; and (iii) permanent-dipole impurities such as OH⁻ and CN⁻ in alkali halides.[5]

A previous formulation[6] of the nonharmonic impurity-phonon coupling problem limited calculations to finite perturbation theory, due to the noncommutativity of the operators characterizing the impurity. The current work involves the use of a new representation which makes calculations involving the use of diagrammatic techniques and infinite-order perturbation feasible. The powerful Wick's theorem and the resulting diagrammatic techniques cannot be used if the problem is phrased in terms of noncommuting operators.

The new representation was obtained by exploiting the formal analogy that exists between the impurity-phonon problem and the Kondo effect. Schematically the correspondence between the two problems can be expressed as

Fermi field (conduction electrons)

> interaction
> $\Rightarrow$ localized spin
>   levels (finite),

> interaction
phonon field $\Rightarrow$ localized-impurity
>   QM levels (finite).
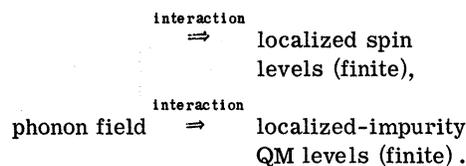
In 1965 Abrikosov,[7] in his paper on the Kondo effect, avoided the problem that the noncommutativity of the spin operators presented by rewriting these operators in terms of Fermi operators, i.e.,

$$\hat{\vec{S}} = c_i^\dagger \vec{S}_{ij} c_j , \qquad (1.1)$$

where the c's are Fermi operators and the S_{ij}^k are spin matrices. Since the operators representing transitions between QM levels of the impurities present the same problem as the spin operators, use will be made of Abrikosov's idea in rewriting these operators in terms of anticommuting Fermi operators.

The scope of the present paper will be limited in several respects in order to make it relatively short and clear. The formalism will be presented

in a form that is particularly suited to the off-center impurity systems, leaving the generalization and application of the formalism to other systems for the future. Only the phonon field will be coupled to the impurity; the problem of the impurity's coupling to the electromagnetic field is completely analogous to the phonon-field problem, as will be pointed out below. Finally, only the effect of the phonon field on the dielectric constant will be considered as a useful application of the formalism.

The remaining part of the text will be divided into three sections. In Sec. II the system's Hamiltonian will be introduced and the formalism for its second quantization discussed; the impurity-"free" thermodynamic Green's function will then be developed in terms of the Fermi operators and its physical significance studied. The impurity's first-order Green's function will then be constructed with the help of a Dyson's equation, using a diagonal self-energy term (diagonal in the impurity's eigenstates). Section III will be devoted to the impurity's dynamic polarizability and its relation to a second-order Green's function; the polarizability of a noninteracting impurity (in the absence of a phonon field) will be discussed to illustrate the use of the formalism. Then, turning the interaction on but without including the four-vertex term (see Fig. 2), the dynamic polarizability will be calculated and a resonance term will be obtained. Finally, in Sec. IV, using techniques developed by Eliashberg and Abrikosov[8-9] for the conductivity of Fermi liquids (which are essentially based on the analytic properties of the second-order Green's function), the polarizability of the impurity is obtained, and is found to contain a dipole relaxation term that was not present when the calculation was done in the absence of the four-vertex part Γ.

II. REPRESENTATION OF IMPURITY QUANTUM-MECHANICAL LEVELS IN TERMS OF FERMI OPERATORS

A. Hamiltonian

The Hamiltonian for the impurity-phonon system can be written as[3(a)]

$$H_T = H_I + H_L + H_{LI} , \qquad (2.1)$$

where H_I is the impurity Hamiltonian, H_L is the lattice Hamiltonian, and H_{LI} is the impurity-phonon term. The impurity Hamiltonian for nonharmonic impurities is taken to be[3(a)]

$$H_I = -\hbar^2 \nabla^2 / 2m_I + V_I(\vec{r}) , \qquad (2.2)$$

where

$$V_I(\vec{r}) = V_{LI}^{(0)} (\{\vec{R}(l, \kappa)\}, \vec{r}) .$$

Here, m_I is the mass of the impurity, $\{\vec{R}(l, \kappa)\}$ is the set of equilibrium positions of the host-lattice ions, and $\vec{r}$ is the spatial coordinate of the impurity

measured from its lattice site. $V_I(\vec{r})$ is nonharmonic by definition, and it is further assumed that the displacements are of such magnitude that the expansion of this potential in terms of small displacements from equilibrium is not feasible.[3(a)] The explicit form of the impurity-phonon Hamiltonian is

$$H_{LI} = \sum_{l,\kappa,\alpha} \frac{\partial V_{LI}(\{\vec{R}(l,\kappa)\},\vec{r})}{\partial R_\alpha(l,\kappa)} u_\alpha(l,\kappa) + O(u^2), \quad (2.3)$$

where $u_\alpha(l,\kappa)$ are the lattice displacements from equilibrium (not including the impurity) in the α direction ($\alpha = 1, 2, 3$).

In what follows it will be assumed that eigenvalues ϵ_{n_i} and eigenfunctions $|n_i\rangle$ of the QM equation

$$H_I |n_i\rangle = \epsilon_i| n_i\rangle, \quad i < \infty \quad (2.4)$$

are known, or that the energies and appropriate matrix elements can be obtained from experiment, and that the number of QM states that are physically relevant are finite. The reader is referred to Ref. 3(a) for a detailed discussion of Eq. (2.4) in the special case of the nonharmonic impurity Li^+ in KCl.

Following Abrikosov,[7] the Hamiltonian can be written in second-quantized form using *one* set of anticommuting Fermi operators for each eigenstate of the impurity. The impurity Hamiltonian is then

$$H_I(k,l) = \sum_{i=1}^{N} \delta_{ik}\delta_{il}\epsilon_i c_i^\dagger c_i, \quad (2.5)$$

where ϵ_i is the energy of the ith level, δ is the Kronecker symbol, N is the number of impurity eigenstates, and the c's are Fermi operators; c_i destroys an impurity in the ith state and $c_i^\dagger$ creates one in the same state of excitation. To facilitate the discussion later on and for emphasis, we have written the conventional second-quantized Hamiltonian in matrix form. Thus H_I is an $N \times N$ diagonal matrix and Eq. (2.5) is the (l,k) matrix element of H_I;

$$H_L = \sum_s \hbar\omega_s (a_s^\dagger a_s + \tfrac{1}{2}), \quad (2.6)$$

where $\hbar\omega_s$ is the energy of the sth phonon mode and the a's are phonon operators. Finally, the impurity-phonon Hamiltonian is

$$H_{LI}(k,l) = \sum_{i,j} \sum_s \delta_{ik}\delta_{jl}\Phi(ij,s)c_i^\dagger c_j A_s, \quad (2.7)$$

$$A_s = a_s^\dagger + a_s$$

where Φ is a matrix element that couples the ith with the jth state of the impurity via an "s" phonon. For the impurity systems that are considered here the energy difference between impurity levels is restricted to energies that fall within the phonon's energy spectrum; in these systems the physical interpretation of H_{LI} is then analogous to that of the electron-phonon Hamiltonian, i.e., $H_{LI}(l,k)$ cor-

responds to a transition from state k to state 1 of the impurity by the absorption or emission of a phonon depending on whether the energy of k is lesser or greater than that of 1. In contrast to the electron-phonon problem, there is no conservation of crystal momentum since the impurity destroys the translational invariance of the crystal.

The explicit form of the coupling parameter Φ can be obtained from Eq. (2.3):

$$\Phi(\beta\beta', s) = \sum_{l,\kappa,\alpha} \left\langle n_i \left| \frac{\partial V_{LI}}{\partial R} \right| n_j \right\rangle B_\alpha^s \binom{l}{\kappa} \left[\hbar/2m \binom{l}{\kappa} \omega_s \right], \quad (2.8)$$

where

$$B_\alpha^s \binom{l}{\kappa}$$

is the αth component of the displacement of the

$$\binom{l}{\kappa} \text{th}$$

atom in the sth mode of the crystal. Direct evaluation of Eq. (2.8) is difficult because of lack of knowledge of V_{LI} and its derivatives, but with the help of acoustic attenuation experiments,[10] estimates of Φ can be obtained.

The introduction of the Fermi operators in the above representation for H_T introduces fictitious or nonphysical states into the impurity's complete set of states: states which have more than one impurity at a given site. More explicitly, the Fermi operators act on the general state

$$|n_1, \ldots, n_i, \ldots, n_N\rangle, \quad n_i = \begin{cases} 1 \\ 0 \end{cases}$$

while only states of the form

$$|0, \ldots, n_j = 1, \ldots, 0\rangle$$

have physical meaning. Fortunately the fictitious states can be eliminated from the problem by defining the ensemble average in the following manner[7]:

$$\langle O(t)\rangle = \lim_{\lambda \to \infty} \frac{e^{\beta\lambda}}{Z} \left[\mathrm{Tr} e^{-\beta(H_T + \lambda\hat{N})} O(t) \right], \quad (2.9)$$

where the number operator $\hat{N}$ is

$$\hat{N}(k,l) = \sum_i \delta_{ik}\delta_{il}c_i^\dagger c_i \; ;$$

$$O(t) = e^{i\beta(H_T + \lambda\hat{N})t} O(0) e^{-i\beta(H_T + \lambda\hat{N})t}, \quad (2.10)$$

$$Z = \lim_{\lambda \to \infty} e^{\beta\lambda} (\mathrm{Tr} e^{-\beta(H_T + \lambda\hat{N})}),$$

$\beta = 1/kT$, "Tr" is the trace, and $O(0)$ is a field operator. The fact that the only states that survive the above limit are the physical ones can be verified by making use of the Lehmann representation for the trace (see Appendix A). Taking the above limit ensures that instead of Fermi statistics we get the required Boltzmann statistics for the impurity.

Note the analogy between λ and a Fermi chemical potential μ; the limit of infinite λ is equivalent to μ going to minus infinity or to the limit of a very-low-density Fermi system.

It must be emphasized that the limiting process described in Eq. (2.9) is to be applied only to the final, physically meaningful ensemble average and not to intermediate Green's-function propagators, since the advantage of the technique lies precisely in having the intermediate propagators behave as Fermi propagators.

The above representation for the impurity-phonon Hamiltonian will prove to be very useful in calculatting dynamic properties of the highly polarizable impurities which are intrinsically many-body in nature. It is also clear that by changing the phonon operators to photon operators in the above Hamiltonian, the coupling of the electromagnetic field to the impurity is obtained.

B. Thermodynamic Green's Function for Impurity and Phonons

With the Hamiltonian of the system expressed in terms of Fermi and phonon operators, it is now possible to make use of Wick's theorem and diagrammatic techniques; thus thermodynamic Green's functions can be used in the solution of the impurity-phonon problem. The first-order thermodynamic Green's functions of the impurity and the phonons will be discussed now, since they will be needed in the calculation of the impurity polarizability.

The impurity Green's function is given by

$$\mathcal{G}_{\beta\beta'}(\tau, \tau') = \langle T[c_\beta(\tau) c_{\beta'}^\dagger(\tau)] \rangle \quad,$$

$$c_\beta(\tau) = e^{\tau(H_T + \lambda\hat{N})} c_\beta e^{-\tau(H_T + \lambda\hat{N})} \qquad (2.11)$$

where τ is the usual imaginary time used in thermodynamic Green's-function calculations and T is the time-ordering operator. Note that as a result of the matrix nature of H_T the $\mathcal{G}$'s are also matrices; in general, $\mathcal{G}_{\beta\beta'}$ will be a nondiagonal matrix because of the H_{LI} term in the Hamiltonian, but this paper will be limited to the special cases where $\mathcal{G}$ is diagonal. $\mathcal{G}_{\beta\beta}$ represents the propagation in time of the impurity state β. The retarded G^R and advanced G^A Green's function will be needed later on; for completeness sake, we define them here as

$$G_{\beta\beta'}^R(t, t') = -\langle \{c_\beta(t), c_{\beta'}^\dagger(t')\} \rangle \Theta(t - t') \quad,$$

$$G_{\beta\beta'}^A(t, t') = -\langle \{c_\beta(t), c_{\beta'}^\dagger(t')\} \rangle \Theta(t' - t) \quad,$$

where $\theta(t)$ is the usual step function. Equation (2.11) can be written in terms of a Fourier series as

$$\mathcal{G}_{\beta\beta'}(\tau) = (1/\beta) \sum_{\omega_n} \mathcal{G}_{\beta\beta'}(\omega_n) e^{-\tau\omega_n},$$

where

$$\omega_n = i(2n + 1)\pi/\beta \quad.$$

It is easy to show[11] that for the case of "free" or noninteracting Green's function the Fourier coefficients are given by

$$\mathcal{G}_{\beta\beta'}^0(\omega_n) = \delta_{\beta\beta'} /[\omega_n - (\epsilon_\beta + \lambda)] \quad. \qquad (2.12)$$

The corresponding expression for a "free" phonon Green's function is

$$\mathcal{D}^0(k, \omega_n) = \omega_0^2(k)/[\omega_n^2 + \omega_0^2(k)], \quad \omega_n = 2\pi n/\beta \qquad (2.13)$$

where $\omega_0(k) = ck$ and c is the speed of sound in the crystal. Figure 1 illustrates the pictorial representation for $\mathcal{D}^0$, $\mathcal{G}^0$, $\mathcal{G}$, and H_{LI} (vertex term) to be used in the construction of diagrams. In applying the vertex term to the construction of diagrams, it will be important to keep in mind that conservation of energy will be required at the vertex while momentum is not conserved.

The self-energy Σ of $\mathcal{G}$, needed in the calculations of the polarizability, will be discussed now. Σ is defined in terms of

$$\mathcal{G}_{\alpha\beta} = \mathcal{G}_{\alpha\alpha}^0 + \mathcal{G}_{\alpha\alpha}^0 \Sigma_{\alpha\gamma} \mathcal{G}_{\gamma\beta} \quad, \qquad (2.14)$$

which is the Dyson equation for $\mathcal{G}$. The evaluation of Σ will be limited to the simplest diagram that contributes to the self-energy; the diagram is shown in Fig. 1. Furthermore, in order to simplify the matrix part of the problem only the diagonal parts of Σ will be considered. The explicit form of Σ in the above approximation is

$$\Sigma_\beta(\mathcal{E}) = \sum_s \sum_{\beta'} \sum_{\mathcal{E}_1} [\Phi(\beta\beta', s)]^2 \mathcal{G}_{\beta'}^0(\mathcal{E}_1) \mathcal{D}_s^0(\mathcal{E} - \mathcal{E}_1). \qquad (2.15)$$
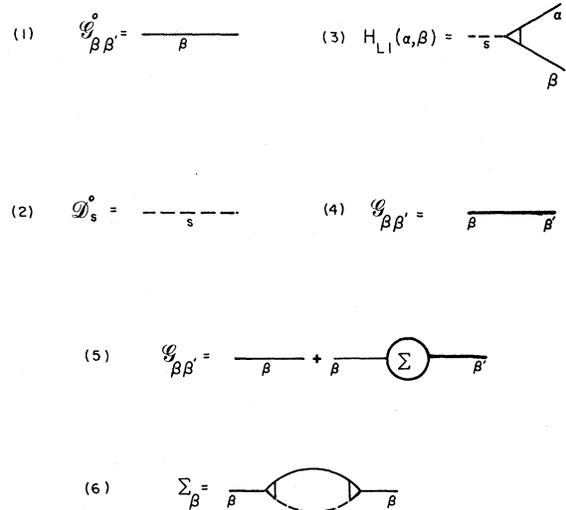
FIG. 1. Pictorial representation for (1) "free" impurity Green's function $\mathcal{G}^0$; (2) "free" phonon Green's function $\mathcal{D}^0$; (3) vertex term H_{LI}; (4) first-order impurity Green's functions $\mathcal{G}$; (5) diagrammatic representation of the Dyson equation for the impurity Green's function; and (6) lowest-order diagram contributing to the impurity self-energy Σ.

Using the Debye approximation for the phonon spectrum, and assuming that

$$\hbar\omega_D \gg \epsilon_\beta, \quad \hbar\omega_D \gg kT,$$

where $\hbar\omega_D$ is the Debye energy, Eq. (2.15) can be evaluated for the case of the retarded self-energy Σ^R. Then the real and imaginary parts of Σ^R are given by

$$\text{Im}\Sigma_\beta^R(\mathcal{E}'+\lambda) = \sum_{\beta'} \overline{[\Phi(\beta\beta', s)]^2} \, \frac{3\pi}{4} \left(\frac{\epsilon_{\beta'} - \mathcal{E}'}{\hbar\omega_D}\right)^3$$

$$\times \{1 + \coth[\beta(\epsilon_{\beta'} - \mathcal{E}')/2]\},$$

$$\text{Re}\Sigma_\beta^R(\mathcal{E}'+\lambda) = \sum_{\beta'} \overline{[\Phi(\beta\beta', s)]^2} \, [\tfrac{1}{2} + \tfrac{3}{4}(kT/\hbar\omega_D)],$$

where the bar over Φ implies an average over those phonon modes "s" that contribute to the matrix element of Eq. (2.8). For more details on the evaluation of Eq. (2.15) the reader is referred to Appendix B.

The above restriction to diagonal Σ (i.e., diagonal in the impurity's eigenstates β), and therefore to a diagonal $\mathcal{G}$, is not as stringent a limitation as it may seem at first sight. Actually for a two-quantum-level system Σ is diagonal, if the diagram shown in Fig. 1 is used. For impurities with non-degenerate eigenstates, the above restriction is expected to be a good approximation in the sense that no new radically different physics is expected to come out if the off-diagonal Σ's are included in the solution of Dyson's equation. But for systems with degenerate eigenstates, the inclusion of the off-diagonal matrix elements in Eq. (2.14) will probably produce dynamic splittings of the degenerate eigenstates, and a possible dynamic Jahn-Teller effect. The author is presently studying these possibilities. It is then fair to state that the conclusions reached in the rest of the article will be strictly valid for two-level systems and systems with nondegenerate eigenstate, but should be interpreted with caution when applied to systems with degenerate states.

III. DYNAMIC POLARIZABILITY OF THE IMPURITY

The dynamic polarizability of the impurity was selected as the first physical quantity to be calculated using the new representation. The reason for this selection is twofold; first, the localized non-harmonic impurities are characterized by an anomalously high polarizability, and second, many-body techniques must be used in order to obtain a dipolar relaxation effect due to phonon drag. This calculation would not be feasible with a noncommuting representation for the operators.

To express the frequency-dependent polarizability $\alpha(\omega)$ in terms of a second-order retarded thermodynamic Green's function, use is made of linear-response theory (LRT). If a perturbation of the

form

$$H' = -e\vec{r} \cdot \vec{\mathcal{E}}(t) = -\vec{\mu} \cdot \vec{\mathcal{E}}(t)$$

[where e is the electron charge, $\vec{r}$ the impurity's coordinate, and $\mathcal{E}(t)$ a time-dependent electric field] is applied to the impurity, then the response of the impurity to this perturbation is the impurity's polarizability and its explicit form can be easily evaluated using LRT. The result of this calculation is

$$\alpha_{\gamma\eta}(\omega) = \sum_{\alpha, \alpha'} \sum_{\beta, \beta'} \langle \epsilon_\alpha | \mu_\gamma | \epsilon_\beta \rangle \langle \epsilon_{\beta'} | \mu_\eta | \epsilon_{\alpha'} \rangle$$

$$\times \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \, \frac{\text{Im}K^R(\alpha, \alpha'; \beta, \beta'; \omega')}{\omega' - \omega - i\delta}, \quad (3.1)$$

where

$$K^R(\alpha, \alpha'; \beta, \beta'; \omega')$$
$$= \text{F. T. } K^R(\alpha, \alpha'; \beta, \beta'; t),$$
$$K^R(\alpha, \alpha'; \beta, \beta'; t)$$
$$= \langle [e^{i(H_T + \lambda\hat{N})t} c_\alpha^\dagger c_\beta e^{-i(H_T + \lambda\hat{N})t}, c_{\beta'}^\dagger c_{\alpha'}] \rangle \Theta(t). \quad (3.2)$$

Here μ is the dipole operator for the impurity, δ is a positive infinitesimal, and K^R is the retarded second-order Green's function for the impurity. Equation (3.1) can be simplified by making use of the integral relation

$$K^R(\alpha, \alpha'; \beta, \beta'; \omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \, \frac{\text{Im}K_R(\alpha, \alpha'; \beta, \beta'; \omega')}{\omega' - \omega - i\delta}. \quad (3.3)$$

Then it becomes clear that the evaluation of the polarizability $\alpha(\omega)$ reduces to the problem of evaluating the second-order Green's function K^R. The function K can be represented by a sum of diagrams that are shown in Fig. 2(a). In the figure, Γ is the four-vertex part; the following section will be devoted to the evaluation of this term. The physical interpretation of the diagram for K in time-space is simple; at time zero the impurity absorbs a quantum of energy $\hbar\omega$, exciting the impurity from state α to state β; Γ corresponds to interaction between state α and β, and other intermediate states via the impurity-phonon term, and finally at time t, state β decays into state α emitting a quantum of energy $\hbar\omega$ and closing the bubble diagram.

Consider first the simple case of no impurity-phonon interaction. Then the term containing Γ vanishes and only the first diagram in Fig. 2(a) contributes to K. In this simple case, K can be written explicitly as

$$K^0(\alpha, \alpha'; \beta, \beta'; \omega_m)$$

$$= \lim_{\lambda \to \infty} \exp(\beta\lambda) \left(-(1/\beta)\sum_n \mathcal{G}_{\alpha\alpha'}^0(\mathcal{E}_n + \omega_m)\mathcal{G}_{\beta\beta'}^0(\mathcal{E}_n)\right), \quad (3.4)$$

where $\omega_m = i2\pi m/\beta$. For details on the evaluation of this sum, the analytic continuation of K into real

ω, and for the application of the limit of λ going to infinity, the reader is referred to Appendix B. The evaluation of Eq. (3.4) gives for K^R the expression

$$K^{0R}(\alpha, \alpha'; \beta, \beta'; \omega + i\delta)$$

$$= \frac{\delta_{\alpha\alpha'}\delta_{\beta\beta'}}{\omega + i\delta - [\epsilon_\beta - \epsilon_\alpha]} \left[\exp(-\beta\epsilon_\alpha) - \exp(-\beta\epsilon_\beta)\right] .$$

$$(3.5)$$

Then using Eq. (3.1), the following expression is obtained for $\alpha(\omega)$:

$$\alpha_{\gamma\eta}(\omega) = \sum_{\beta,\alpha} \frac{\langle \alpha | \mu_\gamma | \beta \rangle \langle \beta | \mu_\eta | \alpha \rangle}{\omega - (\epsilon_\beta - \epsilon_\alpha) + i\delta}$$

$$\times \left[\exp(-\beta\epsilon_\alpha) - \exp(-\beta\epsilon_\beta)\right] . \qquad (3.6)$$

This is the well-known result of LRT for a QM system obeying Boltzmann statistics; thus, although Fermi operators have been used to describe the impurity, the required Boltzmann statistics are recovered.

If now the impurity-phonon interaction is turned on, but the contribution to K of the four-vertex part Γ is neglected, the expression for K is then given by Eq. (3.4) with the "free" propagators $\mathcal{G}^0$ substituted by $\mathcal{G}$ propagators. An explicit form for G^R can be obtained from the Dyson equation [Eq. (2.14)]; thus

$$G_\beta^R(\mathcal{E}) = 1/[\mathcal{E} - (\epsilon_\beta + \mathrm{Re}\Sigma_\beta^R + \lambda) - i\mathrm{Im}\Sigma_\beta^R(\epsilon')] , \quad (3.7)$$

where ϵ' is the solution of the equation

$$\epsilon' - (\epsilon_\beta + \lambda + \mathrm{Re}\Sigma_\beta^R) = 0 . \qquad (3.8)$$

Here it is assumed that $\mathrm{Im}\Sigma^R$ is small enough that $\mathrm{Im}G^R$ can be approximated by a δ function, and

therefore that $\mathrm{Im}\Sigma^R$ can be evaluated at the value of $\mathcal{E}$ given by the resonance condition of Eq. (3.8). If it is further assumed that $\hbar\omega < kT$, then K^R can be evaluated by a procedure analogous to that used in the evaluation of K^{0R} (see Appendix B). The result of this calculation is

$$K^R(\alpha, \alpha'; \beta, \beta'; \omega) = \frac{\delta_{\alpha\alpha'}\delta_{\beta\beta'}[\exp(-\beta\epsilon_\alpha') - \exp(-\beta\epsilon_\beta')]}{\omega - (\epsilon_\beta' - \epsilon_\alpha') - i\,\mathrm{Im}\Sigma_\beta^R} ,$$

$$(3.9)$$

where

$$\epsilon_\alpha' = \epsilon_\alpha + \mathrm{Re}\Sigma_\alpha^R . \qquad (3.10)$$

Upon substituting Eq. (3.9) into Eq. (3.1), the following expression for $\alpha(\omega)$ is obtained:

$$\alpha_{\gamma\eta}(\omega) = \sum_{\alpha,\beta} \frac{\mu_{\alpha\beta}(\gamma)\mu_{\beta\alpha}(\eta)[\exp(-\beta\epsilon_\alpha') - \exp(-\beta\epsilon_\beta')]}{\omega - (\epsilon_\beta' - \epsilon_\alpha') - i\,\mathrm{Im}(\Sigma_\beta^R)} ,$$

where

$$\mu_{\alpha\beta}(\gamma) = \langle \epsilon_\alpha | \mu_\gamma | \epsilon_\beta \rangle . \qquad (3.11)$$

The above expression is composed of resonance terms with the width of the resonance given by the $\mathrm{Im}\Sigma^R$. Note that in the absence of the Boltzmann terms, the above expression would also yield a dipole relaxation term for the special case of $\epsilon_\alpha' = \epsilon_\beta'$. In the next section it will be shown that the diagrams containing Γ change the numerator of Eq. (3.11), producing a dipolar relaxation contribution to $\alpha(\omega)$.

IV. CONTRIBUTION OF Γ TO THE POLARIZABILITY

The diagrams of Fig. 2(a), when the term containing Γ is included, correspond to the expression

$$K(\alpha, \alpha'; \beta, \beta'; \omega_m)$$

(a)

$$K(\omega_m) =$$

(b)

$$\Gamma_1 =$$
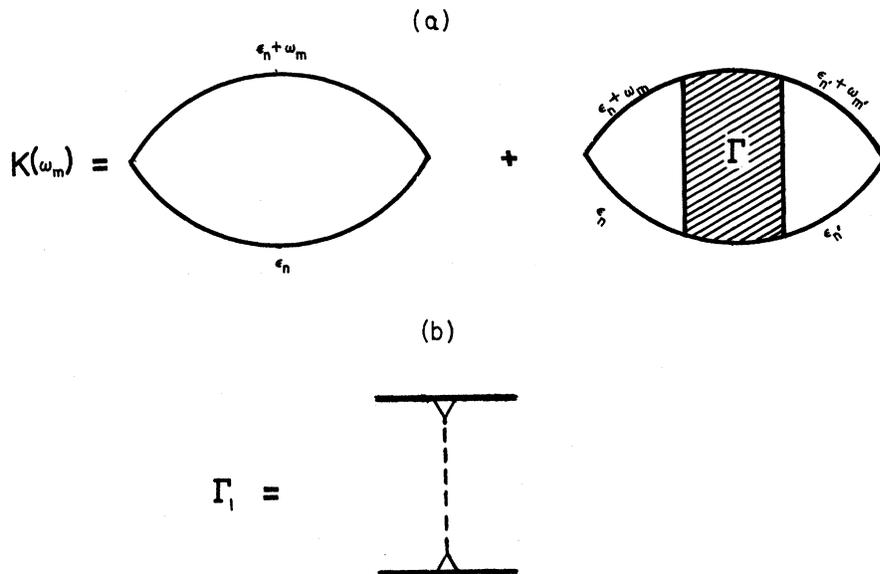
FIG. 2. (a) Diagrams contributing to the second-order impurity Green's function K, shown in energy space. The four-vertex part Γ is shown as a shaded rectangle. (b) Γ_1, the simplest diagram that contributes to the four-vertex part Γ.

$$= -(1/\beta) \sum_{\alpha'',\beta''} \sum_n \delta_{\alpha''\alpha'} \delta_{\beta''\beta'} \, \mathcal{G}_{\alpha\alpha''}(\mathcal{E}_n + \omega_m)$$

$$\times \, \mathcal{G}_{\beta\beta''}(\mathcal{E}_n)$$

$$+ (1/\beta)^2 \sum_{n,n'} \sum_{\substack{\alpha'',\beta'' \\ \alpha''',\beta'''}} \mathcal{G}_{\alpha\alpha''}(\mathcal{E}_n + \omega_m)$$

$$\times \, \mathcal{G}_{\beta\beta''}(\mathcal{E}_n)\, \Gamma(\alpha'', \alpha'''; \beta'', \beta'''; \mathcal{E}_n, \mathcal{E}_{n'}; \omega_m)$$

$$\times \, \mathcal{G}_{\beta'''\beta'}(\mathcal{E}_{n'} + \omega_m) \mathcal{G}_{\beta'''\beta'}(\mathcal{E}_{n'}) \,. \qquad (4.1)$$

In order to evaluate K an analytic continuation of Eq. (4.1) must be performed; therefore, the analytic properties of K and Γ must be known. By considering the Lehmann expansion of K these analytic properties can be obtained.[12] From the expansions it is found that K is a function of the complex variables $\mathcal{E}$, $\mathcal{E}'$ and ω has singularities when

(a) $\mathrm{Im}\,\mathcal{E} = 0$, $\mathrm{Im}(\mathcal{E} + \omega) = 0$, $\mathrm{Im}\,\mathcal{E}' = 0$, $\mathrm{Im}(\mathcal{E}' + \omega) = 0$;

(b) $\mathrm{Im}(\mathcal{E} + \mathcal{E}' + \omega) = 0$; $\qquad\qquad (4.2)$

(c) $\mathrm{Im}\,\omega = 0$, $\mathrm{Im}(\mathcal{E} - \mathcal{E}') = 0$.

These singularities correspond to cuts parallel to the real axis in the complex planes of the appropriate variable. From the analytic properties of K, it then follows that $\Gamma(\mathcal{E}, \mathcal{E}', \omega)$ as a function of $\mathcal{E}$ and $\mathcal{E}'$ will be analytic in 16 different regions of the $\mathrm{Im}\,\mathcal{E}$, $\mathrm{Im}\,\mathcal{E}'$ plane. The regions are separated by the cuts defined in Eq. (4.2), and they are illustrated in Fig. 3(a) for fixed values of ω, with $\mathrm{Im}\,\omega > 0$.

Changing the sum over $\mathcal{E}_n$ in Eq. (4.1) into a contour integral by means of the well-known relation

$$(1/\beta)\sum_{\mathcal{E}_n} \cdots \to (1/4\pi i) \int_C dz \, \tanh(\beta z/2),$$

where $\mathcal{E}_n \to z$ and C, the contour integral for K, is shown in Fig. 3(b), then the expression for K^R is given from Eq. (4.1) by

$$K^R_{(\omega)} = (-1/4\pi i) \int_{-\infty}^{\infty} d\mathcal{E} \, \{\tanh(\beta\mathcal{E}/2)K_1(\mathcal{E}, \omega)$$

$$+ [\tanh(\beta(\mathcal{E} + \omega)/2) - \tanh(\beta\mathcal{E}/2)]K_2(\mathcal{E}, \omega)$$

$$- \tanh(\beta(\mathcal{E} + \omega)/2)K_3(\mathcal{E}, \omega)\} \,, \qquad (4.3)$$

where

$$K_i(\mathcal{E}, \omega) = g_i(\mathcal{E}, \omega)[1 + (1/4\pi i)$$

$$\times \int_{-\infty}^{\infty} d\mathcal{E}' \, \mathcal{T}_{ik}(\mathcal{E}, \mathcal{E}'; \omega)g_k(\mathcal{E}'\omega)] \,, \quad (4.4)$$

$$g_1(\mathcal{E}, \omega) = G^R(\mathcal{E} + \omega) \, G^R(\mathcal{E}),$$

$$g_2(\mathcal{E}, \omega) = G^R(\mathcal{E} + \omega)G^A(\mathcal{E}) \,, \qquad (4.5)$$

$$g_3(\mathcal{E}, \omega) = G^A(\mathcal{E} + \omega)G^A(\mathcal{E}) \,.$$

The quantities $\mathcal{T}_{ik}$ are linearly related to the functions Γ_{ik}, which are the analytic parts of Γ in the regions (i, k) of Fig. 3(a); these terms arise from the analytic continuation of the vertex part Γ. Since the explicit forms of the $\mathcal{T}$'s will not be needed in what follows, they will not be given here. (The reader is referred to Ref. 12 for the explicit form of the $\mathcal{T}$'s.)

(a)

(b)
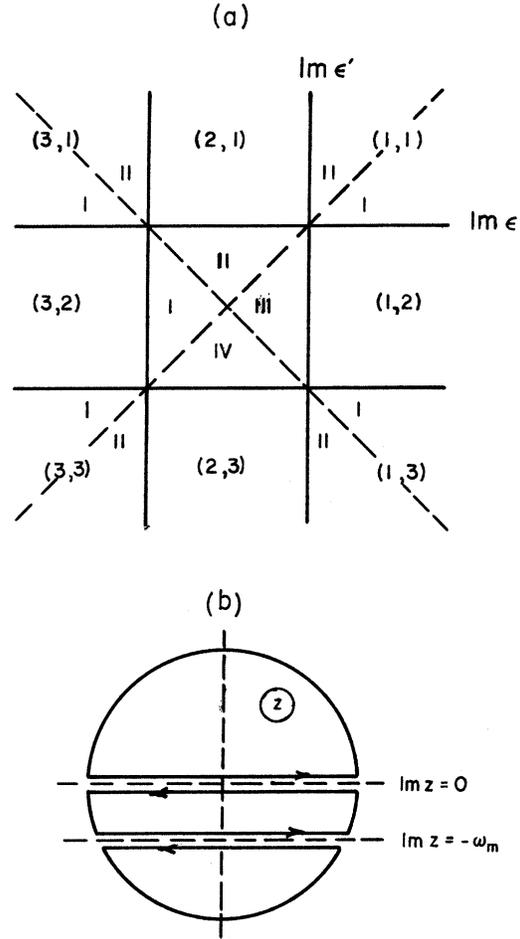
FIG. 3. (a) Plot of the $\mathrm{Im} = \epsilon$, $\mathrm{Im} = \epsilon'$ plane. The lines drawn in the plane divide it into 16 regions, each of which corresponds to a function Γ that is analytic in that region. The rectangular regions are identified by two indexes (i, k). Some of these regions are divided into parts by the diagonal cuts. These parts are denoted by Roman numbers (Ref. 12). (b) Contour of integration used in the evaluation of the functions K and K^0, with branch cuts at $\mathrm{Im}\,z = 0$ and $\mathrm{Im}\,z = \omega_m$.

The evaluation of Eq. (4.3) is now simplified by considering the frequency dependence of the g's. In what follows, Eq. (3.7) for G^R will be used and it will also be assumed that $\mathrm{Im}\Sigma^R$ is small enough that $\mathrm{Im}G^R$ can be approximated by

$$\mathrm{Im}G^R_\beta(\mathcal{E}) = -\pi\delta(\mathcal{E} - (\epsilon'_\beta + \lambda)) \,. \qquad (4.6)$$

It will be further assumed that the system is at relatively high temperatures such that $\hbar\omega < kT$ and $\epsilon'_\alpha - \epsilon'_\beta < kT$ for all α and β. Then by taking into account the effect of the hyperbolic tangents on the domain of integration in Eq. (4.4), the following approximate expressions for the g's are obtained:

$$g_1(\beta, \beta'; \, \mathcal{E}, \omega) \approx G_\beta^R(\mathcal{E}) \, G_{\beta'}^R(\mathcal{E}) \, ,$$

$$g_3(\beta, \beta'; \, \mathcal{E}, \omega) \approx G_\beta^A(\mathcal{E}) \, G_{\beta'}^A(\mathcal{E}) \, , \qquad (4.7)$$

$$g_2(\beta, \beta'; \, \mathcal{E}, \omega)$$

$$\approx \pi i \left\{ \delta(\mathcal{E} - \epsilon_\beta' - \lambda)/[\omega - (\epsilon_\beta' - \epsilon_{\beta'}') - i \, \text{Im}(\Sigma_\beta^R)] \right.$$

$$\left. + \delta(\mathcal{E} - (\lambda + \epsilon_{\beta'}' - \omega))/[\omega - (\epsilon_{\beta'}' - \epsilon_\beta') - i \, \text{Im}(\Sigma_{\beta'}^R)] \right\} \, .$$

The rest of the calculation for K^R will be guided and motivated by the fact that g_1 and g_3 are approximately independent of ω, while g_2 is strongly dependent on ω through a resonance term.

It can be shown that $\mathcal{T}_{ik}$ satisfies the integral equation[12]

$$\mathcal{T}_{ik}(\mathcal{E}, \mathcal{E}'; \omega) = \mathcal{T}_{ik}^{(1)}(\mathcal{E}, \mathcal{E}'; \omega)$$

$$+ [1/2i(2\pi)^4] \int d\mathcal{E}'' \, \mathcal{T}_{il}^{(1)}(\mathcal{E}, \mathcal{E}''; \omega)$$

$$\times g_l(\mathcal{E}'', \omega) \, \mathcal{T}_{lk}(\mathcal{E}'', \mathcal{E}'; \omega) \, , \quad (4.8)$$

where $\mathcal{T}^{(1)}$ are the irreducible parts of $\mathcal{T}_{ik}$. This means that $\mathcal{T}_{ik}$ can be written as the sum of the diagrams containing different numbers or irreducible parts $\mathcal{T}^{(1)}$. In order to take advantage of the fact that of all g_i's only g_2 depends strongly on ω, it will be convenient to express all the $\mathcal{T}_{ik}$'s in terms of $\mathcal{T}_{22}$ and $\mathcal{T}_{ik}^{(0)}$, where $\mathcal{T}_{ik}^{(0)}$ is the totality of diagrams contributing to $\mathcal{T}_{ik}$ that do not contain the pair of lines g_2. Figure 4 is a diagrammatic representation of the above decomposition of the $\mathcal{T}_{ik}$'s. The advantage of this decomposition is that the $\mathcal{T}_{ik}^{(0)}$ will be weakly dependent on ω.

It is relatively easy now to construct the diagrams that will contribute to K^R and that will have a strong ω dependence. This is done by including all diagrams of $\mathcal{T}_{ik}$ that have at least one pair of g_2 lines in the construction of the K^R diagrams. The result of this construction is shown diagrammatically in

FIG. 4. Diagrammatic representation of the quantities $\mathcal{T}_{ik}$ in terms of $\mathcal{T}_{22}$ and $\mathcal{T}_{ik}^{(0)}$. The $\mathcal{T}_{22}$ are represented by shaded circles and $\mathcal{T}_{ik}^{(0)}$ by shaded squares. The connecting pairs of lines are diagrammatic representations of the g_l's and are identified by the label "l," where the l's are numbers that go from 1 to 3 (Ref. 12).

Fig. 5. For convenience the expression for K^R has been separated into two terms: (a) $K_{(1)}^R$, constructed with diagrams that do not contain $\mathcal{T}_{22}$ and which will have a simple physical interpretation, and (b) $K_{(2)}^R$, constructed with all the diagrams that contain $\mathcal{T}_{22}$; this term will have a complicated ω dependence and no simple physical interpretation.

The expression for $K_{(1)}^R$ obtained from the diagrams in Fig. 5(a) is substituted into Eq. (3.1) and the following result is obtained for the polarizability:

$$\alpha_{\gamma\eta}^{(1)}(\omega) = \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}} \frac{[\mu_{\alpha\beta}(\gamma) Q_{\alpha\beta}^{(0)} + Q_{\alpha\beta}^{(1)}(\gamma)][\mu_{\beta\alpha}(\eta) + Q_{\beta\alpha}^{(2)}(\eta)]}{\omega - (\epsilon_\beta' - \epsilon_\alpha') - i \, \text{Im}\Sigma_\beta^R} + \sum_\alpha \frac{Q_{\alpha\alpha}^{(1)}(\gamma)[\mu_{\alpha\alpha}(\eta) + Q_{\alpha\alpha}^{(2)}(\eta)]}{\omega - i \, \text{Im}\Sigma_\alpha^R} \, , \qquad (4.9)$$

where

$$Q_{\alpha\beta}^{(0)} = \exp(-\beta\epsilon_\alpha') - \exp(-\beta\epsilon_\beta') \, ,$$

$$Q_{\alpha\beta}^{(1)}(\gamma) = \sum_{\alpha',\alpha''} \mu_{\alpha'\alpha''}(\gamma) \int \frac{d\mathcal{E}''}{2\pi} \tanh\left(\frac{\beta\mathcal{E}'}{2}\right) [g_1(\alpha', \alpha''; \mathcal{E}'') \, \mathcal{T}_{12}^{(0)}(\alpha', \alpha''; \alpha, \beta; \mathcal{E}''; \omega)$$

$$- g_3(\alpha', \alpha''; \mathcal{E}'') \, \mathcal{T}_{32}^{(0)}(\alpha', \alpha''; \alpha, \beta; \mathcal{E}'', \omega)] \, ,$$

$$Q_{\alpha\beta}^{(2)}(\gamma) = \sum_{\alpha',\alpha''} \mu_{\alpha'\alpha''}(\gamma) \int \frac{d\mathcal{E}''}{2\pi} [\mathcal{T}_{21}^{(0)}(\alpha, \beta; \alpha', \alpha''; \mathcal{E}'', \omega) g_1(\alpha', \alpha''; \mathcal{E}'') - \mathcal{T}_{23}^{(0)}(\alpha, \beta; \alpha', \alpha''; \mathcal{E}'', \omega) g_3(\alpha', \alpha''; \mathcal{E}'')] \, .$$

The Q's are temperature-dependent renormalization terms with a weak ω dependence. They can be associated with the diagrams of Fig. 5(a) as follows: $Q^{(0)}$ with diagram (1), $Q^{(1)}$ with diagrams (3) and (4), and $Q^{(2)}$ with diagrams (2) and (4). The first sum in Eq. (4.9) is a resonance term; the effect of the four-vertex part Γ has been to renor-

malize the dipole matrix elements and make them temperature dependent. In the absence of Γ this sum reduces to the polarizability $\alpha(\omega)$ given in Eq. (3.11), as it should. The second sum in Eq. (4.9) is more interesting than the first; it is a dipole relaxation term due to the phonons, where the relaxa-

(a)

$$K_1^R =$$ $\langle 2 \rangle$ $+$ $\langle 2 \; k \rangle$ $+$ $\langle i \; 2 \rangle$ $+$ $\langle i \; 2 \; k \rangle$

(1)   (2)   (3)   (4)

$i \neq 2$, $k \neq 2$

(b)

$$K_2^R =$$ $\langle 2 \; 2 \rangle$ $+$ $\langle 2 \; 2 \; k \rangle$ $+$ $\langle i \; 2 \; 2 \rangle$

$+$ $\langle i \; 2 \; 2 \; k \rangle$
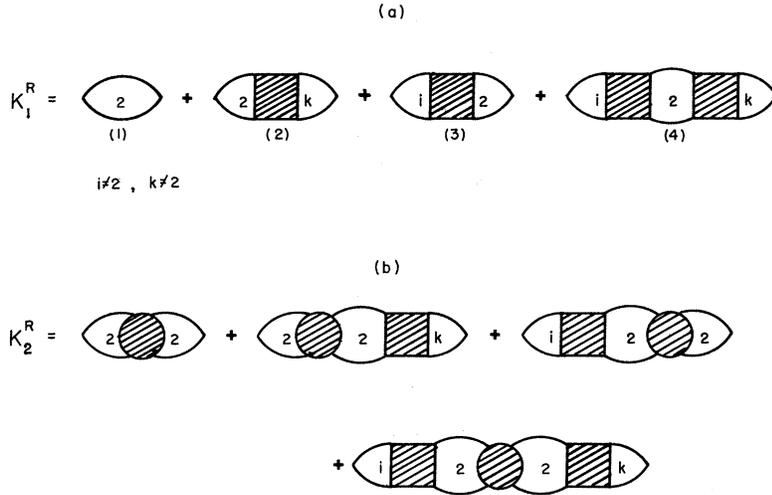
FIG. 5. Diagrammatic representation of K^R in terms of T_{22} and $T_{ik}^{(0)}$:
(a) $K_{(1)}^R$, the sum of all those diagrams that contribute to K^R, that do not contain the T_{22} term but have at least one pair of g_2 lines. (b) $K_{(2)}^R$, the sum of all those diagrams that contribute to K^R and have one T_{22} term. Here the graphic representation of $T_{ik}^{(0)}$, T_{22}, and g_l is the same as that used in Fig. 4.

tion times are given by $\tau_\alpha = 1/\mathrm{Im}\Sigma_\alpha$. The effect of Γ has been to renormalize the diagonal dipole matrix elements $\mu_{\alpha\alpha}$; in the absence of such renormalization the relaxation term will vanish. It should be pointed out that even in the case of the off-center impurities, which in the absence of an external electric field bias do not have a diagonal matrix element, there will be a relaxation term; in this case the diagonal dipole matrix elements are generated by the four-vertex part Γ.

Substituting $K_{(2)}^R$ into Eq. (3.1) gives the following contribution to $\alpha(\omega)$:

$$\alpha_{\gamma\eta}^{(2)}(\omega) = \sum_{\substack{\alpha,\beta \\ \alpha',\beta'}} \frac{[\mu_{\alpha\beta}(\gamma)Q_{\alpha\beta}^0 + Q_{\alpha\beta}^{(1)}(\gamma)]T_{22}(\alpha,\beta;\alpha',\beta';\omega)[\mu_{\alpha'\beta'}(\eta) + Q_{\alpha'\beta'}^{(2)}(\eta)]}{[\omega - (\epsilon_\beta' - \epsilon_\alpha') - i\,\mathrm{Im}\Sigma_\beta^R][\omega - (\epsilon_{\beta'}' - \epsilon_{\alpha'}') - i\,\mathrm{Im}\Sigma_{\beta'}^R]} \quad . \tag{4.10}$$

This contribution to the polarizability will have a complicated ω dependence because of the term T_{22}. Thus, in contrast to the case of $\alpha^{(1)}\omega$ where it was possible to analyze the frequency dependence without explicit knowledge of the Q's, it will not be possible to reach any definite conclusion about the frequency dependence of $\alpha^{(2)}(\omega)$ until T_{22} is evaluated. The evaluation of T_{22} is rather difficult and no attempt will be made to evaluate it here.

Generalizing from the above calculation for the polarizability, the following experimental picture will probably be observed in the particular case of the off-center impurities: (i) At low frequencies, $\omega \ll \Delta\epsilon$ (where $\Delta\epsilon \approx \epsilon_\alpha - \epsilon_\beta$ for $\alpha \neq \beta$), a dipole relaxation term will be observed with temperature-dependent dipole matrix elements. This will be true even for impurities with a center of inversion. (ii) At high frequencies, $\omega \approx \Delta\epsilon$, a resonance term will be observed, with temperature-dependent dipole matrix elements. (iii) At intermediate frequencies, $0 < \omega < \Delta\epsilon$, a complicated frequency behavior will be observed, which will be determined by the polarizability term $\alpha^{(2)}(\omega)$.

V. CONCLUSIONS

The formalism developed in the text for nonhar-

monic impurities interacting with a field has been used for the special case of impurity-phonon interaction. This new formalism permits the use of diagrammatic techniques, which have been used in the calculation of the impurity's dynamic polarizability and self-energy Σ. The results of these calculations are as follows:

(i) A diagonal temperature-dependent self-energy Σ_α for the αth state is obtained to second order in the coupling parameter Φ. To this order the real part of Σ is linear in temperature, while the imaginary part has a hyperbolic tangent temperature dependence [see Eq. (2.16)].

(ii) The impurity polarizability, Eq. (4.9), contains two physically important terms. The first is a dipole relaxation term that will be present even if the impurity has no permanent dipole (i.e., the diagonal dipole matrix elements are zero), with the relaxation time of the αth state given by $\tau_\alpha = 1/\mathrm{Im}\Sigma_\alpha$. The second is a resonance term with the width of the resonance determined by the imaginary part of Σ. In both cases the dipolar matrix elements will be temperature dependent.

It should be emphasized that in the calculation of the polarizability, the resonance and relaxation terms were obtained directly from the total Hamil-

tonian H_T, and not introduced in a heuristic manner.

In order to apply the formalism to the proton in hydrogen-bonded ferroelectrics, several changes will have to be made. The formalism will have to be modified to include more than one impurity (proton); a dipole-dipole interaction term will have to be added to H_T; and the effect of the impurities on the phonon propagator will have to be studied in detail. It appears that although calculations will be more difficult to perform for the ferroelectrics than for the impurity problems, the formalism discussed in the text will be useful in the study of hydrogen-bonded ferroelectrics.

APPENDIX A: SIGNIFICANCE OF LIMIT λ GOING TO INFINITY

To demonstrate that the limit taken in Eq. (2.9) will eliminate all the fictitious states (i.e., states with more than one impurity), the quantity K^R of Eq. (3.2) is considered: K^R has been selected because it fulfills the conditions of being a final, physically meaningful ensemble average, since it is directly related to $\alpha(\omega)$ through Eq. (3.1).

For simplicity only the first term in the commutator of Eq. (3.2) will be studied. Then, by writing K^R in the Lehmann representation, the following expression is obtained:

$$K^R(\alpha, \alpha'; \beta, \beta'; \tau) = \sum_{E_i, E_j, N_i, N_j} \exp[-\beta(E_i + \lambda N_i)]\langle E_i, N_i | c_\alpha^\dagger c_\beta | E_j, N_j\rangle\langle E_j, N_j | c_{\beta'}^\dagger c_{\alpha'} | E_i, N_i\rangle$$

$$\times \exp\{[(E_i - E_j) + \lambda(N_i - N_j)]\tau\}\Theta(\tau) \quad , \tag{A1}$$

where E_i is the ith eigenstate of the total Hamiltonian H_T and N_i is the number of impurities in that state. It will be more convenient to work in ω_n space instead of τ space; for that reason a Fourier transformation of K^R into ω_n space is performed, giving

$$K^R(\alpha, \alpha'; \beta, \beta'; \omega_m) = \sum_{i,j} \frac{\exp[-\beta(E_i + \lambda N_i)]\langle E_i, N_i | c_\alpha^\dagger c_\beta | E_j, N_j\rangle\langle E_j, N_j | c_{\beta'}^\dagger c_{\alpha'} | E_i, N_i\rangle}{\omega_m + (E_i - E_j) + \lambda(N_i - N_j)} \quad . \tag{A2}$$

Now multiplying by the normalization factor $e^{\beta\lambda}$ and taking the limit as λ goes to infinity of Eq. (A2), the following result is obtained:

$$\lim_{\lambda \to \infty} e^{\beta\lambda} \exp[-\beta(E_i + \lambda N_i)]$$

$$= \begin{cases} 0 & \text{for } N_i > 1 \\ \exp(-\beta E_i) & \text{for } N_i = 1 \end{cases} \tag{A3}$$

and

$$\lim_{\lambda \to \infty} \frac{1}{\omega_m + (E_i - E_j) + \lambda(N_i - N_j)}$$

$$= \begin{cases} 0 & \text{for } N_i \neq N_j \\ 1/[\omega_m + (E_i - E_j)] & \text{for } N_i = N_j \end{cases} \quad . \tag{A4}$$

Therefore, K^R will be zero unless $N_i = N_j = 1$ for all i's and j's; thus, all states with more than one impurity do not contribute to the expression for K^R

after the limit has been taken. This proof can be generalized to include an ensemble average containing any number of time-dependent operators. This can be easily verified by including one more time-dependent operator in Eq. (A1); this will add one more intermediate state E_j that upon Fourier transformation will produce another term of the same form as the one in the right-hand side of Eq. (A4). Upon taking the limit of the new and old terms the condition

$$N_i = N_j = N_{j'} = 1$$

is obtained.

Finally, it is interesting to point out that, since the matrix element

$$\langle E_i, N_i = 1 | c_\alpha | E_j, N_j = 1\rangle = 0 \quad ,$$

the impurity Green's function will vanish when the limit of λ going to infinity is taken.

APPENDIX B: EVALUATION OF K^R FOR THE NONINTERACTING IMPURITY AND OF $\Sigma\alpha$

The sum over ω_n in Eq. (3.4) can be converted into a contour integral by well-known procedures to give

$$K(\alpha, \alpha'; \beta, \beta'; \omega_m) = \lim_{\lambda \to \infty} e^{\beta\lambda}\left[\left(\frac{1}{4\pi i}\right)\int_C d\mathcal{E} \tanh\left(\frac{\beta\mathcal{E}}{2}\right)G^{0RA}(\alpha, \alpha'; \mathcal{E})G^{0RA}(\beta, \beta'; \mathcal{E} + \omega_m)\right] \quad , \tag{B1}$$

where the contour of integration C is given by Fig. 3(b). The function $G^{RA}(\mathcal{E})$ must be understood as G^R if $\text{Im}\,\mathcal{E} > 0$ and G^A if $\text{Im}\,\mathcal{E} < 0$. Since the integral over the outer circumference of C vanishes, only the integrals over the lines $\text{Im}\,\mathcal{E} = 0$ and $\text{Im}\,\mathcal{E} = -\omega_n$ remain. Performing a change of variable for the integral over the line $\text{Im}\,\mathcal{E} = -\omega_m$ and making use of the integral representation of G^A and G^R, the following expression for K is obtained:

$$K(\alpha, \alpha'; \beta, \beta'; \omega_m) = \lim_{\lambda \to \infty} e^{\beta\lambda} \left(\frac{\delta_{\alpha\alpha'}\delta_{\beta\beta'}}{2\pi^2}\right) \int_{-\infty}^{\infty} d\mathcal{E} \int_{-\infty}^{\infty} d\mathcal{E}' \tanh\left(\frac{\beta\mathcal{E}}{2}\right)$$

$$\times \left(\frac{\mathrm{Im}G^{0R}(\alpha, \mathcal{E})\,\mathrm{Im}G^{0R}(\beta, \mathcal{E}')}{\mathcal{E}' - (\mathcal{E}+\omega_m) - i\delta} - \frac{\mathrm{Im}G^{0R}(\beta, \mathcal{E})\,\mathrm{Im}G^{0A}(\alpha, \mathcal{E}')}{\mathcal{E}' - (\mathcal{E}-\omega_m) + i\delta}\right) \quad . \tag{B2}$$

Upon performing the analytic continuation from ω_n to real ω and making use of the expressions

$$\mathrm{Im}G^{0R}(\alpha, \mathcal{E}) = -\pi\delta(\mathcal{E} - (\epsilon_\alpha + \lambda)), \quad \mathrm{Im}G^{0A}(\alpha, \mathcal{E}) = -\mathrm{Im}G^{0R}(\alpha, \mathcal{E}) \quad , \tag{B3}$$

the integrations in (B2) can be carried out, yielding the following result:

$$K^R(\alpha, \alpha'; \beta, \beta'; \omega) = \left(\frac{\delta_{\alpha\alpha'}\delta_{\beta\beta'}}{\omega - (\epsilon_\beta - \epsilon_\alpha) + i\delta}\right) \lim_{\lambda \to \infty} \left(\frac{e^{\beta\lambda}}{2}\right) \left[\tanh\left(\frac{\beta(\epsilon_\alpha + \lambda)}{2}\right) - \tanh\left(\frac{\beta(\epsilon_\beta + \lambda)}{2}\right)\right] \quad . \tag{B4}$$

Upon taking the limit, K^R becomes

$$K^R(\alpha, \alpha'; \beta, \beta'; \omega) = \frac{\delta_{\alpha\alpha'}\delta_{\beta\beta'}}{\omega - (\epsilon_\beta - \epsilon_\alpha) + i\delta}(e^{-\beta\epsilon_\alpha} - e^{-\beta\epsilon_\beta}) \quad , \tag{B5}$$

which is the desired result.

Following a procedure for the self-energy Σ similar to that used in obtaining Eq. (B2), the following expression results:

$$\Sigma_\beta^R(\mathcal{E}) = \sum_{\beta'} \sum_s \Phi^2\binom{\beta\beta'}{s} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\mathcal{E}_1 \left(\frac{\mathrm{Im}G^{0R}(\beta, \epsilon_1)\,\mathrm{Im}D^{0R}(\omega, s)}{\omega + \epsilon_1 - \mathcal{E} - i\delta}\right)\left[\tanh\left(\frac{\beta\epsilon_1}{2}\right) + \coth\left(\frac{\beta\omega}{2}\right)\right] \quad . \tag{B6}$$

With the help of Eq. (B3) and the equation

$$\mathrm{Im}D^{0R}(\omega, k) = -\pi\omega_0^2(k)\delta(\omega^2 - \omega_0^2(k)) \quad ,$$

the integrals in Eq. (B6) can be easily evaluated to give

$$\Sigma_\beta^R(\mathcal{E}) = \sum_{\beta'} [\overline{\Phi(\beta\beta', s)}]^2 \sum_s \omega_0(k)\left[\tanh\left(\frac{\beta(\epsilon_\beta' + \lambda)}{2}\right)\left(\frac{1}{\omega_0(k) + (\epsilon_\beta + \lambda) - \mathcal{E} + i\delta} + \frac{1}{-\omega_0(k) + (\epsilon_\beta' + \lambda) - \mathcal{E} - i\delta}\right)\right.$$

$$\left. + \coth\left(\frac{\beta\omega_0(k)}{2}\right)\left(\frac{1}{\omega_0(k) + (\epsilon_\beta' + \lambda) - \mathcal{E} - i\delta} - \frac{1}{-\omega_0(k) + (\epsilon_\beta + \lambda) - \mathcal{E} - i\delta}\right)\right] \quad . \tag{B7}$$

Here the coupling constant Φ has been averaged over the lattice normal modes s in order to facilitate the evaluation of the sum over s. Upon transforming the sum over s into an integral, using the Debye approximation for the phonon spectrum, assuming that $\hbar\omega_D \gg \epsilon_\beta$ and $\hbar\omega_D \gg kT$, and remembering that λ is a large parameter, Eq. (B7) can be evaluated to give Eq. (2.16).

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