

## Raman Scattering from Localized-Mode Polaritons

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In a crystal containing a finite concentration of impurities which give rise to localized vibration modes, the coherent motion of the impurity system can result in the generation of a macroscopic electric field, if the local modes are infrared-active. In this case, the true normal modes of the impurity system are collective modes with a wavelike character. We show that the transverse local modes have the character of polariton modes, with properties very similar to the properties of the phonon-polariton modes of pure crystals. We also present the theory of the Raman scattering of light from local-mode polaritons. We estimate the Raman efficiency for the scattering of light from local-mode polaritons, and make comparisons between the scattering from these excitations and the scattering from phonon polaritons in pure crystals.

### I. INTRODUCTION

It is well known by now that the vibrational spectrum of a crystal with a small concentration of impurities often contains modes with frequencies that lie outside the band of vibrational frequencies associated with the host crystal.<sup>1</sup> The displacement field associated with these modes is localized in space, and is nonzero only in the vicinity of an impurity ion. In the limit that the impurity concentration  $f$  is small compared to unity, it is generally assumed that the impurities vibrate independently, when a localized mode is excited. As a first approximation, one can assume that a number of independent oscillators with frequency above the vibrational continuum of the host has been randomly distributed through the crystal.

Consider an infrared-active localized mode associated with a single, isolated impurity in an otherwise perfect crystal. Since a dipole moment which is first order in the impurity displacement is associated with the impurity motion, a finite electric field is present when the localized mode is excited. Maradudin and Oitmaa<sup>2</sup> have recently pointed out that when the impurity concentration  $f$  is finite, a macroscopic electric field is generated by coherent motions of the entire impurity system. As a consequence, the true normal modes of the impurity system have a wavelike character for long wavelengths, with the motion of the impurities correlated through the macroscopic electric field. If the electric field is treated in the static approximation, one obtains normal modes of transverse and longitudinal character in the long-wavelength limit, with a Lyddane-Sachs-Teller (LST) splitting between the frequencies of these modes.<sup>2</sup>

Our purpose in the present paper is to point out that when retardation effects are included in the calculation of the electric field, then the transverse collective modes

of the system have the character of polariton modes, with properties very similar to the polariton modes of pure crystals.<sup>3</sup> Since the technique of Raman scattering has proved useful<sup>4</sup> in the study of polaritons of pure crystals, we have examined the theory of the Raman scattering of light from local-mode polaritons. We show that light scattering will also provide a useful means of probing local-mode polaritons, although we shall see that there are important differences between the local-mode polaritons and polaritons in ordered systems. When light is scattered by local-mode polaritons, the Raman cross section contains a sizable contribution from incoherent scattering of the radiation from the array of impurities, in addition to the coherent scattering from which one obtains detailed information about the dispersion relation of the normal modes. In pure crystals, of course, the scattering is purely coherent.

In their calculation of the LST splitting of the collective modes of the impurity system, Maradudin and Oitmaa<sup>2</sup> employed a model in which only the impurities oscillate, while the host lattice remains at rest. We shall employ the same model in this work, since it is clear that it contains all the features essential to the phenomena we consider.

### II. LOCALIZED MODES IN PRESENCE OF RETARDATION

If we make here the assumptions concerning the vibrations of impurity ions in localized modes that were made in Ref. 1, the equations of motion of one of the impurity ions can be written in the form

$$m\ddot{u}_\alpha(lt) = -m\omega_0^2 u_\alpha(lt) - eE_\alpha^{(e)}(lt). \quad (2.1)$$

In these equations  $m$  is the mass of an impurity ion,  $u_\alpha(lt)$  is the  $\alpha$  Cartesian component of the displacement of the ion on the  $l$ th site of the impurity sublattice from its equilibrium position,  $\omega_0$  is the localized-mode frequency associated with an isolated impurity ion,  $e$  is the magnitude of the electronic charge, and  $\mathbf{E}^{(e)}(lt)$

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<sup>1</sup> See A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963).

<sup>2</sup> A. A. Maradudin and J. Oitmaa, *Solid State Commun.* (to be published).

<sup>3</sup> M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Sec. 8.

<sup>4</sup> C. H. Henry and J. J. Hopfield, *Phys. Rev. Letters* **15**, 964 (1965).

is the exciting field at the  $l$ th site due to the other impurities in the crystal. It is with the calculation of  $\mathbf{E}^{(e)}(lt)$  when the retardation of the Coulomb interaction is taken into account that we will be concerned in this section.

It is convenient to perform this calculation by determining first the Hertz vector of the electromagnetic field set up by the impurity atoms vibrating in localized modes, and deriving the electric field from it. The Hertz vector  $\mathbf{\Pi}(\mathbf{x},t)$  satisfies the equation

$$\nabla^2 \mathbf{\Pi}(\mathbf{x},t) - (1/c^2)(\partial^2/\partial t^2)\mathbf{\Pi}(\mathbf{x},t) = -4\pi \mathbf{P}(\mathbf{x},t), \quad (2.2)$$

where  $c$  is the speed of light and  $\mathbf{P}(\mathbf{x},t)$  is the polarization density at the point  $\mathbf{x}$  at the time  $t$ . The solution of Eq. (2.2) can be written formally as

$$\mathbf{\Pi}(\mathbf{x},t) = \int \frac{\delta(t'+1/c|\mathbf{x}-\mathbf{x}'|-t)}{|\mathbf{x}-\mathbf{x}'|} \mathbf{P}(\mathbf{x}',t') d^3x' dt'. \quad (2.3)$$

The electric field at the point  $\mathbf{x}$  at time  $t$  is obtained from  $\mathbf{\Pi}(\mathbf{x},t)$  through the relation

$$E_\alpha(\mathbf{x},t) = \sum_\beta \left( \frac{\partial^2}{\partial x_\alpha \partial x_\beta} - \delta_{\alpha\beta} \nabla^2 \right) \Pi_\beta(\mathbf{x},t). \quad (2.4)$$

The polarization density at the space-time point  $(\mathbf{x},t)$  is given by

$$\mathbf{P}(\mathbf{x},t) = -e \sum_{l'} c(l') \mathbf{u}(l') \delta(\mathbf{x}-\mathbf{x}(l')). \quad (2.5)$$

The sum on  $l'$  in this expression runs over all the lattice sites of the sublattice on which the impurity ions are situated (an fcc lattice for crystals possessing the rock-salt or zinc-blende structures);  $c(l)$  equals unity if the site  $l$  is occupied by an impurity ion, and vanishes otherwise.

If we assume for  $u_\alpha(lt)$  the expression

$$u_\alpha(lt) = u_\alpha e^{i\mathbf{k} \cdot \mathbf{x}(l) - i\omega t}, \quad (2.6)$$

substitution of Eqs. (2.5) and (2.6) into Eq. (2.3) yields the result

$$\Pi_\alpha(\mathbf{x},t) = -e u_\alpha e^{-i\omega t} \sum_{l'} c(l') e^{i\mathbf{k} \cdot \mathbf{x}(l')} \frac{e^{ik_0|\mathbf{x}-\mathbf{x}(l')|}}{|\mathbf{x}-\mathbf{x}(l')|}, \quad (2.7)$$

where we have set  $k_0 = \omega/c$ . It follows from Eq. (2.4) that  $E_\alpha(\mathbf{x},t)$  is given by

$$E_\alpha(\mathbf{x},t) = -e e^{i\mathbf{k} \cdot \mathbf{x} - i\omega t} \sum_\beta u_\beta \sum_{l'} c(l') e^{-i\mathbf{k} \cdot (\mathbf{x}-\mathbf{x}(l'))} \times \left[ (x_\alpha - x_\alpha(l'))(x_\beta - x_\beta(l')) \left( \frac{3}{|\mathbf{x}-\mathbf{x}(l')|^5} - \frac{3ik_0}{|\mathbf{x}-\mathbf{x}(l')|^4} - \frac{k_0^2}{|\mathbf{x}-\mathbf{x}(l')|^3} \right) - \delta_{\alpha\beta} \left( \frac{1}{|\mathbf{x}-\mathbf{x}(l')|^3} - \frac{ik_0}{|\mathbf{x}-\mathbf{x}(l')|^2} \right) + \delta_{\alpha\beta} \frac{k_0^2}{|\mathbf{x}-\mathbf{x}(l')|} + 4\pi \delta_{\alpha\beta} \delta(\mathbf{x}-\mathbf{x}(l')) \right] e^{ik_0|\mathbf{x}-\mathbf{x}(l')|}. \quad (2.8)$$

At this point we recall that it is the exciting field at the site  $l$  that enters into the equations of motion (2.1). We obtain  $E_\alpha^{(e)}(lt)$  by setting  $\mathbf{x} = \mathbf{x}(l)$  in Eq. (2.8), and omitting the term with  $l' = l$  from the right-hand side of Eq. (2.8). Finally, since the value of  $E_\alpha^{(e)}(lt)$  obtained in this way depends on the distribution of impurity ions over the sites of the impurity sublattice, which is unknown, we follow the procedure of Ref. 1 and average the exciting field over all impurity configurations. We obtain in this way the result that

$$E_\alpha^{(e)}(lt) = -e f e^{i\mathbf{k} \cdot \mathbf{x}(l) - i\omega t} \sum_\beta u_\beta \sum_{l' (\neq l)} e^{-i\mathbf{k} \cdot \mathbf{r}} e^{ik_0 r} \times \left[ x_\alpha x_\beta \left( \frac{3}{r^5} - \frac{3ik_0}{r^4} - \frac{k_0^2}{r^3} \right) - \delta_{\alpha\beta} \left( \frac{1}{r^3} - \frac{ik_0}{r^2} \right) + \delta_{\alpha\beta} \frac{k_0^2}{r} \right]_{\mathbf{r}=\mathbf{x}(l)-\mathbf{x}(l')}, \quad (2.9)$$

where  $f = n/N$ , with  $n$  the number of impurity ions and  $N$  the number of primitive unit cells in the crystal.

We are interested in only the long-wavelength limit of the expression (2.9) for  $E_\alpha^{(e)}(lt)$ , since it is only this limit which is susceptible to experimental study by light-scattering techniques. In the limit of small  $\mathbf{k}$ , the summand on the right-hand side of Eq. (2.9) changes slowly as the summation variable  $\mathbf{x}(l) - \mathbf{x}(l')$  ranges over the sites of the impurity ion sublattice. In this limit we can replace summation over  $\mathbf{x}(l')$  by integration, and we have the integral

$$I_{\alpha\beta}(\mathbf{k}) = \frac{1}{\Omega_0} \int d^3r e^{-i\mathbf{k} \cdot \mathbf{r}} e^{ik_0 r} \left[ x_\alpha x_\beta \left( \frac{3}{r^5} - \frac{3ik_0}{r^4} - \frac{k_0^2}{r^3} \right) - \delta_{\alpha\beta} \left( \frac{1}{r^3} - \frac{ik_0}{r^2} \right) + \delta_{\alpha\beta} \frac{k_0^2}{r} \right] \quad (2.10)$$

to evaluate, where  $\Omega_0$  is the volume of a primitive unit cell.

It is convenient to rewrite Eq. (2.10) as

$$I_{\alpha\beta}(\mathbf{k}) = -\frac{\partial^2}{\partial k_\alpha \partial k_\beta} \frac{1}{\Omega_0} \int d^3r e^{-i\mathbf{k} \cdot \mathbf{r}} e^{ik_0 r} \left( \frac{3}{r^5} - \frac{3ik_0}{r^4} - \frac{k_0^2}{r^3} \right) - \delta_{\alpha\beta} \frac{1}{\Omega_0} \int d^3r e^{-i\mathbf{k} \cdot \mathbf{r}} e^{ik_0 r} \left( \frac{1}{r^3} - \frac{ik_0}{r^2} - \frac{1}{3} \frac{k_0^2}{r} \right) + \delta_{\alpha\beta} \frac{2}{3} k_0^2 \frac{1}{\Omega_0} \int d^3r e^{-i\mathbf{k} \cdot \mathbf{r}} \frac{e^{ik_0 r}}{r}, \quad (2.11)$$

and to evaluate the integrals over angles by choosing the polar axis along the direction of  $\mathbf{k}$ . In this way we

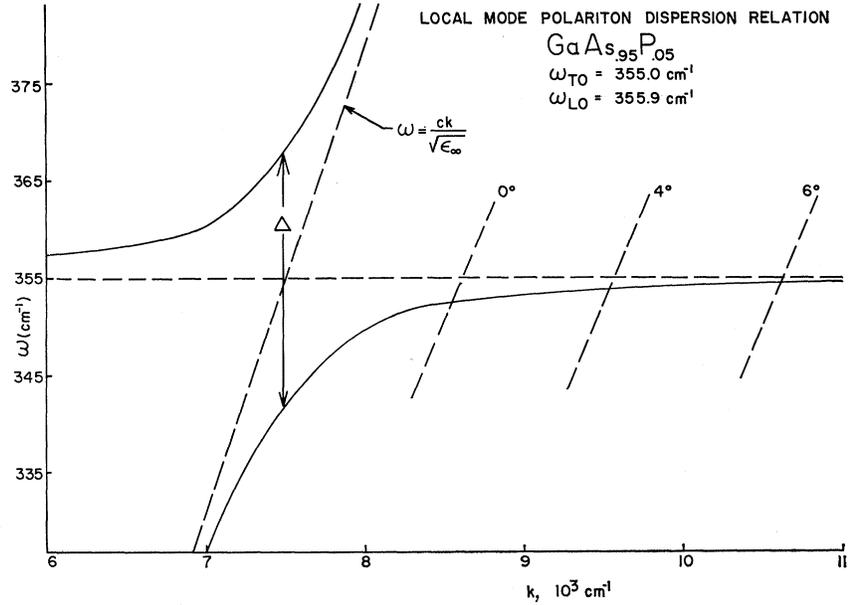


FIG. 1. Local-mode polariton dispersion relation for a sample of GaAs, doped with 5% P. Superimposed on the graph are curves that denote the values of frequency and wave-vector transfer allowed at fixed scattering angle for 1.06- $\mu$  radiation.

obtain

$$\Omega_0 I_{\alpha\beta}(\mathbf{k}) = \delta_{\alpha\beta} \frac{8\pi}{3} \frac{\xi^2}{1-\xi^2} - 4\pi(3\hat{k}_\alpha\hat{k}_\beta - \delta_{\alpha\beta}) \times \int_0^\infty d\rho e^{i\xi\rho} (1/\rho - i\xi - \frac{1}{3}\xi^2\rho) j_2(\rho), \quad (2.12)$$

where  $\xi = k_0/k = \omega/c k$  and  $j_n(\rho)$  is a spherical Bessel function. The last integral is readily evaluated, and we obtain, finally,

$$I_{\alpha\beta}(\mathbf{k}) = \frac{4\pi}{\Omega_0} \left[ -\frac{2}{3}\hat{k}_\alpha\hat{k}_\beta + (\delta_{\alpha\beta} - \hat{k}_\alpha\hat{k}_\beta) \left( \frac{1}{3} + \frac{\xi^2}{1-\xi^2} \right) \right]. \quad (2.13)$$

The exciting field  $E_\alpha^{(e)}(l)$ , therefore, is given by

$$E_\alpha^{(e)}(l) = -\frac{4\pi e f}{\Omega_0} e^{i\mathbf{k}\cdot\mathbf{x}(l) - i\omega t} \times \sum_\beta \left[ -\frac{2}{3}\hat{k}_\alpha\hat{k}_\beta + (\delta_{\alpha\beta} - \hat{k}_\alpha\hat{k}_\beta) \left( \frac{1}{3} + \frac{\xi^2}{1-\xi^2} \right) \right] u_\beta. \quad (2.14)$$

If we substitute Eq. (2.14) together with Eq. (2.6) into the equations of motion (2.1), we find that the equations determining the displacement amplitude  $\mathbf{u}$  are

$$(\omega^2 - \omega_0^2)u_\alpha + \omega_p^2 \sum_\beta \left[ -\frac{2}{3}\hat{k}_\alpha\hat{k}_\beta + (\delta_{\alpha\beta} - \hat{k}_\alpha\hat{k}_\beta) \left( \frac{1}{3} + \frac{\xi^2}{1-\xi^2} \right) \right] u_\beta = 0, \quad (2.15)$$

where we have introduced the plasma frequency of the collective impurity mode,  $\omega_p^2 = 4\pi e^2 f / m\Omega_0$ . For longi-

tudinal modes, in which  $\mathbf{u} \parallel \mathbf{k}$ , we obtain the dispersion relation

$$\omega^2 = \omega_0^2 + \frac{2}{3}\omega_p^2 = \omega_l^2, \quad (2.16)$$

and we see that retardation has no effect on these modes. For transverse modes, in which  $\mathbf{u} \perp \mathbf{k}$ , the dispersion relation can be written in the form

$$c^2 k^2 / \omega^2 = \epsilon(\omega) = 1 + \omega_p^2 / (\omega_l^2 - \omega^2), \quad (2.17)$$

where  $\omega_l^2 = \omega_0^2 - \frac{1}{3}\omega_p^2$  is the transverse localized-mode frequency in the absence of retardation. This equation has two solutions

$$\omega^2 = \omega_\pm^2(\mathbf{k}) = \frac{1}{2} \{ \omega_l^2 + \omega_p^2 + c^2 k^2 \pm [(\omega_l^2 + \omega_p^2 + c^2 k^2)^2 - 4\omega_l^2 c^2 k^2]^{1/2} \}. \quad (2.18)$$

The elementary excitations whose dispersion relations are given by the two branches  $\omega^2 = \omega_\pm^2(\mathbf{k})$  can be called localized-mode polaritons by analogy with the coupled-photon-transverse-phonon modes in pure crystals. A plot of the dispersion curves given by Eq. (2.18) is displayed in Fig. 1 for GaAs containing 5% P impurities in the As sublattice.<sup>5</sup>

For each value of  $\mathbf{k}$  the eigenvalue equation (2.15) possesses three real eigenvectors, which we denote by  $e_\alpha(\mathbf{k}j)$  ( $j=1, 2, 3$ ). They are mutually orthogonal, can be normalized to unity

$$\sum_\alpha e_\alpha(\mathbf{k}j) e_\alpha(\mathbf{k}j') = \delta_{jj'}, \quad (2.19)$$

<sup>5</sup> We have assumed the effective charge of the P impurity is  $2e$ , where  $e$  is the charge of the electron. This is reasonable, since the effective charge of both As and P in pure GaAs and GaP is close to  $2e$ . We have also replaced the factor of unity on the right-hand side of Eq. (2.21) by  $\epsilon_\infty$ , the dielectric of GaAs in the absence of the P impurities. Following Mooradian and Wright [Phys. Rev. Letters 16, 999 (1966)], we have used the value  $\epsilon_\infty = 11.3$ .

and, consequently, obey the closure condition

$$\sum_j e_\alpha(\mathbf{k}j)e_\beta(\mathbf{k}j) = \delta_{\alpha\beta}. \quad (2.20)$$

The eigenvector  $\mathbf{e}(\mathbf{k}l)$  describes purely longitudinal displacements and is given by  $\mathbf{e}(\mathbf{k}l) = \hat{\mathbf{k}}$ . These results will be useful in Sec. III.

There is one feature of the local-mode polariton spectrum we would like to point out at this stage in the discussion. First consider the LST splitting. From the preceding results we see that for low impurity concentrations, the LST splitting  $\Delta\omega$  is given by

$$\Delta\omega = \omega_l - \omega_t = \frac{1}{2}(\omega_p^2/\omega_0) = 4\pi e^2 f / 2\omega_0 m \Omega_0. \quad (2.21)$$

If this expression is applied to the case where GaAs has been doped with P,<sup>5</sup> the splitting  $\Delta\omega$  is 0.9 cm<sup>-1</sup>, as one can see from Fig. 1. The LST splitting is thus quite small for this case. However, the separation  $\Delta$  between the two polariton branches at a value of the wave vector  $\mathbf{k}$  for which  $ck = \omega_t$  is found from Eq. (2.18) to be

$$\Delta = \omega_+ \left( \frac{\omega_t}{c} \right) - \omega_- \left( \frac{\omega_t}{c} \right) = \omega_p = f^{1/2} \left( \frac{4\pi e^2}{m\Omega_0} \right)^{1/2}. \quad (2.22)$$

The frequency splitting  $\Delta$ , which is indicated in Fig. 1, is a measure of the width of the frequency region within which the polariton contains a strong admixture of impurity motion. Notice that  $\Delta$  varies as the square root of  $f$ , while  $\Delta\omega$  is proportional to  $f$ . Thus, when  $f \ll 1$ ,  $\Delta$  may be considerably larger than the LST splitting. From Fig. 1, one sees that  $\Delta = 24$  cm<sup>-1</sup> for GaAs<sub>0.95</sub>P<sub>0.05</sub>. Even though  $\Delta\omega$  in some circumstances can be small compared to the intrinsic width of the local mode, so that the observation of the LST splitting would be difficult, the quantity  $\Delta$  may be much larger than the intrinsic width.

### III. RAMAN SCATTERING BY LOCALIZED-MODE POLARITONS

At the present time the Raman scattering of light from polaritons in pure crystals is the only experimental technique available for determining the dispersion relation for these elementary excitations. It is natural, therefore, to explore the possibility of using this technique for the experimental study of the localized-mode polaritons derived in Sec. II.

The intensity of Raman scattering per unit solid angle in the frequency range from  $\omega_s$  to  $\omega_s + d\omega_s$  is given by<sup>6</sup>

$$I(\omega_s)d\omega_s = \frac{\omega_s^4}{2\pi c^3} \sum_{\alpha\gamma} \sum_{\beta\lambda} n_\alpha n_\beta i_{\alpha\gamma, \beta\lambda}(\omega) E_\gamma^- E_\lambda^+ d\omega_s, \quad (3.1)$$

where  $\omega_i$  is the frequency of the incident light,  $\omega = \omega_s - \omega_i$

is the shift in the frequency of the light on scattering,  $\mathbf{n}$  is a unit vector describing the polarization of the scattered light, and  $\mathbf{E}^+$  and  $\mathbf{E}^- = (\mathbf{E}^+)^*$  are the amplitudes of the positive and negative frequency components of the incident light. The tensor  $i_{\alpha\gamma, \beta\lambda}(\omega)$  is given by

$$i_{\alpha\gamma, \beta\lambda}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle p_{\beta\lambda}^+(t) p_{\alpha\gamma}^-(0) \rangle, \quad (3.2)$$

where

$$p_{\alpha\gamma}^- = \int d^3x e^{-i\mathbf{q}\cdot\mathbf{x}} \delta\chi_{\alpha\gamma}(\mathbf{x}) = (p_{\alpha\gamma}^+)^*, \quad (3.3)$$

and  $\delta\chi_{\alpha\beta}(\mathbf{x})$  is the change in the electronic susceptibility of the crystal at the point  $\mathbf{x}$ . The vector  $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i$  is the difference between the wave vectors of the scattered and incident light. The angular brackets in Eq. (3.2) denote an average over the canonical ensemble defined by the vibrational Hamiltonian for the impurity system.

Let us now restrict our attention to crystals of the zinc-blende structure. Such crystals possess the correct symmetry to give rise to Raman-active polaritons in pure samples; they can have Raman-active localized vibration modes in the presence of suitable substitutional impurities, and these localized modes will have Raman-active polaritons associated with them. For such crystals the change in the electronic susceptibility at the point  $\mathbf{x}$  is made up of two contributions, namely, an elasto-optic and an electro-optic contribution:

$$\delta\chi_{\alpha\gamma}(\mathbf{x}) = \sum_{l\kappa\mu} \delta(\mathbf{x} - \mathbf{x}(l\kappa)) \times [P_{\alpha\gamma, \mu}(l\kappa) u_\mu(l\kappa) + Q_{\alpha\gamma\mu}(l\kappa) E_\mu^M(l\kappa)]. \quad (3.4)$$

In this expression  $\mathbf{x}(l\kappa)$  is the position vector of the equilibrium position of the  $\kappa$ th ion in the  $l$ th primitive unit cell. We choose the basis vectors  $\{\mathbf{x}(\kappa)\}$  such that  $\mathbf{x}(-) = 0$  and  $\mathbf{x}(+) = \frac{1}{4}a_0(1,1,1)$ , where  $a_0$  is the lattice parameter, and assume that the impurities occupy the negative-ion sublattice. The coefficient  $P_{\alpha\gamma, \mu}(l\kappa)$  is the first derivative of the electronic polarizability with respect to the displacement amplitude  $u_\mu(l\kappa)$ , and  $Q_{\alpha\gamma\mu}(l\kappa)$  is the contribution of the lattice site  $(l\kappa)$  to the lowest-order nonlinear susceptibility (it is an electro-optic coefficient).  $\mathbf{E}^M(l\kappa)$  is the macroscopic field at the site  $(l\kappa)$ . Combining Eqs. (3.3) and (3.4), we find that

$$p_{\alpha\gamma}^- = \sum_{l\kappa\mu} e^{-i\mathbf{q}\cdot\mathbf{x}(l\kappa)} [P_{\alpha\gamma, \mu}(l\kappa) u_\mu(l\kappa) + Q_{\alpha\gamma\mu}(l\kappa) E_\mu^M(l\kappa)]. \quad (3.5)$$

The macroscopic field  $\mathbf{E}^M(l\kappa)$  is set up by the vibrations of the impurity ions. From the results of Sec. II, we find that a collective motion of the impurity ions described by Eq. (2.6) gives rise to a macroscopic field

<sup>6</sup> Reference 3, Secs. 19 and 49.

at the site ( $lk$ ) given by

$$E_{\alpha}^M(lk) = -\frac{4\pi ef}{\Omega_0} e^{i\mathbf{k}\cdot\mathbf{x}(lk)} \times \sum_{\beta} \left( -\hat{k}_{\alpha}\hat{k}_{\beta} + (\delta_{\alpha\beta} - \hat{k}_{\alpha}\hat{k}_{\beta}) \frac{\xi^2}{1-\xi^2} \right) u_{\beta}, \quad (3.6)$$

irrespective of whether the site ( $lk$ ) is an impurity site or not. Consequently, if we expand the impurity displacement field in normal coordinates,

$$u_{\alpha}(l) = \frac{1}{(Nm)^{1/2}} \sum_{\mathbf{k}j} e_{\alpha}(\mathbf{k}j) e^{i\mathbf{k}\cdot\mathbf{x}(l)} Q(\mathbf{k}j), \quad (3.7)$$

the corresponding macroscopic field is

$$E_{\alpha}^M(lk) = \frac{4\pi ef}{\Omega_0} \frac{1}{(Nm)^{1/2}} \sum_{\mathbf{k}j\beta} \left( \hat{k}_{\alpha}\hat{k}_{\beta} - (\delta_{\alpha\beta} - \hat{k}_{\alpha}\hat{k}_{\beta}) \frac{\xi^2}{1-\xi^2} \right) \times e_{\beta}(\mathbf{k}j) e^{i\mathbf{k}\cdot\mathbf{x}(lk)} Q(\mathbf{k}j). \quad (3.8)$$

We have assumed that the impurity ions occupy the negative-ion sublattice and are the only ions vibrating in the localized modes and in the localized-mode polariton modes. We now assume in addition that the coefficient  $Q_{\alpha\gamma\mu}(lk)$  for an impurity ion differs from that for an ion of the host crystal, so that for any ion it can be written as

$$Q_{\alpha\gamma\mu}(lk) = Q_{\alpha\gamma\mu}^{(0)}(k) + c(l)\Delta Q_{\alpha\gamma\mu}. \quad (3.9)$$

With these assumptions we find that we can write  $p_{\alpha\gamma}^{-}$  in the form

$$p_{\alpha\gamma}^{-} = \sum_{\mathbf{k}j} \sum_{\mu} P_{\alpha\gamma\mu}(\mathbf{k}|\mathbf{q}) e_{\mu}(\mathbf{k}j) Q(\mathbf{k}j), \quad (3.10)$$

where

$$P_{\alpha\gamma\mu}(\mathbf{k}|\mathbf{q}) = \frac{1}{(Nm)^{1/2}} \sum_{l\nu} e^{-i(\mathbf{q}-\mathbf{k})\cdot\mathbf{x}(l)} \left\{ c(l) \left[ P_{\alpha\gamma\nu} \delta_{\nu\mu} + \frac{4\pi ef}{\Omega_0} \Delta Q_{\alpha\gamma\nu} \times \left( \hat{k}_{\nu}\hat{k}_{\mu} - (\delta_{\nu\mu} - \hat{k}_{\nu}\hat{k}_{\mu}) \frac{\xi^2}{1-\xi^2} \right) \right] + \frac{4\pi ef}{\Omega_0} \sum_{\kappa} e^{-i(\mathbf{q}-\mathbf{k})\cdot\mathbf{x}(\kappa)} Q_{\alpha\gamma\mu}^{(0)}(\kappa) \times \left( \hat{k}_{\nu}\hat{k}_{\mu} - (\delta_{\nu\mu} - \hat{k}_{\nu}\hat{k}_{\mu}) \frac{\xi^2}{1-\xi^2} \right) \right\}. \quad (3.11)$$

The expression (3.2) for  $i_{\alpha\lambda,\beta\lambda}(\omega)$  can therefore be

rewritten as

$$i_{\alpha\gamma,\beta\lambda}(\omega) = \frac{1}{2\pi} \sum_{\mathbf{k}j} \sum_{\mathbf{k}'j'} \sum_{\mu\nu} P_{\beta\lambda\mu}^*(\mathbf{k}|\mathbf{q}) P_{\alpha\gamma\nu}(\mathbf{k}'|\mathbf{q}) e_{\mu}(\mathbf{k}j) \times e_{\nu}(\mathbf{k}'j') \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle Q^*(\mathbf{k}j; t) Q(\mathbf{k}'j'; 0) \rangle. \quad (3.12)$$

To evaluate the Fourier transform of the correlation function, we introduce the (retarded) double-time Green's function

$$G(\mathbf{k}j; \mathbf{k}'j'; t) = \langle \langle Q^*(\mathbf{k}j; t); Q(\mathbf{k}'j'; 0) \rangle \rangle = -i\theta(t) \langle [Q^*(\mathbf{k}j; t), Q(\mathbf{k}'j'; 0)] \rangle, \quad (3.13)$$

where  $\theta(t)$  is the Heaviside unit step function. If we introduce the Fourier transform of this function by

$$G(\mathbf{k}j; \mathbf{k}'j'; t) = \int_{-\infty}^{\infty} dE \hat{G}(\mathbf{k}j; \mathbf{k}'j'; E) e^{-iEt}, \quad (3.14)$$

then it is the case that

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle Q^*(\mathbf{k}j; t) Q(\mathbf{k}'j'; 0) \rangle = [i/(e^{\beta\hbar\omega} - 1)] [\hat{G}(\mathbf{k}j; \mathbf{k}'j'; \omega + i0) - \hat{G}(\mathbf{k}j; \mathbf{k}'j'; \omega - i0)]. \quad (3.15)$$

The Green's function  $G(\mathbf{k}j; \mathbf{k}'j'; t)$  obeys the equation of motion

$$-\hbar^2 (d^2/dt^2) G(\mathbf{k}j; \mathbf{k}'j'; t) = i\hbar^2 \delta(t) \langle [\dot{Q}^*(\mathbf{k}j), Q(\mathbf{k}'j')] \rangle - \hbar^2 \langle \langle \dot{Q}^*(\mathbf{k}j; t); Q(\mathbf{k}'j'; 0) \rangle \rangle. \quad (3.16)$$

The commutator of  $\dot{Q}^*(\mathbf{k}j)$  and  $Q(\mathbf{k}'j')$  is

$$[\dot{Q}^*(\mathbf{k}j), Q(\mathbf{k}'j')] = -i\hbar\Delta(\mathbf{k}-\mathbf{k}')\delta_{jj'}, \quad (3.17)$$

where  $\Delta(\mathbf{k})$  equals unity if  $\mathbf{k}$  is  $2\pi$  times a reciprocal lattice vector, and vanishes otherwise. If we assume a harmonic time dependence  $e^{-i\omega t}$  for  $Q(\mathbf{k}j; t)$ , the equation of motion of this normal coordinate obtained by combining Eq. (3.7) with the analysis that led from Eq. (2.1) to Eq. (2.19) is

$$\ddot{Q}(\mathbf{k}j) = -\omega_0^2 Q(\mathbf{k}j) + \omega_P^2 V(\mathbf{k}j) Q(\mathbf{k}j), \quad (3.18a)$$

where

$$V(\mathbf{k}1) = -\frac{2}{3}, \quad (3.18b)$$

$$V(\mathbf{k}2) = V(\mathbf{k}3) = \frac{1}{3} + \omega^2 / (c^2 k^2 - \omega^2). \quad (3.18c)$$

Consequently, taking the Fourier transform of Eq. (3.16) and making use of Eqs. (3.17) and (3.18), we obtain

$$\hat{G}(\mathbf{k}j; \mathbf{k}'j'; E) = \frac{\hbar}{2\pi} \frac{\Delta(\mathbf{k}-\mathbf{k}')\delta_{jj'}}{E^2 - \omega_0^2 + \omega_P^2 V(\mathbf{k}j)}. \quad (3.19)$$

Combining the results given by Eqs. (3.12), (3.15), and (3.19), we obtain for  $i_{\alpha\gamma,\beta\lambda}(\omega)$  the result that

$$i_{\alpha\gamma,\beta\lambda}(\omega) = \hbar \operatorname{sgn}\omega n(\omega) \sum_{\mathbf{k}} \sum_{\mu\nu} P_{\beta\lambda\mu}^*(\mathbf{k}|\mathbf{q}) P_{\alpha\gamma\nu}(\mathbf{k}|\mathbf{q}) \times \{ \hat{k}_\mu \hat{k}_\nu \delta(\omega^2 - \omega_l^2) + (\delta_{\mu\nu} - \hat{k}_\mu \hat{k}_\nu) S_{\text{ph}}(\omega) \times [\delta(\omega^2 - \omega_+^2(\mathbf{k})) + \delta(\omega^2 - \omega_-^2(\mathbf{k}))] \}. \quad (3.20)$$

$$\frac{\omega_\pm^2(\mathbf{k}) - c^2 k^2}{\omega_+^2(\mathbf{k}) - \omega_-^2(\mathbf{k})} \delta(\omega^2 - \omega_\pm^2(\mathbf{k})) = \pm S_{\text{ph}}(\omega) \delta(\omega^2 - \omega_\pm^2(\mathbf{k})). \quad (3.22)$$

We have introduced the photon strength function

$$S_{\text{ph}}(\omega) = \frac{\omega^2 \omega_p^2}{(\omega_l^2 - \omega^2)} \left( 1 + \frac{\omega_p^2 \omega_l^2}{(\omega^2 - \omega^2)^2} \right)^{-1} \quad (3.21)$$

that has been utilized in previous discussions of polariton theory.<sup>7</sup> This function may be introduced

This identity follows from Eq. (2.17) and Eq. (2.18).

It remains to average the expression given by Eq. (3.20) over all possible impurity configurations. This means that we must average the product  $P_{\beta\lambda\mu}^*(\mathbf{k}|\mathbf{q}) \times P_{\alpha\gamma\nu}(\mathbf{k}|\mathbf{q})$  over all impurity configurations. When this is done, we find that  $i_{\alpha\gamma,\beta\lambda}(\omega)$  can be written as the sum of an expression which describes coherent scattering of light and an expression which describes incoherent scattering, where

$$i_{\alpha\gamma,\beta\lambda}(\omega)_{\text{coh}} = \frac{f^2 \hbar N}{m} \operatorname{sgn}\omega n(\omega) \sum_{\mu\nu} \left[ \left( P_{\beta\lambda\mu} + \frac{4\pi e}{\Omega_0} (Q_{\beta\lambda\mu}^{(0)} + f\Delta Q_{\beta\lambda\mu}) \right) \left( P_{\alpha\gamma\nu} + \frac{4\pi e}{\Omega_0} (Q_{\alpha\gamma\nu}^{(0)} + f\Delta Q_{\alpha\gamma\nu}) \right) \hat{q}_\mu \hat{q}_\nu \delta(\omega^2 - \omega_l^2) + \left( P_{\beta\lambda\mu} - \frac{4\pi e}{\Omega_0} (Q_{\beta\lambda\mu}^{(0)} + f\Delta Q_{\beta\lambda\mu}) \frac{\omega^2}{c^2 q^2 - \omega^2} \right) \left( P_{\alpha\gamma\nu} - \frac{4\pi e}{\Omega_0} (Q_{\alpha\gamma\nu}^{(0)} + f\Delta Q_{\alpha\gamma\nu}) \frac{\omega^2}{c^2 q^2 - \omega^2} \right) \times (\delta_{\mu\nu} - \hat{q}_\mu \hat{q}_\nu) S_{\text{ph}}(\omega) (\delta(\omega^2 - \omega_+^2(\mathbf{q})) + \delta(\omega^2 - \omega_-^2(\mathbf{q}))) \right], \quad (3.23a)$$

$$i_{\alpha\gamma,\beta\lambda}(\omega)_{\text{incoh}} = f(1-f) \frac{\hbar}{m} \operatorname{sgn}\omega n(\omega) \sum_{\mathbf{k}} \sum_{\mu\nu} \left[ \left( P_{\beta\lambda\mu} + \frac{4\pi e f}{\Omega_0} \Delta Q_{\beta\lambda\mu} \right) \left( P_{\alpha\gamma\nu} + \frac{4\pi e f}{\Omega_0} \Delta Q_{\alpha\gamma\nu} \right) \hat{k}_\mu \hat{k}_\nu \delta(\omega^2 - \omega_l^2) + \left( P_{\beta\lambda\mu} - \frac{4\pi e f}{\Omega_0} \Delta Q_{\beta\lambda\mu} \frac{\omega^2}{c^2 k^2 - \omega^2} \right) \left( P_{\alpha\gamma\nu} - \frac{4\pi e f}{\Omega_0} \Delta Q_{\alpha\gamma\nu} \frac{\omega^2}{c^2 k^2 - \omega^2} \right) \times (\delta_{\mu\nu} - \hat{k}_\mu \hat{k}_\nu) S_{\text{ph}}(\omega) (\delta(\omega^2 - \omega_+^2(\mathbf{k})) + \delta(\omega^2 - \omega_-^2(\mathbf{k}))) \right], \quad (3.23b)$$

where we have defined  $Q_{\alpha\gamma\delta}^{(0)}$  by

$$Q_{\alpha\gamma\delta}^{(0)} = \sum_{\kappa} Q_{\alpha\gamma\delta}^{(0)}(\kappa). \quad (3.24)$$

For crystals of the zinc-blende structure each of the third-rank tensors  $P_{\alpha\gamma\nu}$ ,  $Q_{\alpha\gamma\nu}^{(0)}$ , and  $\Delta Q_{\alpha\gamma\nu}$  has only one independent nonzero component

$$P_{\alpha\gamma\nu} = P |\epsilon_{\alpha\gamma\nu}|, \quad Q_{\alpha\gamma\nu}^{(0)} = Q^{(0)} |\epsilon_{\alpha\gamma\nu}|, \quad \Delta Q_{\alpha\gamma\nu} = \Delta Q |\epsilon_{\alpha\gamma\nu}|, \quad (3.25)$$

where  $\epsilon_{\alpha\gamma\nu}$  is the Levi-Civita symbol. Consequently, for these crystals we find that

$$i_{\alpha\gamma,\beta\lambda}(\omega)_{\text{coh}} = \frac{f^2 \hbar N}{m} \operatorname{sgn}\omega n(\omega) \left[ \left( P + \frac{4\pi e}{\Omega_0} (Q^{(0)} + f\Delta Q) \right)^2 \delta(\omega^2 - \omega_l^2) \sum_{\mu\nu} |\epsilon_{\beta\lambda\mu}| |\epsilon_{\alpha\gamma\nu}| \hat{q}_\mu \hat{q}_\nu + \left( P - \frac{4\pi e}{\Omega_0} (Q^{(0)} + f\Delta Q) \frac{\omega^2}{c^2 q^2 - \omega^2} \right)^2 S_{\text{ph}}(\omega) [\delta(\omega^2 - \omega_+^2(\mathbf{q})) + \delta(\omega^2 - \omega_-^2(\mathbf{q}))] \times \sum_{\mu\nu} |\epsilon_{\beta\lambda\mu}| |\epsilon_{\alpha\gamma\nu}| (\delta_{\mu\nu} - \hat{q}_\mu \hat{q}_\nu) \right], \quad (3.26a)$$

$$i_{\alpha\gamma,\beta\lambda}(\omega)_{\text{incoh}} = \frac{f(1-f)n\hbar}{3m} \operatorname{sgn}\omega n(\omega) \left( P + \frac{4\pi e f}{\Omega_0} \Delta Q \right)^2 \delta(\omega^2 - \omega_l^2) \sum_{\mu} |\epsilon_{\beta\lambda\mu}| |\epsilon_{\alpha\gamma\mu}| + \frac{2f(1-f)\hbar}{3m} \operatorname{sgn}\omega n(\omega) \times \sum_{\mathbf{k}} \left( P - \frac{4\pi e f}{\Omega_0} \Delta Q \frac{\omega^2}{c^2 k^2 - \omega^2} \right)^2 S_{\text{ph}}(\omega) [\delta(\omega^2 - \omega_+^2(\mathbf{k})) + \delta(\omega^2 - \omega_-^2(\mathbf{k}))] \sum_{\mu} |\epsilon_{\beta\lambda\mu}| |\epsilon_{\alpha\gamma\mu}|. \quad (3.26b)$$

<sup>7</sup> E. Burstein, S. Ushioda, and A. Pinczuk, *Solid State Commun.* **6**, 407 (1968).

Being dispersionless, the longitudinal localized mode contributes a sharp peak at the frequency  $\omega_i$  to both the coherent and incoherent scattering cross sections. However, the polarization selection rules for the two kinds of scattering processes are different, so that it should be possible to observe the longitudinal-mode peak in the coherent scattering cross section at the same time that the incoherent scattering has been suppressed.

The detailed information on the polariton dispersion relation is contained in the coherent part of the scattering. To see this, note that the incoherent part exhibited in Eq. (3.26) contains an unrestricted sum over wave vector. The volume of  $\mathbf{k}$  space within which the polariton effects are important is very small. Thus, for our model, the incoherent cross section consists of peaks at  $\omega_i$  and  $\omega_l$ , and the polariton contribution provides wings of small amplitude on the transverse peak. Note that for  $f \ll 1$ , the intensities of the incoherent peaks are proportional to the concentration  $f$ .

Now consider the coherent scattering cross section of Eq. (3.26a). This expression describes the coherent scattering from collective excitations of the impurity array; the wave vector is conserved in this scattering process. The presence of the coherent scattering contribution allows one to study the local-mode polariton dispersion relation by exactly the same technique employed in the study of polaritons in pure crystals. One observes the shift in frequency of the transverse mode as a function of scattering angle, for angles near the forward direction.

Let us consider the concentration dependence of the coherent scattering from the local-mode polariton. First suppose that  $Q^{(0)} \equiv 0$ , i.e., we ignore the electro-optic scattering from the bulk of the crystal. Then, for  $f \ll 1$ , we have  $P \gg (4\pi e f / \Omega_0) \Delta Q$ , and in this limit the scattering comes primarily from the elasto-optic scattering associated with the motion of the impurity ion. For this case, the coherent scattering is proportional to  $f^2$ . Hence, for  $f \ll 1$ , the coherent scattering cross section should be smaller than the incoherent cross section by roughly a factor of  $f$ . Next consider the effect of the bulk electro-optic scattering represented by the  $Q^{(0)}$  term in Eq. (3.18a). Upon noticing the presence of the  $\delta$  functions in Eq. (3.26a) we may

replace  $[4\pi e \omega^2 / \Omega_0 (c^2 q^2 - \omega^2)] Q_0$  by

$$\frac{4\pi e}{\Omega_0} \frac{Q_0}{\epsilon(\omega) - 1} = \frac{m}{f e} (\omega_i^2 - \omega^2) Q_0. \quad (3.27)$$

For large scattering angles, where  $\omega$  is very close to  $\omega_i$  in value, the bulk electro-optic scattering may be ignored, and the preceding remarks apply. As the scattering angle is decreased, and the polariton region is entered, then  $\omega$  shifts below  $\omega_i$  and the bulk electro-optic scattering becomes important. For the case where the scattering vector  $q = \omega_i / c$ , the right-hand side of Eq. (3.27) becomes  $(m\omega_i / f e) Q_0 \Delta \equiv [(4\pi m)^{1/2} \omega_i / f^{1/2}] Q_0$ . For  $f \ll 1$ , the bulk electro-optic scattering thus dominates the elasto-optic scattering for this wave-vector transfer. The coherent part of the cross section at this point is proportional to  $f$  rather than to  $f^2$ , as it is in the large-angle region.

The following picture of the scattering from the transverse local modes thus emerges: At large scattering angles, one sees a peak at the TO frequency  $\omega_i$ . In the general case, the scattered intensity contains a contribution from the coherently scattered light, and the incoherently scattered radiation. The intensity of the former is proportional to  $f^2$  and the latter to  $f$ , for  $f \ll 1$ . As the scattering angle is decreased into the polariton regime, the incoherent peak remains at  $\omega_i$  since its position is insensitive to the scattering angle. The coherent peak shifts to lower frequencies and at the same time grows in intensity from the increasing importance of the bulk electro-optic scattering. When the scattering vector  $q = \omega_i / c$ , the incoherent and coherent peaks are comparable in intensity.

In Fig. 1, we indicate the position of the coherent peak as a function of scattering angle for GaAs doped with 5% P. We have assumed the incident radiation is  $1.06 \mu$  in wavelength. For this crystal, the frequency shift is only  $2.5 \text{ cm}^{-1}$  even in the forward-scattering limit. The small frequency shift that can be realized in this case is a consequence of the strong variation of the refractive index of GaAs with frequency in the vicinity of the  $1.06\text{-}\mu$  line.<sup>8</sup>

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<sup>8</sup> D. T. F. Marple, J. Appl. Phys. **35**, 1241 (1964).