Another important case is the possibility of diffraction occurring resonantly in and out of an intermediate bound state b, of energy $E_b \simeq E_i$ and parallel momentum $\vec{P}_i + \vec{G}$. Through solving another set of equations similar to (5) we find that the essential features of the specular elastic beam are well described by

$$R(\vec{p}_s, \vec{p}_i) = |1 - 2i\Gamma_{el}/(E_i - E_b + i\Gamma_{tot})|^2, \qquad (7)$$

where $\Gamma_{el} = N_i |(U\vec{G})_{sb}|^2$ and Γ_{tot} is Γ_{el} plus the contribution of phonon scattering. The inelastic one-phonon absorption coefficient is similar to (4) except that $(\nabla U\vec{Q})_{fi}$ is replaced by $(\nabla U\vec{Q})_{fi} + (\nabla U\vec{G} + \vec{Q})_{fb}(U\vec{G})_{bi}/(E_i - E_b + i\Gamma_{tot})$. The general case of several diffracted and several bound states can be treated in a manner similar to the simpler cases outlined above.

In conclusion, we have shown that surface scattering can be treated by taking matrix elements of the effective potential (1) between wave functions of the smoothed average potential U. The essential point is the introduction of the reduced matrix t. These results generalize previous treatments of surface scattering.[8] The angular distribution and intensity of the one-phonon scattering have been computed as an example in the simplest possible case. For actual experiments it is better to use nonnormal incidence so as to increase the angular separation between elastic and one-phonon beams, and there is really no need to use an incoming beam of very low energy.

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EXCITON-ENHANCED RAMAN SCATTERING BY OPTICAL PHONONS

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The theory of exciton-enhanced Raman scattering is formulated in terms of the scattering of polaritons by optical phonons via the exciton part of the coupled modes. The expression for the exciton contribution to the scattering tensor is given, within a constant factor, in terms of the same parameters that determine the exciton contribution to the frequency-dependent dielectric constant. The theory also provides a new mechanism for the exciton contribution to the electro-optic effect.

Leite and Porto[1] have reported a marked enhancement of Raman scattering by LO phonons in CdS at low temperatures (77°K) at frequencies near the absorption edge, and have explained their results in terms of Loudon's theory[2] of resonant Raman scattering via electron-hole-pair intermediate states. Birman and Ganguly[3] have, however, pointed out that the creation of virtual excitons dominates the resonance Raman scattering by LO to TO phonons and have interpreted Leite and Porto's data on this basis. More recent data[4] for CdS indicate that the ratio of the

first-order scattering intensities of LO and TO phonons I_{LO}/I_{TO} increases rapidly and becomes greater than unity in the resonance region. The data imply that the electro-optic contribution to the Raman scattering tensor $\chi^{(1)}(\vec{E})$ is much larger than the atomic-displacement (deformation-potential) contribution $\chi^{(1)}(\vec{u})$. A large enhancement of I_{LO}/I_{TO} is also observed in InSb at frequencies near the E_1 energy gap.[5] We attribute the large values of $\chi^{(1)}(\vec{E})/\chi^{(1)}(\vec{u})$ to the role played by excitons in the scattering processes at frequencies near the exciton absorption band, and to the fact that the exciton–LO-phonon interaction via the macroscopic electric field is considerably stronger than that via the deformation potential.

We present here a theory of exciton-enhanced Raman scattering by LO and TO phonons which is formulated in terms of the scattering of polaritons by optical phonons (or by coupled photon–TO-phonon modes) via interaction with the exciton parts of the coupled modes. Ovander and co-workers[6] have also treated scattering from this point of view.[7] The theory which involves optical-phonon–induced transitions between exciton levels is also applicable to bound exciton-enhanced scattering by optical phonons and to exciton-enhanced Brillouin scattering by acoustical phonons. It leads to a frequency dispersion of the scattering efficiency that is qualitatively different from that of Birman and Ganguly who use a perturbation theoretic approach to treat the exciton-photon coupling. The theory also provides a new mechanism for the exciton contribution to the electro-optic coefficient $(\partial\chi/\partial\vec{E})_{\vec{u}}$ $= b$ and leads to an expression for b valid in the resonance region.

The dispersion relation for the polariton modes $\Omega(k)$ in a crystal (assumed to be optically isotropic) exhibiting several exciton bands has the form

$$k^2c^2 = \Omega^2 \epsilon(\Omega)$$

$$= \Omega^2\left[\epsilon_0(\Omega) + \sum_i \frac{4\pi\beta_{xi}\omega_{xi}^2}{\omega_{xi}^2 - \Omega^2 - i\Omega/\tau_{xi}}\right], \quad (1)$$

where $\epsilon_0(\Omega)$ is the frequency-dependent dielectric constant in the absence of exciton-photon coupling, ω_{xi} and τ_{xi} are the frequency and lifetime of excitons of type i, β_{xi} is the zero-frequency contribution of the ith exciton band to the electric susceptibility, and we have neglected the wave-vector dispersion of the exciton bands. The normal modes $\Omega(\vec{q})$ are sketched in Fig. 1 for infinite
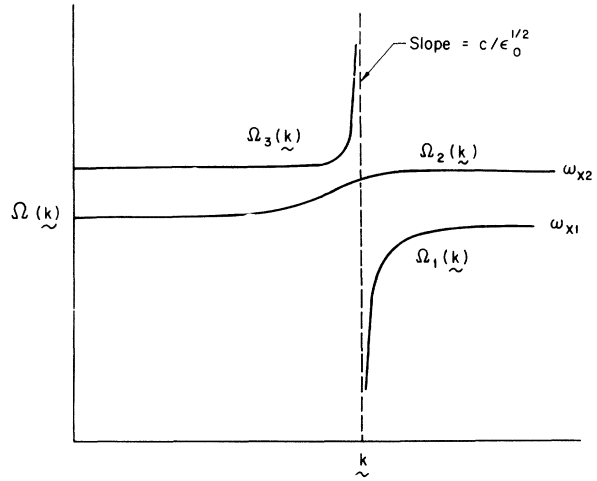

FIG. 1. The Ω vs q curves of polaritons in the vicinity of the exciton absorption bands for a two-exciton band model.

τ_{xi}. The lowest frequency branch is labeled $\Omega_1(\vec{K})$; the next highest $\Omega_2(\vec{K})$; etc.

In order to compute the cross section for the Raman scattering of polaritons by phonons via interaction with the exciton part of the polaritons (Fig. 2), we write the polariton-phonon interaction potential in the form

$$V_{pol-ph} = (i/V^{1/2})\sum \bar{M}_{nm}(\vec{K}, \vec{K}+\vec{q})$$

$$\times \alpha^\dagger(\vec{K}+\vec{q})\alpha(\vec{q})[c(\vec{q})-c^\dagger(-\vec{q})], \quad (2)$$

where $\bar{M}_{nm}(\vec{K}, \vec{K}+\vec{q})$ is the polariton-phonon scattering matrix element; V is the volume of the crystal; $\alpha_n(\vec{k})$, $\alpha_n^\dagger(-\vec{k})$, and $c(\vec{q})$, $c^\dagger(-\vec{q})$ are the polariton and phonon creation and annihilation operators, respectively, and $\vec{k}_i = \vec{k}_0 + \vec{q}$. We find that $\bar{M}_{nm}(\vec{K}, \vec{K}+\vec{q})$ may be expressed in terms of the exciton-phonon matrix element[8] $M_{ij}(\vec{q})$ and
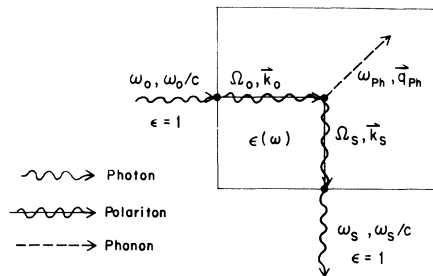

FIG. 2. Schematic diagram showing the Raman scattering of polaritons by optical phonons.

the exciton strengths $s_{\chi i}[\Omega_n(\vec{k})]$ as

$$\bar{M}_{nm}(\vec{k}, \vec{k}+\vec{q}) = \tfrac{1}{2}\sum_{ij} s_{\chi i}^{1/2}[\Omega_n(\vec{k})]M_{ij}(\vec{q})\left[1 + \frac{\omega_{\chi i}\omega_{\chi j}}{\Omega_n(\vec{k})\Omega_m(\vec{k}+\vec{q})}\right]s_{\chi j}^{1/2}[\Omega_m(\vec{k}+\vec{q})],\tag{3}$$

where $s_{\chi i}[\Omega_n(\vec{k})]$ is the strength of the ith exciton level in the polariton mode $\Omega_n(\vec{k})$. $s_{\chi i}[\Omega_n(\vec{k})]$ is defined by

$$\langle P_{\chi i}^2[\Omega_n(\vec{k})]\rangle = s_{\chi i}[\Omega_n(\vec{k})]\langle P_{\chi i}^2(\omega_{\chi i})\rangle,\tag{4}$$

where $P_{\chi i}$ is the dipole-moment density of the ith exciton level and the averages are taken in one-polariton states at the indicated frequencies.

In the case of TO phonons, the exciton-phonon matrix element corresponds to a deformation-potential matrix element $M_{ij}{}^D(\vec{q})$, while for LO phonons it consists of a contribution from the Fröhlich (macroscopic electric field) interaction, in addition to the deformation-potential contribution, $M_{ij}{}^F(\vec{q}) + M_{ij}{}^D(\vec{q})$. Since the scattering wave vector $\vec{k}_0 - \vec{k}_s = \vec{q}$ is small, we are concerned with the limit of $M_{ij}(\vec{q})$ as $\vec{q} \to 0$. In the long-wavelength limit the Fröhlich matrix element becomes proportional to the electric-dipole matrix element $r_{ij} = \langle i|\vec{r}|j\rangle$, where $\vec{r}$ is the relative coordinate of the electron-hole pair. Since the i and j exciton states involved are states which are coupled to photons to form polaritons, r_{ij} is nonzero only in crystals lacking a center of inversion, in

which the exciton wave functions do not have well-defined parity. Furthermore, for this case, one may have $r_{ii} \neq 0$. The deformation-potential matrix elements are nonzero for Raman active photons, with both interband $(i \neq j)$ and intraband $(i = j)$ matrix elements allowed.

We now compute the Stokes scattered polariton flux $\Phi_S(\Omega_S)$ assuming that $\Phi_0(\Omega_0)$ is the flux of the incident polariton mode. For simplicity we consider Ω_0 to be below the first exciton level at $\omega_{\chi i}$ [i.e., both the initial and final states are associated with the $\Omega_1(k)$ branch] and to be outside of the strongly absorbing region.

The energy flux density associated with a given polariton mode $[\Omega_n(k)]$ is given by

$$\Phi(\Omega_n(\vec{k})) = v_g(\Omega_n(\vec{k}))\hbar\Omega_n(\vec{k})\bar{n}(\Omega_n(\vec{k})),\tag{5}$$

where $\bar{n}(\Omega_n(\vec{k}))$ is the occupation number of the mode and $v_g(\Omega_n(\vec{k}))$ is the velocity of energy transport.[2,9] At frequencies outside of the strongly absorbing region, i.e., where $[\omega_{\chi i}^2 - \Omega_n^2(\vec{k})]^2 > [\Omega_n(\vec{k})/\tau_{\chi i}]^2$, but within the region of anomalous dispersion, the expression for $v_g(\Omega_n(k))$ takes the approximate form

$$v_g(\Omega_n(k)) \approx c\eta(\Omega_n(k))\left\{\epsilon_0 + \sum_i \frac{4\pi\beta_{\chi i}\omega_{\chi i}^4}{[\omega_{\chi i}^2 - \Omega_n^2(k)]^2}\right\}^{-1} \approx v_g(\Omega_n(k)),\tag{6}$$

where $v_g(\Omega_n(\vec{k}))$ is the group velocity of the mode, c is the velocity of light, and $\eta(\Omega_n(\vec{k}))$ is the real part of the complex refractive index.

Application of the golden rule to Eq. (2) yields the following expression for the rate at which polaritons are scattered into the solid angle $d\Theta$ within the crystal:

$$\frac{d^2N_S}{d\Theta dt} = \frac{2\pi}{\hbar^2}|\bar{M}_{11}(k_s, \vec{k}_0)|^2\rho(\Omega_S)\bar{n}_0(n_{\text{ph}}+1),\tag{7}$$

where $\Omega_S = \Omega_0 - \omega_{\text{ph}}$ and $\vec{k}_s = \vec{k}_0 - \vec{q}_{\text{ph}}$ are the frequency and wave vector of the scattered polariton; $\bar{n}_0$ is the number of incident polaritons per unit volume; N_S is the number of scattered polaritons; $\bar{n}_{\text{ph}}$, ω_{ph}, and $\vec{q}_{\text{ph}}$ are the occupation number, frequency, and wave vector, respectively, of the optical phonons; and $\rho(\Omega_S)$ is the density

of the scattered polariton modes. Outside the absorbing region $\rho(\Omega_S)$ is given by

$$\rho(\Omega_S) = \frac{V}{(2\pi)^3}\frac{k_s^2}{V_g(\Omega_S)}.\tag{8}$$

From Eq. (7), we obtain the following expression for the Raman-scattering efficiency, defined as the ratio of the number of scattered polaritons per unit solid angle per unit crystal length per unit time to the number of incident polaritons crossing unit area in unit time[10]:

$$S = \frac{(\bar{n}_{\text{ph}}+1)}{4\pi^2\hbar^2}\left(\frac{\Omega_S}{c}\right)^2\frac{|\bar{M}_{11}(\vec{k}_s, \vec{k}_0)|^2}{V_g(\Omega_0)V_g(\Omega_S)}.\tag{9}$$

We consider a model in which the photon field is coupled to two exciton excitations at ω_{x2} corresponding, for example, to the ground and first-excited states of the direct exciton.[11] For this model, the exciton strengths $S_{xi}[\Omega_n(\vec{k})]$ are given by

$$S_{xi}[\Omega_n(\vec{k})] = \frac{4\pi\beta_{xi}\omega_{xi}^3\Omega_n(\vec{k})}{[\omega_{xi}^2 - \Omega_n^2(\vec{k})]^2}\left\{\epsilon_0 + \sum_{i=1}^{2}\frac{4\pi\beta_{xi}\omega_{xi}^4}{[\omega_{xi}^2 - \Omega_n^2(k)]^2}\right\}^{-1}.$$ (10)

We note, in the limit $\tau_{xi} \to \infty$, that as the incident frequency Ω_0 approaches ω_{xi} from below, $S_{x1}(\Omega_0) \to 1$ and $S_{x2}(\Omega_0) \to 0$. At $\Omega_0 = \omega_{x1}$, the polariton is a "pure" exciton level-1 mode.

Since $M_{ij}(\vec{q})$ depends only on the scattering wave vector, and since $(1 + \omega_{x1}\omega_{x2}/\Omega_0\Omega_s)$ is slowly varying over the resonance region, all of the frequency dependence of the Raman tensor resides in the exciton strength parameters, and in the group-velocity factor. One sees from Eq. (6) and Eq. (9) that the exciton strengths and the group velocity depend only on $\epsilon_0(\Omega)$ and the parameters β_{xi}, ω_{xi}, and τ_{xi} that determine the exciton contribution to the dielectric constant.

It should be noted that the matrix element of Eq. (9) is never infinite, since the exciton strengths only vary from 0 to 1. This behavior of the matrix element differs qualitatively from that of Birman and Ganguly[3] which diverges as $(\omega_{xi} - \omega)^{-1}$. Also, we have $v_g(\Omega_0)v_g(\Omega_s)$ in the denominator of the expression for the scattering efficiency, whereas Birman and Ganguly have c^2/ϵ_0. Since $v_g(\Omega)$ decreases as the resonance region is approached one obtains an additional strong enhancement from this source. Our result reduces to the Birman-Ganguly form outside the resonance region where the normal modes are predominantly of photon character.

The behavior of the scattering efficiency as $\Omega_0 \to \omega_{x1}$ will depend on whether inter- or intraband exciton-phonon scattering dominates. In the case of scattering by LO phonons, the Fröhlich interaction is the important one, as can be seen from the experimental data on phonon assisted exciton absorption and fluorescence,[12] where LO sidebands show clearly, but no structure from TO phonons is observed. If the r_{12} transition matrix element is the dominant one, then from the character of $S_{x1}^{1/2}(\Omega_0)M_{12}(\vec{q})S_{x2}^{1/2}(\Omega_s)$ we may expect the enhancement in the Raman efficiency, in the limit $\tau_{x1} \to \infty$, to have a peak at a frequency $\Omega_0 < \omega_{x1}$. This might account for the difference between the value of 2.521 eV reported by Leite and Porto[1] for the photon energy at which the enhancement has a peak and the value of the exciton energy 2.544 eV. If the r_{11} transition matrix element is the dominant one, as may be the case for the deformation potential mechanism, we may expect the enhancement, in the limit $\tau_{x2} \to \infty$, to have a peak at ω_{x1}.

We now consider the effect of the exciton lifetimes τ_{xi} on the scattering efficiency. The magnitude of τ_{xi} controls the magnitudes of $S_{xi}(\Omega)$, $v_g(\Omega)$, and $\rho(\Omega)$.[13] The lifetime of excitons are known to decrease rapidly with increase in temperature due to phonon-exciton scattering processes and to the increasing rate of thermal ionization.[14] We may therefore expect $S_{xi}(\Omega)$, $v_g(r)$, and $\rho(\Omega)$ to decrease and, thereby, the exciton enhancement of Raman scattering to decrease with increasing temperature and to become negligible at temperatures where the τ_{xi} become relatively small and the absorbing region spreads beyond the region of anomalous dispersion. Specifically we expect the exciton enhancement from a given exciton absorption band to be small when $(4\pi\beta_{xi}/\epsilon_0)(\omega_{xi}\tau_{xi}) < 1$. Since Raman scattering via continuum electron-hole-pair excitations should be relatively insensitive to temperature, the effect of temperature on the scattering efficiency can be used to establish whether excitons or continuum excitations are involved in the scattering process.[5]

Finally we note that the electro-optic contribution to the scattering efficiency can be expressed in terms of the electro-optic coefficient, $b = (\partial\chi/\partial\vec{E})_{\vec{u}}$,[10]

$$S_x(E) = (\omega_s^4/2c^4)|bE|^2(\bar{n}_{ph} + 1),$$ (11)

where $\vec{E}$ is the macroscopic electric field of the optical phonon. It is therefore possible by comparing Eq. (10) with Eq. (8) to obtain an expression for b in terms of $|\bar{M}_{nm}^F(\vec{k}_s\vec{k}_0)|^2/v_q(\Omega)^2$, where $\bar{M}_{nm}(\vec{k}_s\vec{k}_0)$ is the matrix element for the scattering of polaritons by optical phonons via the Fröhlich interaction. The low-frequency form of b is obtained by computing $\bar{M}_{nm}^F(\vec{k}_s, \vec{k}_0)$ in the limit $\omega_0 - \omega_s = 0$ and $\vec{k}_s = \vec{k}_0$. The large exciton-enhanced R-scattering efficiencies of LO phonons which are observed at $\Omega_0 \approx \omega_{x1}$ imply large val-

ues of the electro-optic coefficient. Such large values may, in part, account for the structure due to excitons in electroreflectance spectra.[15]

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ISOSPIN-NONCONSERVING DECAYS IN MIRROR NUCLEI*

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We have measured branching ratios for the isospin-nonconserving particle decays of the 15.1-MeV $T = \frac{3}{2}$ states in ^{13}N and ^{13}C to the $(0.0, 0^+)$ and $(4.44, 2^+)$ states of ^{12}C. By comparing ratios of reduced widths with the 0^+ and 2^+ states of ^{12}C for the mirror decays, we show that the form of the isospin impurity in the 15.1-MeV states depends on T_z.

One of the more intriguing ideas in nuclear physics is the suggestion that the isospin impurities observed in nuclear wave functions may be useful in understanding the charge dependence of the internucleon force itself.[1] That the exploitation of this suggestion has not been entirely successful is largely due to the scarcity of sufficiently detailed experimental information on the size and form of these impurities. Our present knowledge of the magnitude of isospin admixtures is primarily obtained from three sources: (1) β-decay matrix elements,[2] (2) electromagnetic selection rules (especially for $\Delta T = 0$, $E1$ transitions in self-conjugate nuclei),[3,4] (3) comparison of isospin-allowed and -forbidden reaction rates.[5-7]

We have employed a new technique for studying the form of isospin impurities in nuclear wave functions by comparing isospin-nonconserving decays from analog levels in mirror nuclei. In this Letter we present results for the decays of the lowest $T = \frac{3}{2}$ levels in ^{13}C and ^{13}N. Similar experiments are presently under way in mass 9 and mass 17.

Decay branching ratios (BR's) to the ground and 4.44-MeV states of ^{12}C were measured using the reactions ^{11}B(^{3}He, n)^{13}N(15.07) → p + ^{12}C and ^{11}B(^{3}He, p)^{13}C(15.11) → n + ^{12}C. Coincidences between neutrons and protons were stored in a 64 ×64-channel array, one variable being neutron flight time, the other proton energy. Protons