where $\beta = 2.7 \mp 1$, $\omega_p = 2.73 \times 10^{12}$ sec^{-1}, and, if we take $\beta = 2$, $a = (1.8 \mp 0.4) \times 10^{11}$ sec^{-1}, $\tau_{\mathrm{imp}} = (3 \mp 0.5) \times 10^{-11}$ sec.

Let us point out that our experiment has been tested with copper samples[17] from 4- to 0.6-mm wavelength. We have observed there an effective mass and a relaxation time independent of frequency, as would be expected from the high Debye temperature of copper.

Conclusion.—Our experiments on mercury give evidence of the change of the electron effective mass in the vicinity of the Debye frequency. The related decrease of the relaxation time in this region has also been put in evidence in lead and mercury. The fact that we observe an electron-phonon–limited relaxation time proportional to the inverse of the square of the frequency does not agree with the previous theories.

It is a great pleasure to express appreciation to Professor A. Libchaber, Professor P. Nozieres, and Professor Y. Sharvin for helpful discussions, to Mr. J. Brochard for his exceptional skill in mechanical design, and to Mr. H. Thome for his technical assistance.

Note added in proof.—Experiments on cyclotron linewidth dependence in frequency and temperature have been performed on bismuth by V. S. Edel'mann and J. M. Tcheremicin, Pis'ma Zh. Eksp. Teor. Fiz. 11, 373 (1970). The observed relaxation time τ varies as $\tau^{-1} = \tau_0^{-1} + \tau^{-1}(F, T)$, where $\tau^{-1}(F) \propto F^{2.5}$ and $\tau^{-1}(T) \propto T^2$. These variations are attributed mainly to electron-electron interaction.

---

*Permanent address: Centre Universitaire de Marseille-Luminy, 13-Marseille 9°, France.

†Laboratoire associé au Centre National de la Recherche Scientifique.

[1] H. Scher and T. Holstein, Phys. Rev. 148, 598 (1966).

[2] G. Grimvall, Phys. Kondens. Mater. 9, 283 (1969).

[3] P. B. Allen and M. L. Cohen, Phys. Rev. B 1, 1329 (1970).

[4] J. J. Sabo, Phys. Rev. B 1, 1325 (1970).

[5] P. Goy, "Temperature Dependence of the Cyclotron Effective Mass and of the Relaxation Time in Lead" (to be published); I. Krasnopolin, to be published.

[6] W. L. MacMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), p. 561.

[7] Thomson-C. S. F. We particularly thank Dr. A. Schaer for his very helpful collaboration.

[8] Y. Couder and P. Goy, in *Proceedings of the International Symposium on Submillimeter Waves, Brooklyn, N. Y., 31 March-2 April 1970* (Polytechnic, Brooklyn, 1970).

[9] Y. Sharvin and V. F. Gantmakher, Cryogen. 5, 278 (1965).

[10] Cominco.

[11] Mercure Industrie.

[12] R. T. Mina and M. S. Khaikin, Zh. Eksp. Teor. Fiz. 45, 1304 (1963) [Sov. Phys. JETP 18, 896 (1964)].

[13] R. G. Chambers, Proc. Phys. Soc., London 86, 305 (1965).

[14] A. E. Dixon and W. R. Datars, Phys. Rev. 175, 928 (1968).

[15] A. F. Kip, D. N. Langenberg, and T. W. Moore, Phys. Rev. 124, 359 (1961).

[16] P. Haussler and S. J. Welles, Phys. Rev. 152, 675 (1966).

[17] P. Goy and G. Weisbuch, Phys. Kondens. Mater. 9, 200 (1969).

RAMAN SCATTERING IN RESONANCE WITH THE EXCITON TRANSITION IN PURE POLAR CRYSTALS*

E. Mulazzi†
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 26 May 1970)

A study of the Raman scattering near resonance with the exciton transition in pure polar crystals is presented. The following conclusions are obtained, independently of the crystal symmetry: (I) The resonant Raman spectra should show multiphonon structures at energy multiples of the first-order peak. The repetition of the peaks depends on the strength of the exciton-phonon coupling. (II) For the case of large-radius excitons, these spectra should show the same peaks for any polarization of the light.

In pure crystals, Raman scattering spectra far from resonance with an electronic transition have been always interpreted by following the usual selection rules.[1] Here we show that for the Raman scattering in resonance with the exciton transition in a pure polar crystal, the usual selection rules are no longer applicable. Rather, the following conclusions are reached: (I) Resonant Raman spectra should show multiphonon structures at energy multiples of the first-order peak. The repetition of the peaks depends on the strength of the exciton-phonon linear interaction. (II) For the case of large-radius excitons, these spectra should show the same peaks for any polarization of the light. These properties depend only on the conservation of the total momentum of the exciton-phonon system so that in pure polar crystals of high symmetry like O_h, the Raman-scattering spectra in resonance with the exciton transition should show these peculiarities. Under opportune resonance conditions these spectra should, therefore, give much information both on the crystal lattice dynamics seen by the exciton and on the exciton-phonon coupling, even when such information is not readily available from absorption and excitation spectra.

In the present work, we study Raman scattering in resonance with the exciton transition in the framework of the adiabatic approximation by extending the theory for defect-induced resonance Raman scattering.[2] We consider the properties of the Raman scattering in resonance with those excitons for which only the "diagonal"[3] part of the linear interaction with the phonons is strong. A detailed investigation[4,5] of the exciton absorption bands justifies this assumption. In polar crystals these excitons are characterized by a large radius and a large difference between the effective masses for the hole and the electron. In the following discussion, we restrict our attention to this kind of exciton. A more extended theory, including the effects on Raman-scattering structures due to the change of the lattice dynamics by the exciton-phonon interaction,[6] will be presented in a forthcoming paper.[7]

It is well known that the function $i_{\alpha\gamma,\beta\delta}(\omega_0\Omega)$, which determines the intensity of the scattered radiation, is connected with the polarizability tensor $P_{\alpha\gamma}$ in the following way:

$$i_{\alpha\gamma,\beta\delta}(\omega_0\Omega)=\sum_{v v'} w(v)\,\langle v'|P_{\alpha\gamma}{}^*|v\rangle\,\langle v|P_{\beta\delta}|v'\rangle\,\delta(\omega-\omega_{v v'}). \tag{1}$$

In this equation ω_0 and Ω are the incident and scattered radiation frequencies, $w(v)$ is the Boltzmann factor, $\Omega-\omega_0=\omega$, and $\omega_{vv'}=E_0{}^v-E_0{}^{v'}$; $E_0{}^{v(v')}$ denotes the vibrational energy of the v, v' level in the ground electronic state $|0\rangle$. The tensor $P_{\alpha\gamma}$ may be written as

$$P_{\alpha\gamma}=\sum_{n v''}\left\{\frac{\langle 0|M_\gamma|nv''\rangle\langle nv''|M_\alpha|0\rangle}{\Omega_{n0}{}^0+\omega_{v''v}-\omega_0+\frac{1}{2}i\gamma_n}+\frac{\langle 0|M_\alpha|nv''\rangle\langle nv''|M_\gamma|0\rangle}{\Omega_{n0}{}^0+\omega_{v''v}+\omega_0+\frac{1}{2}i\gamma_n}\right\}, \tag{2}$$

where $\vec{\mathrm{M}}$ is the dipole-moment operator, $|nv''\rangle$ denotes the excited electronic and vibrational states, $\Omega_{n0}{}^0$ is the pure electronic transition energy, and γ_n is the radiative width of the excited electronic level. The electronic transition causes a change in the electron-phonon linear interaction and the resultant change in the system Hamiltonian is denoted by $\omega_{v''v}$. When the exciting frequency is in resonance with the exciton absorption due to the direct transition $|0\rangle\to|1\rangle$, we must consider all the contributions to the polarizability coming from the change in the Hamiltonian of the system. Equation (1) becomes

$$i_{\alpha\gamma,\beta\delta}(\omega_0\Omega)=\langle 0|M_\gamma{}^0|1\rangle\langle 1|M_\alpha{}^0|0\rangle\langle 0|M_\delta{}^0|1\rangle\langle 1|M_\beta{}^0|0\rangle\sum_{v v' v''} w(v)\left|\frac{\langle v|v''\rangle\langle v''|v'\rangle}{\omega_{v''v}+\Omega_{10}{}^0-\frac{1}{2}i\gamma_1}\right|^2\delta(\Omega-\omega_0+\omega_{vv'}). \tag{3}$$

Since we study the Raman scattering in resonance with an exciton direct transition, the sum over n in Eq. (2) drops out and only electric dipole matrix elements are considered. Moreover, by using the integral representation for the δ function and recalling that $(\epsilon-\frac{1}{2}i\gamma)^{-1}=-i\int_0^\infty dt\exp\{-(i\epsilon+\frac{1}{2}\gamma)t\}$, (3) can be written

$$\begin{aligned}i_{\alpha\gamma,\beta\delta}(\omega_0,\Omega)={}&(1/2\pi)\,\langle 0|M_\gamma{}^0|1\rangle\langle 1|M_\alpha{}^0|0\rangle\langle|M_\delta{}^0|1\rangle\langle 1|M_\beta{}^0|0\rangle\\&\times\int_{-\infty}^{+\infty}d\mu\int_0^\infty dt\int_0^\infty dt'\exp\{i\Omega\mu-i\omega_0(\mu+t'-t)-\tfrac{1}{2}\gamma_1(t+t')\}B(t,t',\mu),\end{aligned} \tag{4}$$

where

$$B(t,t',\mu)=\frac{\mathrm{Tr}\langle e^{it'H_1}e^{i\mu H_0}e^{-itH_1}e^{-i(\mu+t'-t)H_0}e^{-H_0/kT}\rangle}{\mathrm{Tr}\langle e^{-H_0/kT}\rangle}, \tag{5}$$

t is the time related to the absorption process, t' is the time for the inverse process, and μ is the time of the Raman scattering response; H_0 is the Hamiltonian for the electronic and vibrational ground state,

$$H_1=E_{\mathrm{exc}}+\sum_{\vec{q}j}\omega_{\vec{q}j}(b_{\vec{q}j}{}^\dagger b_{\vec{q}j}+\tfrac{1}{2})+\sum_{qj}(V_{\vec{q}j}b_{\vec{q}j}+\mathrm{H.c.})\quad(\hbar=1).$$

Here $E_{\text{exc}} = \langle \varphi(\vec{r}_e, \vec{r}_h) | H_{\text{eff}}^{\text{exc}} | \varphi(\vec{r}_e, \vec{r}_h) \rangle$, $H_{\text{eff}}^{\text{exc}}$ is the effective Hamiltonian for the exciton in the rigid lattice, $\varphi(\vec{r}_e, \vec{r}_h) = \psi(\vec{r})\chi(\vec{R})$, where e and h indicate the electron and hole particles, with effective masses m_e and m_h, and coordinates $\vec{r}_e$ and $\vec{r}_h$, respectively; $\vec{r}$ and $\vec{R}$ are, respectively, the exciton relative coordinate and the center-of-mass coordinate. $V_{\vec{q}j}$ is the interaction between the electron-hole pair and the $\vec{q}j$ phonon; $b_{\vec{q}j}$ and $b_{\vec{q}j}{}^\dagger$ are the creation and annihilation operators of the phonon of wave vector $\vec{q}$; j designates the vibrational branches; and $\omega_{\vec{q}j}$ are the frequencies of the phonon modes. We consider first the electron-hole pair interacting with LO phonon field according to the Fröhlich interaction. With this assumption,

$$V_{\vec{q}j} \equiv V_{\vec{q}} = \left[\frac{\omega_{\text{LO}}}{4\pi}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\right]^{1/2} [A_{\vec{q}}{}^e - A_{\vec{q}}{}^h]$$

and $\omega_{\vec{q}j} \equiv \omega_{\text{LO}}$; $A_{\vec{q}}{}^{e(h)}$ are the Fourier transform of

$$A^{e(h)}(\vec{r}\,') = e\left\langle \varphi(\vec{r}_e, \vec{r}_h) \left| \frac{|\vec{r}_{e(h)} - \vec{r}\,'|}{(r_{e(h)} - r')^3} \right| \varphi(\vec{r}_e, \vec{r}_h) \right\rangle.$$

Whether or not the study of the exciton-phonon interaction requires a more careful examination of the discrete properties of the lattice, as for instance in alkali-halide crystals, it is not possible to consider the lattice as a continuous polarizable dielectric. So in the present case the $V_{\vec{q}j}$'s are related to the forces $[\vec{F}^e(\vec{x}_{lk}) - \vec{F}^h(\vec{x}_{lk})]$ that the electron-hole pair exerts on the lk ions through the standard transformation from the $\vec{u}_{lk}$ space to the $\vec{q}$ space.[8] ($\vec{x}_{lk}$ are the equilibrium positions of the lk ions in the ground state.) By performing the evaluation of Eq. (5), it is found that

$$B(t, t', \mu) = \exp[i\Omega_{\text{exc}}{}^0(t'-t)] \exp\{g^*(t) + g(t') + g(\mu) + g(\mu + t' - t) - g(\mu - t) - g(\mu + t')\},$$

where $\Omega_{\text{exc}}{}^0$ is the exciton frequency for the direct transition, and the g functions are given by

$$g(s) = A\{e^{i\omega_{\text{LO}}s}[n_T(\omega_{\text{LO}}) + 1] + e^{-i\omega_{\text{LO}}s} n_T(\omega_{\text{LO}}) - [2n_T(\omega_{\text{LO}}) + 1]\}, \tag{6}$$

$$n_T(\omega) = [\exp(\omega/kT) - 1], \quad A = (4\pi\omega_{\text{LO}})^{-1}(\epsilon_\infty{}^{-1} - \epsilon_0{}^{-1}) |\textstyle\sum_q [A_q{}^e - A_q{}^h]|^2;$$

or

$$g(s) = \int_0^\infty A_{\Gamma_1}{}^2(\omega)\{e^{i\omega s}[n_T(\omega) + 1] + e^{-i\omega s} n_T(\omega) - [2n_T(\omega) + 1]\} \rho_{\Gamma_1}{}^0(\omega) d\omega. \tag{6'}$$

Here, $A_{\Gamma_1}(\omega) = F_{\Gamma_1}(2\omega^3)^{-1/2}$, and F_{Γ_1} are the Γ_1 components of the forces (normalized to the ion masses) that the electron-hole pair exerts on the surrounding lattice. (Γ_1 is the identity representation in the O_h group.) $\rho_{\Gamma_1}{}^0(\omega)$ is the Γ_1 unperturbed crystal phonon density of states in the region of the crystal in which the electron-hole pair applies non-negligible forces. Only the forces transforming as the Γ_1 representation are different from zero; in fact, we find that the large-radius exciton[9] couples mainly with the phonons of the Γ_1 density of states when $n = 1$ as well as when $n = 2$. (See, for instance, the experimental results for $n = 1$ and $n = 2$ exciton absorption bands in KI and LiI, respectively, in Ref. 4.) In order to obtain the intensity of the pth-order Raman scattering, we have to evaluate the integral in Eq. (4). First we consider the g function given by Eq. (6). We obtain for the Stokes Raman spectra

$$i_{\alpha\gamma,\delta\beta}(\omega_0\Omega) = (M_\gamma{}^0)_{01}(M_\alpha{}^0)_{10}(M_\delta{}^0)_{01}(M_\beta{}^0)_{10} \sum_{p=1}^{\infty} C_p \,\delta(\Omega - \omega_0 + p\omega_{\text{LO}}). \tag{7}$$

Here the C_p coefficients at $T = 0°\text{K}$ are given by

$$C_p = \frac{(A)^p}{p!} \left| \sum_{s=0}^{p} (-1)^s \binom{p}{s} \Phi(\omega_0 - s\omega_{\text{LO}}) \right|^2. \tag{7'}$$

Here $\Phi(x) = \text{P}\int_{-\infty}^{+\infty} [I(\omega)/(\omega - x)] d\omega + i\pi I(x)$; $I(x)$ is the normalized absorption intensity at the frequency x and zero temperature. Note that if the polarization is changed there is no substantial change in the Raman spectra, because the C_p coefficients and the structures at ω_{LO} frequency are polarization independent. For all polarizations, the spectra should show the structures at the same frequencies. It must be emphasized, of course, that this conclusion applies exactly when $\omega_0 > \Omega_{\text{exc}}{}^0$.

By considering the g functions in Eq. (6′), the following intensities for the first- and second-order

Raman scattering at $T = 0°\mathrm{K}$ are obtained:

$$i^{(1)}(\omega_0, \Omega) \propto A_{\Gamma_1}{}^2(\Omega)\rho_{\Gamma_1}{}^0(\Omega)\left|\sum_{s=0}^{1}(-)^s\Phi(\omega_0 - s\Omega)\right|^2,$$

$$i^{(2)}(\omega_0, \Omega) \propto \tfrac{1}{2}\left\{\int_0^{+\infty} d\omega\, A_{\Gamma_1}{}^2(\omega) A_{\Gamma_1}{}^2(\Omega-\omega)\rho_{\Gamma_1}{}^0(\Omega-\omega)\rho_{\Gamma_1}{}^0(\omega)\left|\Phi(\omega_0) + \Phi(\omega_0 - \Omega) - \Phi(\omega_0 + \omega - \Omega) - \Phi(\omega_0 - \omega)\right|^2\right\}. \quad (8)$$

From Eqs. (7), (7′), and (8) it is possible to see that the most important features of resonance Raman scattering depend on features other than the peculiarities of the Γ_1 densities and the delta peaks in $\Omega - \omega_0 = p\omega_{\mathrm{LO}}$. Consider for simplicity Eqs. (7) and (7′), although similar conclusions follow from Eq. (8). From these equations it is possible to see that the multiphonon scattering induced by the exciton-phonon interaction would be observed only when A is not small and the ω_0 frequency is in resonance, i.e., the p order of scattering induced by the interaction should be observed when, to this order, $\Phi(\omega_0 - p\omega_{\mathrm{LO}})$ and $A^p/p!$ are different from zero. It is also possible to predict a particular peak in the intensity of the p-order scattering, whether $\Phi(\omega_0 - p\omega_{\mathrm{LO}})$ has its maximum at (or near) this frequency, provided p is of low order. Usually $\Phi(x)$ for exciton transitions considered here has a maximum at the pure exciton frequency $\Omega_{\mathrm{exc}}{}^0$. A maximum in the intensity at or near to the pure exciton frequency should then be observed when the resonant frequency ω_0 is near $\Omega_{\mathrm{exc}}{}^0$, or larger than $\Omega_{\mathrm{exc}}{}^0$ by a few times the phonon frequencies. When $\omega_0 \lesssim \Omega_{\mathrm{exc}}{}^0$ we have to consider two different cases for the polarized spectra: (I) when the one-phonon scattering due to the ω_{LO} phonon is forbidden off resonance, and (II) when the one-phonon scattering due to the ω_{LO} phonon is allowed off resonance. In the first case the resonance-scattering process at ω_{LO} is determined only by the exciton-phonon interaction considered here, and the intensity of this process increases in going towards the resonance condition with the direct transition. To obtain the appropriate intensity law for the scattering processes in the second case, a study of a more complicated correlator than that shown in Eq. (5) is required. If the effect of exciton-phonon coupling on indirect transitions is included in the correlator, then we find that only the $2\omega_{\mathrm{LO}}$ scattering intensity increases on approaching resonance, whereas the ω_{LO} scattering intensity can decrease. Whether or not the frequency ω_0 remains in resonance with the exciton transition when the system temperature is increased, it should be noted that for a given ω_0, the spectral intensities change with an increase in temperature because of both the change in the phonon population and the temperature dependence of $\Phi(x)$.

It seems that some peculiarities of the Raman scattering spectra[10,11] in CdS may be explained by means of Eq. (7) and the above conclusions about the features of the Raman-scattering response. This follows from a consideration of the I_1 trapped exciton-phonon coupling, the interaction between the continuum excitons and the phonons, and the change of $\Omega_{\mathrm{exc}}{}^0(T)$ of the excitons with the temperature.

We thank Professor J. A. Krumhansl for helpful comments on the manuscript.

---

*Research sponsored by a North Atlantic Treaty Organization—Consiglio Nazionale delle Richerche Fellowship. Additional support received from the U. S. Atomic Energy Commission through Contract No. AT(30-1)-3699, NYO-3699-48.

†On leave from Istituto di Fisica dell'Università, Milano, Italy.

[1] R. Loudon, Advan. Phys. 13, 423 (1964).

[2] A. T. Lubchenko and B. P. Pavlik, Fiz. Tverd. Tela 5, 1714 (1963) [Sov. Phys. Solid State 5, 1246 (1964)].

[3] E. Mulazzi, G. F. Nardelli, and N. Terzi, Phys. Rev. 172, 847 (1968).

[4] G. Baldini, A. Bosacchi, and B. Bosacchi, Phys. Rev. Lett. 23, 846 (1969).

[5] See papers quoted in Ref. 4.

[6] These effects are mainly important for the Raman scattering in resonance with $n = 1$ exciton transition in alkali halides, if the $n = 1$ exciton radius is not large.

[7] E. Mulazzi, to be published.

[8] A. A. Maradudin, E. W. Montroll, and G. M. Weiss, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1963), Suppl. 3.

[9] When the radius of the exciton in alkali-halide crystals is not large, other force components are expected to be different from zero.

[10] J. F. Scott, R. C. C. Leite, and T. C. Damen, Phys. Rev. 188, 1285 (1969). Note particularly Fig. 7 and the related discussion.

[11] See papers quoted in Ref. 10.