Resonant Raman Scattering from LO Phonons in Polar Semiconductors*

DAVID C. HAMILTON
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173
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Multiphonon Raman scattering from LO phonons has previously been observed in CdS in the case where the laser frequency lies near the energy gap. The combined effects of finite wave vector and resonant energy denominators are offered as the explanation for certain features of the scattering. These features include the unusual polarization properties of the single-phonon scattering and the unexpected sharpness of the two-phonon line. The effects of the Fröhlich interaction are calculated in lowest-order perturbation theory under the assumption of spherical, parabolic bands. The important part of the scattering amplitude is due to terms where the laser is resonant to interband transitions. Since the parameter qv/ω_l is of order unity, the dipole approximation $q \to 0$ is not applicable. (Here v is the electron velocity at that point in the zone where the laser can cause real transitions.) In the single-phonon scattering, $\mathbf{q}$ is the difference between the wave vectors of the incident and scattered photons, while for the double-phonon case, $\mathbf{q}$ is the wave vector of one of the two final-state phonons. No exciton effects are included. The temperature is taken to be zero throughout.

INTRODUCTION

An observation has been made by Leite and Porto[1] of Raman scattering in CdS at integral or nearly integral multiples n of the longitudinal optical-phonon frequency $n=1, 2, 3, 4$. For convenience, a line which occurs at a frequency n times the fundamental LO frequency, or nearly so, is referred to as the n-LO line. Subsequently, Leite, Scott, and Damen[2] have observed harmonics as high as $n=9$. A large number of harmonics is observed when the laser frequency does not differ from the energy-gap frequency by more than a few multiples of the LO frequency ω_l. Leite *et al.* also stated that the frequency of the second harmonic is about 1% less than exactly twice the fundamental LO frequency.[2a] Our treatment implies that the shift of the 2-LO line should be less than this and should be a function of laser frequency.

A number of authors[3-5] have found deviations from the usual polarization selection rules in that 1-LO scattering is observed when incident and scattered light have parallel polarization vectors in a geometry where this would not be expected. Pinczuk and Burstein[5] have presented convincing evidence that this can be caused by a surface electric field. Here we give an alternative mechanism whereby 1-LO scattering can occur with $\epsilon_1 \| \epsilon_2$.

In all these experiments, the 2-LO line and higher harmonics are quite sharp. If LO phonons from the entire Brillouin zone were participating in the scattering, one may conclude from the dispersion curve of Nusimovici and Birman[6] that the 2-LO line would be as broad as 50 cm^{-1}. Leite *et al.* have concluded that only zone-center phonons participate in the scattering, while Klein and Porto did not assign the multiphonon features to the zone center. Our treatment gives heavy weight to zone-center phonons.

In order to explain these facts, Leite *et al.*[2] had suggested that virtual photon absorption followed by n-fold iteration of the usual Fröhlich interaction might account for the n-LO line. This is, in fact, the approach taken here, except that we allow one or both of the two interband transitions to be real (energy-conserving), and we retain finite wave vector. Since it has been demonstrated[2,3] that exciton effects are important for the relative magnitude of the various n-LO lines, there is no doubt that exciton effects should be included in an accurate treatment. However, it is argued here that the striking features of the scattering mentioned above are not primarily dependent on exciton effects, and no such effects are included.

ONE-PHONON SCATTERING

We start from the usual Fröhlich Hamiltonian supplemented by th einteraction between the electrons and the radiation field, and the Hamiltonian of the free radiation field. In this approach, the electrons interact with LO phonons only via their electric field, and the deformation potential coupling is ignored. Only one-band (intraband) matrix elements of the Fröhlich interaction are retained, just as is usually done in the effective-mass treatment of the polaron problem. This procedure has the practical advantage that it simplifies the calculation, since fewer terms need be retained. The one-band matrix elements of the Fröhlich interaction

* Work sponsored by the U. S. Air Force.
[1] R. C. C. Leite and S. P. S. Porto, Phys. Rev. Letters **17**, 10 (1966).
[2] R. C. C. Leite, J. F. Scott, and T. C. Damen, Phys. Rev. Letters **22**, 780 (1969); R. C. C. Leite, T. C. Damen, and J. F. Scott, in *Proceedings of the International Conference on Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer-Verlag, New York, 1969), p. 359.
[2a] This effect in CdS has subsequently been ascribed to anisotropy. See J. F. Scott *et al.*, Phys. Rev. **188**, 1285 (1969).
[3] M. V. Klein and S. P. S. Porto, Phys. Rev. Letters **22**, 782 (1969).
[4] R. C. C. Leite and J. F. Scott, Phys. Rev. Letters **22**, 130 (1969).
[5] A. Pinczuk and E. Burstein, Phys. Rev. Letters **21**, 1073 (1968).
[6] M. A. Nusimovici and J. L. Birman, Phys. Rev. **156**, 925 (1967), Fig. 10.

do make a contribution to the Raman scattering even when the laser frequency and wave vector tend to zero.[7]

$$\mathcal{H}=\mathcal{H}_0+V,$$

$$\mathcal{H}_0=\sum_{\mathbf{p}n}\epsilon_{\mathbf{p}n}c_{\mathbf{p}n}^{\dagger}c_{\mathbf{p}n}+\sum_{\mathbf{q}}\omega_l b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}}+\sum_{\mathbf{k}}\omega(k)a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}},$$

$$V=V_F+V_{\mathrm{rad}},$$

$$V_F=\sum_{\mathbf{q}\mathbf{p}n}V(q)(b_{\mathbf{q}}-b_{-\mathbf{q}}^{\dagger})c_{\mathbf{p}+\mathbf{q}\,n}^{\dagger}c_{\mathbf{p}n},$$

$$V(q)=-(ie/|\mathbf{q}|)[2\pi\omega_l(1/\epsilon_\infty-1/\epsilon_0)]^{1/2},\quad \omega^2(k)=c^2k^2/\epsilon_\infty,$$

$$V_{\mathrm{rad}}=\frac{e}{m}\sum_{\mathbf{k}\mathbf{p}nn'}\left[\frac{2\pi}{\epsilon_\infty\omega(k)}\right]^{1/2}(\mathbf{p}+\mathbf{k}\,n|e^{i\mathbf{k}\cdot\mathbf{x}}\hat{\epsilon}_{\mathbf{k}}\cdot\mathbf{p}|\mathbf{p}n')\times(a_{\mathbf{k}}+a_{-\mathbf{k}}^{\dagger})c_{\mathbf{p}+\mathbf{k}\,n}^{\dagger}c_{\mathbf{p}n'}.$$

In the above, factors of $\hbar$ and the volume of the system have not been written explicitly. Strictly speaking, V_{rad} should contain another term quadratic in the photon operators a, $a^{\dagger}$; but this term does not contribute to our calculation, and it has been dropped. Polarization indices have been dropped from the photon operators. The electron operators are $c^{\dagger}$, c; the phonon operators are $b^{\dagger}$, b. We calculate the scattering efficiency in perturbation theory with two orders in V_{rad} and one additional order in V_F for each phonon.

In the initial and final states, the system is in its ground state as far as the electrons are concerned. Hence the first and last transitions must be interband transitions, and these can only be due to V_{rad}, since V_F has no interband terms. Thus, for the 1-LO process, the dimensionless scattering amplitude is

$$M_{fi}^{\mathrm{LO}}=(-i)^3\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\times\langle f|V_{\mathrm{rad}}(t_1)V_F(t_2)V_{\mathrm{rad}}(t_3)|i\rangle,$$

$$|i\rangle=|n_1\rangle,\quad |f\rangle=a_{k_2}^{\dagger}b_{\mathbf{q}}^{\dagger}|n_1-1\rangle,$$

$$V_F(t)=e^{iH_0t}V_Fe^{-iH_0t}.$$

Here, a photon of frequency and wave vector ω_1, $\mathbf{k}_1$ scatters to ω_2, $\mathbf{k}_2$ with emission of a phonon of wave vector $\mathbf{q}$; $|n_1\rangle$ is the state in which there are n_1 photons present and the electronic system is in its ground state. Since the incident and scattered photons are assumed to be in plane-wave states, we implicitly assume that the imaginary part of the optical dielectric constant is less than the real part.

Third-order perturbation theory involves two energy denominators. We assume that the laser frequency is greater than the energy gap and pick out only that part of M_{fi}^{LO} where at least one of the energy denominators vanishes. Loudon[8] has given a discussion of resonant Raman scattering using the principal value part of an expression like $(\epsilon_{\mathbf{p}n}-\epsilon_{\mathbf{p}n'}-\omega_1-i\eta)^{-1}$, while we are using the δ-function part. We evaluate the momentum matrix elements at the center of the Brillouin zone, and this will not be a bad approximation if the laser frequency is not too much greater than the energy gap. Furthermore, we expand terms in the energy denominator for small but finite photon wave vector, e.g., $\epsilon_{\mathbf{p}+\mathbf{k}_1}\cong\epsilon_{\mathbf{p}}+\mathbf{k}_1\cdot\nabla_{\mathbf{p}}\epsilon_{\mathbf{p}}=\epsilon_{\mathbf{p}}+\mathbf{v}\cdot\mathbf{k}_1$.

With these approximations we obtain

$$M_{fi}^{\mathrm{LO}}=-V(q)\frac{e^2}{m}\frac{2\pi^2n_1^{1/2}}{\epsilon_\infty(\omega_1\omega_2)^{1/2}}2\pi\delta(\omega_2+\omega_l-\omega_1)\delta_{\mathbf{q},\mathbf{k}_1-\mathbf{k}_2}\sum_{nn'}f_n(1-f_{n'})\frac{(n|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|n')(n'|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|n)}{m}$$

$$\times\sum_{\mu}\left[\left(\frac{1}{\omega_l-\mathbf{q}\cdot\mathbf{v}'}-\frac{1}{\omega_l-\mathbf{q}\cdot\mathbf{v}}\right)[\delta(\epsilon_{\mathbf{p}n'}-\epsilon_{\mathbf{p}n}+\mathbf{k}_1\cdot\mathbf{v}-\omega_1)-\delta(\epsilon_{\mathbf{p}n'}-\epsilon_{\mathbf{p}n}+\mathbf{k}_2\cdot\mathbf{v}-\omega_2)]\right.$$

$$\left.+i\pi\delta(\epsilon_{\mathbf{p}n'}-\epsilon_{\mathbf{p}n}+\mathbf{k}_2\cdot\mathbf{v}-\omega_2)[\delta(\omega_l-\mathbf{q}\cdot\mathbf{v}')-\delta(\omega_l-\mathbf{q}\cdot\mathbf{v})]\right],$$

$$\mathbf{v}=\mathbf{v}_{n\mathbf{p}},\qquad \mathbf{v}'=\mathbf{v}_{n'\mathbf{p}}.$$

Here the factors $(\omega_l-\mathbf{q}\cdot\mathbf{v})^{-1}$ are to be interpreted as principal values. The various velocities are to be evaluated at that point in the band where the argument of the δ function vanishes. It is clear that M^{LO} has its major contribution when $\mathbf{e}_1\|\mathbf{e}_2$. A new polarization component is obtained, since M^{LO} depends on the new vector $\mathbf{q}$.

We express the result in terms of the dimensionless scattering efficiency[9] S^{LO}, defined as the number of scattered photons per incident photon:

$$M_{fi}=W_{fi}2\pi\delta(E_f-E_i),$$

$$S^{\mathrm{LO}}=\frac{L\epsilon_\infty^{1/2}}{n_1c}\sum_f|W_{fi}|^2 2\pi\delta(E_f-E_i).$$

For simplicity, we assume flat valence bands, i.e.,

[7] The cancellation of electron and hole contributions which has been mentioned in the literature actually does not occur, but results in the taking of a derivative of certain matrix elements with respect to crystal momentum.

[8] R. Loudon, J. Phys. (Paris) **26**, 677 (1965).

[9] Defined in R. Loudon, Proc. Roy. Soc. (London) **A275**, 218 (1963), Eq. (45).

$\mathbf{v}\to 0$. The factor involving interband matrix elements of $\mathbf{e}_2\cdot\mathbf{p}$ and $\mathbf{e}_1\cdot\mathbf{p}$ can be rewritten using the effective-mass sum rule.[10] Then we find

$$S^{\mathrm{LO}}=L\Delta\Omega(4/\pi)(m^*e^2/\hbar^2)(e^2/mc^2)^2q^2(1/\epsilon_\infty-1/\epsilon_0)\times[E_g^2/(\hbar\omega_l)^2](m/m^*-1)^2F(\omega_1),$$

$$F(\omega_1)=\left(\frac{m^*\omega_l}{2q^2}\right)^3\left[\left(\tfrac{1}{2}\ln\frac{|1+z_1|}{|1-z_1|}-\tfrac{1}{2}\ln\frac{|1+z_2|}{|1-z_2|}-z_1+z_2\right)^2+\tfrac{1}{4}\pi^2\theta(z_2-1)\right],$$

$$z_1^2=\frac{2\hbar q^2}{m^*\omega_l}\frac{\omega_1-E_g}{\omega_l},\qquad z_2^2=\frac{2\hbar q^2}{m^*\omega_l}\frac{\omega_1-E_g-\omega_l}{\omega_l}.$$

Here, $\theta(z)=1$ if $z>0$, and $\theta(z)=0$ if $z<0$. We assume that $z_1^2>0$ and $z_2^2>0$. The length of the crystal in the direction of the incident beam is L, and $\Delta\Omega$ is the solid angle over which the scattered light is collected. Let us consider parameters[11] for back scattering with 4579 Å light;

$$\epsilon_\infty=5.10,\quad q=6.2\times10^5\ \mathrm{cm}^{-1},\quad \omega_l/2\pi c=304\ \mathrm{cm}^{-1},$$
$$m^*/m=0.20,\quad \epsilon_0=8.87,\quad E_g=2.5\ \mathrm{eV},$$
$$2\hbar q^2/m^*\omega_l=0.078.$$

Then $S^{\mathrm{LO}}=(7.63\times10^{-3}\ \mathrm{cm}^{-1})\times L\times\Delta\Omega\times F_1(\omega_1)$, and the frequency-dependent factor $F_1(\omega_1)$ is shown in Fig. 1.

There is a sharp rise in $F_1(\omega_1)$ at the point where $qv_e=\omega_l$ with v_e in the conduction band.[12] If we had not assumed $v_h=0$ in the valence band, there would be a sharp decrease where $qv_h=\omega_l$.

TWO-PHONON SCATTERING

The significant feature of the 2-LO line is that it is so sharp[13]—much sharper than would be expected if phonons from the entire Brillouin zone participated in the scattering. It will be shown that the wave vectors of the two phonons involved in the 2-LO line are each required to be of order $\omega_l/v\sim10^5$–$10^6\ \mathrm{cm}^{-1}$, owing to the various weighting factors that occur in the scattering efficiency. This accounts for the sharpness of the line and implies that the 2-LO line should occur at slightly less than twice the zone-center frequency. This effect can be estimated as follows: Let the dispersion be described by

$$\omega(q_1)=\omega_l-Aq_1^2/2m,$$

where m is the free-electron mass and A is dimensionless. Here, q_1 is the wave vector of one of the two scattered phonons. If we assume $q_1v=\omega_l$ and $\frac{1}{2}m^*v^2=\omega_1-E_g$, which will be shown to be reasonable, then

$$\frac{\omega(q_1)-\omega_l}{\omega_l}\approx-\frac{1}{4}\frac{m^*}{m}A\frac{\omega_l}{\omega_1-E_g}.$$

This expression is not valid for $\omega_1-E_g<\omega_l$. One may estimate $A=0.006$ from the dispersion curves of Nusimovici and Birman.[6] This yields

$$[\omega(q_1)-\omega_l]/\omega_l=-0.03\%$$

for $\omega_1-E_g=\omega_l$. This is probably too small a deviation from exactly twice the zone-center frequency to show up in the experiments.

In an unpublished discussion,[14] Leite *et al.* emphasized the importance of wave-vector-dependent weighting factors, but their argument differed from that given here. They assumed that the phonon wave vector $\mathbf{q}_1$ was equal to the wave vector of the electron or hole in the pair created by the incident photon, rather than the difference between these wave vectors.

The scattering amplitude is given by

$$M_{fi}^{2\mathrm{LO}}=(-i)^4\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\int_{-\infty}^{t_3}dt_4,$$
$$\langle f|V_{\mathrm{rad}}(t_1)V_F(t_2)V_F(t_3)V_{\mathrm{rad}}(t_4)|i\rangle,$$
$$|i\rangle=|n_1\rangle,\quad |f\rangle=a_{\mathbf{k}_2}{}^\dagger b_{\mathbf{q}_1}{}^\dagger b_{\mathbf{q}_2}{}^\dagger|n_1-1\rangle.$$

The two final-state phonons have wave vectors $\mathbf{q}_1$ and $\mathbf{q}_2$.

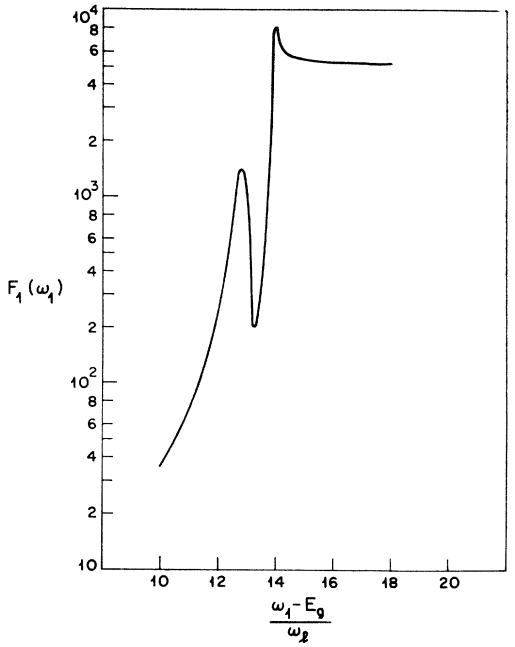

FIG. 1. Frequency dependence of the one-phonon scattering. A more realistic calculation with finite relaxation time would show a smooth rise instead of the structure shown here.

[10] C. Kittel, *Quantum Theory of Solids* (Wiley-Interscience, Inc., New York, 1963), p. 186.

[11] Parameters for CdS are quoted in B. Segall, Phys. Rev. **163**, 769 (1967).

[12] R. Martin (private communication) on some properties of $F(\omega_1)$.

[13] A. Pine (private communication).

[14] R. C. C. Leite, J. F. Scott, and T. C. Damen (private communication).

For simplicity we take the limit $\mathbf{k}_1, \mathbf{k}_2 \to 0$, thus making a dipole approximation for the radiation. As before, we write $\epsilon_{\mathbf{p}+\mathbf{q}} \to \epsilon_{\mathbf{p}}+\mathbf{q}\cdot\mathbf{v}$ and assume constant momentum matrix elements. We assume flat valence bands, and we only consider terms which have at least one resonant energy denominator:

$$M_{fi}^{2\mathrm{LO}} = -4\pi^2 \frac{e^2}{m}\frac{n_1^{1/2}}{\epsilon_\infty(\omega_1\omega_2)^{1/2}} V(q_1)V(-q_1)2\pi\delta(\omega_2+2\omega_l-\omega_1)\delta(\mathbf{q}_1+\mathbf{q}_2)\frac{1}{m}\sum_{nn'} f_{n'}(1-f_n)(n'|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|n)(n|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|n')$$

$$\times\Bigg\{\sum_{\mathbf{p}}[\delta(\epsilon_{\mathbf{p}n}-\epsilon_{\mathbf{p}n'}-\omega_2)+\delta(\epsilon_{\mathbf{p}n}-\epsilon_{\mathbf{p}n'}-\omega_1)]\left(\frac{1}{2\omega_l}-\frac{1}{2\omega_l+\mathbf{q}_1\cdot\mathbf{v}}\right)\left(\frac{1}{\omega_l}+\frac{1}{\omega_l+\mathbf{q}_1\cdot\mathbf{v}}\right)-\sum_{\mathbf{p}}\delta(\epsilon_{\mathbf{p}n}-\epsilon_{\mathbf{p}n'}-\omega_1+\omega_l)$$

$$\times\left(\frac{1}{\omega_l}-\frac{1}{\omega_l+\mathbf{q}_1\cdot\mathbf{v}}\right)\left(\frac{1}{\omega_l}-\frac{1}{\omega_l-\mathbf{q}_1\cdot\mathbf{v}}\right)+\frac{i\pi}{2\omega_l}\sum_{\mathbf{p}}[\delta(\epsilon_{\mathbf{p}n}-\epsilon_{\mathbf{p}n'}-\omega_2)-\delta(\epsilon_{\mathbf{p}n}-\epsilon_{\mathbf{p}n'}-\omega_1)]\delta(\omega_l-\mathbf{q}_1\cdot\mathbf{v})\Bigg\}.$$

After the scattering amplitude is squared, the sum over final states involves an integral over q_1. Each factor $V(q_1)$ contributes q_1^{-1}, so that at large q_1, the integral converges at least as fast as $\int q_1^2 dq_1 q_1^{-4}$. This heavy weighting of zone-center phonons is characteristic of the Frohlich interaction and would not be true of the deformation potential interaction. If the assumption of flat valence bands had not been made, i.e., $q_1 v'/\omega_l \to 0$, the term in curly brackets would decrease as q_1^{-1} for large q_1 rather than q_1^0, giving an additional q_1^{-2} dependence when squared. We have, then, finally for the integrated scattering efficiency

$$S^{2\mathrm{LO}} = L\Delta\Omega(1/2\pi^2)(e^2/mc^2)^2(1/\epsilon_\infty-1/\epsilon_0)^2(2\omega_l m^*/\hbar)^{3/2}$$
$$\times(e^4m^*/\hbar^3\omega_l)(E_g/\hbar\omega_l)^2(m/m^*-1)^2F_2(\omega_1)$$
$$=\Delta\Omega\times LF_2(\omega_1)\times(2.47\times10^{-2}\ \mathrm{cm}^{-1}),$$

$$F_2(\omega_1)=\left(\frac{\omega_1-E_g}{\omega_l}\right)^{3/2}\int_0^\infty\frac{dx}{x^4}\{[g(x)+g(x\cdot R_1)-2g(x\cdot R_2)]^2$$
$$+\tfrac{1}{4}\pi^2[\theta(x-1)-\theta(x\cdot R_1-1)]^2\},$$

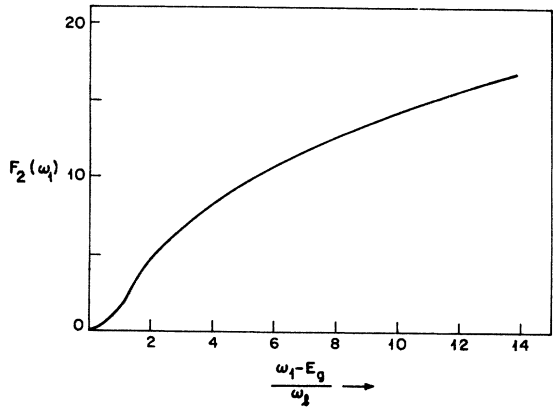

FIG. 2. Frequency dependence of the two-phonon scattering.

$$g(x)=x-\tfrac{1}{2}\ln\frac{|1+x|}{|1-x|},$$

$$R_1=[1-2\omega_l/(\omega_1-E_g)]^{1/2},\quad R_2=[1-(\omega_l/\omega_1-E_g)]^{1/2}.$$

In the integration over q_1 we have changed variables to $x=q_1v/\omega_l$. The dependence of $F_2(\omega_1)$ on laser frequency is shown in Fig. 2.

The fact that many LO phonon lines are observed and that the polaron coupling constant α is 1.4 in CdS suggest that lowest-order perturbation theory is not quantitatively reliable.

SUMMARY

The presence of 1-LO scattering when $\mathbf{e}_1\|\mathbf{e}_2$ and the sharpness of the 2-LO line can be explained in terms of finite wave-vector effects caused by resonance in one or more of the energy denominators. Finite wave vector effects are important since the relevant parameter is qv/ω_l rather than qa, where a is a lattice constant. The frequency of the 2-LO line is found to be slightly shifted from twice the zone-center frequency. The fact that zone-center phonons are heavily weighted indicates that the electron-phonon coupling occurs via the Fröhlich interaction.

In the present treatment, no account has been taken of a surface electric field, which can also cause deviations from the usual 1-LO selection rules.[5]

In the present approach, the scattering efficiency should increase monotonically as the laser frequency increases above the energy gap. However, the measurements[1] indicate that S peaks near $\omega_1=E_g$ for CdS and then decreases. This discrepancy in the frequency dependence is then a failure of the theory.

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