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# Multiphonon processes in YbS

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The resonance of the Raman scattering by the 1 LO(Γ) phonon and its overtones has been investigated in YbS. The results are interpreted in terms of a configuration-coordinate model which considers a strongly interacting exciton–LO-phonons system. The model is also able to account for multiphonon structure in the wavelength-modulated reflectance. The phonon energy observed in the reflectance spectrum is, however, somewhat smaller than that observed in Raman scattering, a fact which is attributed to a frequency renormalization in the excited state of the exciton.

## I. INTRODUCTION

The Yb$X$ ($X$ = S, Se, Te) compounds crystallize in the rocksalt structure where the optical phonons at $q = 0$ have odd parity and thus are Raman inactive. The interest in light-scattering experiments for the Yb monochalcogenides originated in the work of Vitins and Wachter[1,2] who showed that these compounds exhibit features similar to those of the magnetic fcc Eu monochalcogenides. Both families of compounds show strong first-order Raman scattering (RS) and, in addition, multiphonon structures at energy multiples of the first-order peak.[3,4] In the paramagnetic phase of the Eu compounds the first-order peak appears at a frequency $\Omega_0 \simeq \Omega_{\mathrm{LO}}(L)$ implying a breakdown of $\vec{k}$ conservation.[4] Vitins and Wachter reported the observation of a somewhat similar breakdown of $\vec{k}$ conservation for the Yb$X$ compounds in RS experiments.[1,2] These authors reported structure centered between the TO(Γ) and LO(Γ) phonon frequencies in YbTe.[1,2] Moreover, they also observed a shift in the first-order peak frequency with exciting laser energy in YbS.[1] The apparent similarities in the light-scattering experiments of both families of compounds led Vitins and Wachter to invoke a common mechanism in order to explain the various features of both Eu and Yb monochalcogenides.[1,2] They considered a modified version of the "cascade model"[5] in order to account for the origin of the multiphonon processes. Moreover, a lattice relaxation as well as a localization of the excited $d$ electron was invoked in order to explain the breakdown in $\vec{k}$ conservation.[1,2] The apparent similar behavior of the Yb and Eu monochalcogenides noticed by Vitins and Wachter, however, appears questionable in the light of considerable experimental and theoretical evidence[3,4,6-8] which indicates that the unusual features observed in RS in the paramagnetic phase of the Eu monochalcogenides originate in the disorder of spins as originally proposed by Tsang *et al.*[3] Clearly such an origin cannot explain the breakdown of translational symmetry in the diamagnetic Yb$X$ compounds.

In this work we present measurements of the reflectivity in the visible and infrared, RS and resonant RS spectra in YbS and YbTe. No evidence for the previously reported[1,2] breakdown in $\vec{k}$ conservation could be observed. We show that the breakdown of Raman selection rules is the same as that observed in many other polar compounds (i.e., "forbidden" LO scattering) which is due to an effect dependent upon the finite wave vector of the light.[9] Moreover, we report the observation of multiphonon processes in the optical reflectivity spectrum of YbS. We find that the results can be quantitatively explained by a model in which the relevant electronic state is an exciton which interacts strongly with LO phonons.

## II. EXPERIMENTAL TECHNIQUES AND SAMPLES

Single crystals of YbS and thin films of YbS and YbTe were used in the experiments. Raman measurements were made using a Jarrell-Ash double monochromator and photon counting detection. A Spex single monochromator was used to obtain the optical reflectivity data in the visible and a Perkin Elmer Model 180 spectrometer for the infrared reflectivity measurements.

The results we present here concern essentially the YbS single crystal. The lattice constant of this sample was measured to be $a = 5.691$ Å and corresponds to that of the stoichiometric composition.[10] The YbS thin films were used in the absorption measurements necessary for the data reduction in the resonant RS experiments. Although the Raman measurements in YbTe agree qualitatively with those reported previously.[1,2] we found that these spectra strongly depend on the sample quality, indicating that the processes are dominated by impurity effects.

## III. EXPERIMENTAL RESULTS

In Fig. 1 we show RS spectra of YbS at liquid-nitrogen temperature for different laser lines. The energies of the multiphonon structure are multiples of 275 $\text{cm}^{-1}$ which agree, within the limits of the experimental error, with the frequency of the LO($\Gamma$) phonon determined from infrared reflectivity data (see Table I). The weak sidebands observed in Fig. 1 slightly above the 1 LO, 2 LO, 3 LO... frequencies will be the subject of a future publication. In previous works RS selection rules have not been investigated in detail.[1,2] It is, however, important to remark that the overtone spectrum appears only in the $\Gamma_1^+$ RS component. This is what one expects for the "forbidden" LO($\Gamma$) RS due to the Fröhlich electron-phonon interaction.[11] We did not observe the shift of the first-order line with laser energy reported by Vitins,[1] who found an 8-$\text{cm}^{-1}$ shift as the exciting energy changes from 2.345 to 2.729 eV. We believe this shift is caused either by impurities in their samples or by an experimental artifact. Support for an impurity effect is provided by a comparison of the 20-$\text{cm}^{-1}$ linewidth (at $T = 4.2$ K) of the first-order peak reported by Vitins[1] and the 3.5-$\text{cm}^{-1}$ linewidth (at $T = 77$ K) measured in our samples. In our experiments we have used cleaved surfaces. We have, however, observed an increase in linewidth when polished samples are used. This effect is probably due to a relaxation of the $\vec{k}$-conservation rule because of surface damage, which may extend beyond the penetration depth of the light (~$10^3$ Å, at $\omega = 2.8$ eV). In any case, the linewidth we measured in polished samples was never larger than 8 $\text{cm}^{-1}$ (at $T = 77$ K). In Fig. 2 the resonant enhancement of the 1 LO($\Gamma$) and 2 LO($\Gamma$) peaks is shown as a function of photon energy for room and liquid-nitrogen temperatures. The data have been corrected for absorption. The frequency region where the resonant enhancement occurs corresponds to the $E_2$ peak in the reflectivity and absorption spectra.[12,13] This structure has been assigned to the $4f^{14}(^1S) \rightarrow 4f^{13}(^2F_{7/2})5d^1(e_g)$ electronic transition.[12,13] Our results differ from those reported by Vitins[1] in the position of the maximum in the resonance curve (in Vitins' paper $\omega_{\max} \sim 2.55$ eV) and the magnitude of the resonant enhancement. These differences are probably due to dif-

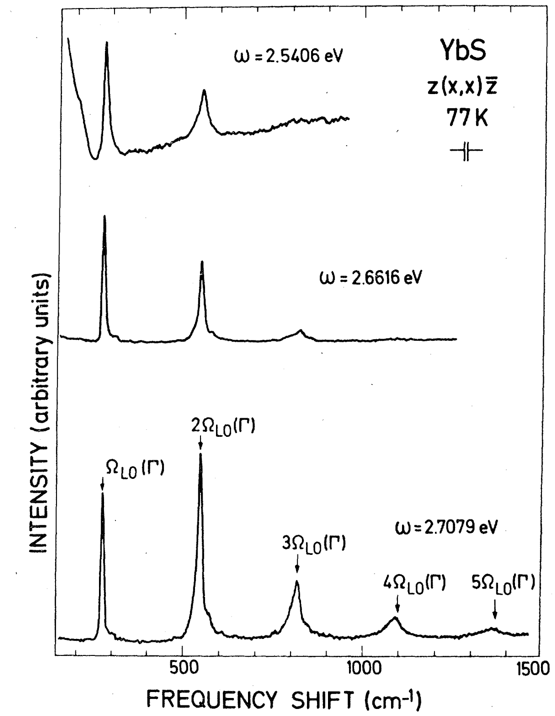

FIG. 1. Raman spectra of YbS at 77 K for different exciting energies.

TABLE I. Energies of optical phonons (in units of $\text{cm}^{-1}$) and dielectric constants.

| | YbS | | | | YbTe | |
|---|---|---|---|---|---|---|
| | Raman | | Infrared[a] | | Raman | Infrared[a] |
| | 300 K | 77 K | 300 K | 77 K | 4.2 K | 300 K |
| $\omega_{TO}$ | | | 199 ± 3 | 203 ± 3 | | 98 ± 3 |
| $\omega_{LO}$ | 271 ± 2 | 275 ± 1 | 272 ± 3 | 276 ± 3 | 142[b] | 145 ± 3 |
| Linewidth | 13 ± 2 | 3.5 ± 0.5 | 14 ± 2 | 4 ± 1 | | |
| $\epsilon_0$ | | | 9.5 ± 0.5 | 9.6 ± 0.5 | | |
| $\epsilon_\infty$ | | | 5 ± 0.5 | 5 ± 0.5 | | |

[a] Oscillator parameters from the fit of the reststrahlen band.

[b] Reference 1.

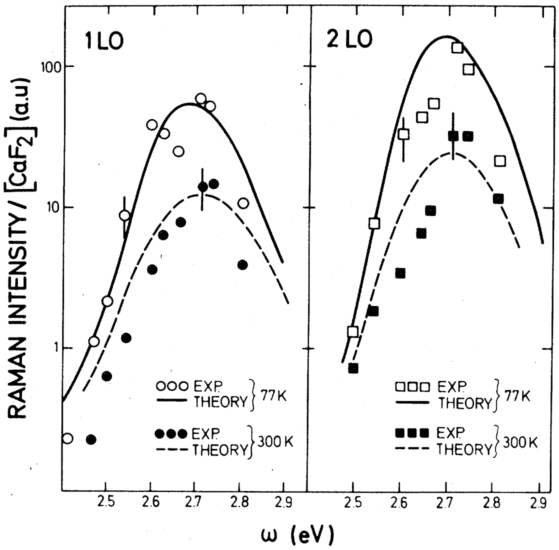

FIG. 2. Raman scattering efficiencies of YbS normalized to that of $CaF_2$ as a function of laser energy for two different temperatures. The calculated curves were obtained with Eqs. (10) and (11).

ferent sample preparations or to absorption corrections. In fact, we observed that the maximum in the resonant curve shifts towards 2.6 eV in the polished samples.

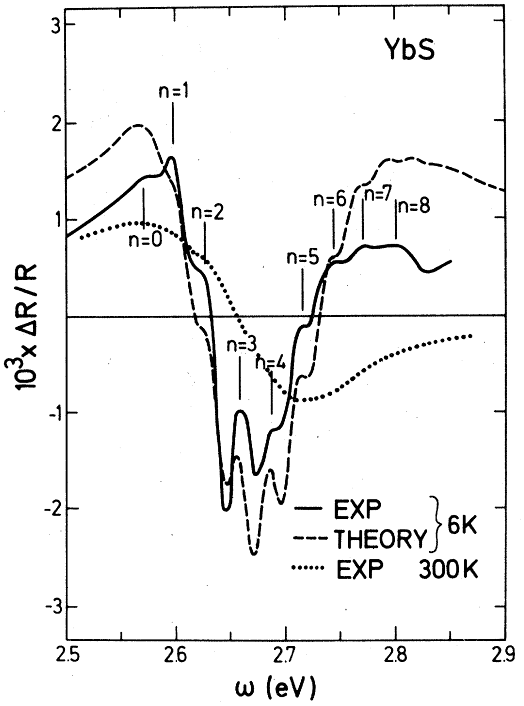

FIG. 3. Wavelength derivative reflectance curve of YbS. The calculated curve was obtained with the expression for the electrical susceptibility [Eq. (11)].

We have also investigated the reflectivity of YbS and, in order to improve the resolution, its first derivative using wavelength modulation. Figure 3 shows the wavelength modulated reflectance spectrum of YbS measured at 6 K and at room temperature. This spectrum contains structure at nearly equal intervals of 235 $cm^{-1}$. We assign the different structures to optical excitations of an electronic transition with the simultaneous creation of $n$ phonons. The value of 235 $cm^{-1}$ is 15% lower than the frequency of the LO(Γ) phonon. A similar situation has been found in a number of ionic compounds and has been generally explained in terms of exciton-phonon bound states.[14]

## IV. THEORY AND DISCUSSION

Multiple-order processes in RS experiments and above the band edge have been observed in a large number of ionic compounds.[15-18] The significant features observed in these experiments are the following[15]: (i) the multiphonon lines appear at energies which are almost exact multiples of a first-order LO(Γ) phonon line; (ii) the observed polarization selection rules $(\vec{E}_l \| \vec{E}_s)$ are independent of crystal symmetry. This holds for one-LO-phonon scattering near resonance even in configurations in which it is forbidden if the scattering is determined by a second-rank Raman tensor. The selectivity in $\vec{k}$, i.e., the fact that only overtones of the $\vec{k} \simeq 0$ phonons are observed, has been considered by Hamilton.[19] This author showed that when Fröhlich terms dominate over deformation potential terms, the multiphonon processes involve participation of phonons having wave vectors $\lesssim 10^6$ $cm^{-1}$ (this value is for CdS). On the other hand, the breakdown in RS selection rules for one phonon scattering can be caused by: (a) impurity states (bound excitons) near the band gap,[20] (ii) by an intrinsic effect dependent upon the finite wave vector of the phonon[21] as originally proposed by Martin and Damen,[22] or (iii) by a surface electric field,[23] a situation which cannot hold for our insulating samples. Theoretical explanations of the origin of the multiphonon processes have been given in terms of a cascade model,[5] configuration models,[24] or an interband transitions model in which it is difficult to treat explicitly exciton effects.[25]

In the configuration-coordinate models it is assumed that the phonon wave functions in the excited electronic state are obtained from those of the ground electronic state by displacing the phonon coordinate by an amount Δ. This mechanism is the basis of the Franck-Condon principle in molecular spectroscopy. Similar mechanisms have been discussed in connection with resonant RS experiments in II-VI compounds,[24] III-V alloys,[26] and multiphonon scattering from a local mode in $MnO_4^{2}$-doped CsI.[27] In addition, the same theory was applied to the case of the paramagnetic phase of Eu-monochalcogenide compounds[3] where $\vec{k}$ is not conserved in the scattering process. In all cases the displacement of the phonon coordinate, which is the fundamental parameter of the theory, is considered to be a phenomenological parameter to be determined after a fit to the experimental data. It is, however, important to remark that basically the same theory can be applied to the case of a single localized phonon state and to the case of a phonon band. For the latter, *all* phonons can be excited in the Raman process, provided the sum of their $\vec{k}$'s is zero. The experiments, nevertheless, show only overtones of the $\vec{k}=0$ phonons (except for the paramagnetic phase of the Eu monochalcogenides).[3-4] In what follows, we show how this fact derives from our model and describes a way to estimate theoretically $\Delta$, the basic parameter of the theory. The formalism we discuss is analogous to that proposed for the absorption by color centers in alkali halides.[28]

Let us consider the Fröhlich interaction between the LO phonons and a dispersionless exciton, a case which is likely to apply to the Yb monochalcogenides where the hole is in a strongly localized $4f$ state. This problem can be approximated by the interaction of LO phonons with a static charge distribution. The corresponding Hamiltonian is[29]

$$H=\sum_{\vec{k}}\Omega(\vec{k})a_{\vec{k}}^{\dagger}a_{\vec{k}}+\sum_{\vec{k}}\left(V_{\vec{k}}\rho_{\vec{k}}a_{\vec{k}}+V_{\vec{k}}^{*}\rho_{\vec{k}}^{*}a_{\vec{k}}^{\dagger}\right), \qquad (1)$$

where $\Omega(\vec{k})$ is the phonon energy, $a_{\vec{k}}$ ($a_{\vec{k}}^{\dagger}$) the destruction (creation) operator for the phonon, $\rho_{\vec{k}}$ is the Fourier transform of the static charge distribution and

$$V_{\vec{k}}=(i/|\vec{k}|)(2\pi/V)^{1/2}[\Omega(\vec{k})]^{1/2}e(\epsilon_{\infty}^{-1}-\epsilon_{0}^{-1})^{1/2} \qquad (2)$$

is the well-known Fröhlich interaction term, $V$ is the volume of the crystal, and $\epsilon_0$ ($\epsilon_\infty$) the low- (high-) frequency dielectric constant. The Hamiltonian (1) can be trivially diagonalized by the transformation[29]

$$a_{\vec{k}}\rightarrow a_{\vec{k}}+\frac{V_{\vec{k}}^{*}\rho_{\vec{k}}^{*}}{\Omega(\vec{k})}, \qquad (3)$$

i.e., the phonons are "displaced" in the excited electronic state. For a $1s$ exciton state

$$\rho(\vec{r})=(1/\pi a_0^3)\exp(-2|\vec{r}-\vec{r}_0|/a_0)-\delta(\vec{r}-\vec{r}_0) \qquad (4)$$

and one obtains

$$\Delta_{\vec{k}}=\frac{V_{\vec{k}}^{*}\rho_{\vec{k}}^{*}}{\Omega(\vec{k})}$$
$$=\frac{-i}{|\vec{k}|}\left(\frac{2\pi}{V}\right)^{1/2}e\left(\frac{\epsilon_{\infty}^{-1}-\epsilon_{0}^{-1}}{\Omega(\vec{k})}\right)^{1/2}\left[(1+\tfrac{1}{4}a_0^2k^2)^{-2}-1\right]$$
$$\times e^{i\vec{k}\cdot\vec{r}_0}, \qquad (5)$$

where $a_0$ is the exciton radius and $\vec{r}_0$ is the position vector of a lattice site. The parameter $\Delta_{\vec{k}}$ represents the displacement in the phonon momentum coordinate measured in units of the zero-point vibration amplitude.

The RS cross section will be determined by Franck-Condon overlap integrals which are algebraic expressions involving $\Delta_{\vec{k}}$. The Raman matrix element for an $n$-order phonon process is, to terms of first order in $V^{-1/2}$:

$$R^{(n)}(\omega,\Omega)=|P_0|^2\sum_{\alpha,\vec{r}_0}\frac{\langle 1_{k_1}\cdots 1_{k_1}|\alpha,\vec{r}_0\rangle\langle\alpha,\vec{r}_0|0\rangle}{E_0+E_\alpha-\omega+i\Gamma}. \qquad (6)$$

Where $\Omega=\Omega(\vec{k}_1)+\cdots+\Omega(\vec{k}_n)$, $\alpha$ is some intermediate phonon state and $\langle 1_{\vec{k}_1}\cdots 1_{\vec{k}_1}|$ is the phonon state with one phonon each of wave vectors $\vec{k}_1$, $\vec{k}_2$, etc.; $P_0$ is the dipole matrix element between the ground and the excited electronic state, $\omega$ is the energy of the incoming photon, and $E_0$ and $\Gamma$ are the energy and lifetime of the excited electronic state, respectively. In Eq. (6), $T=0$ is assumed. By performing in Eq. (6) the sum over all lattice sites $\vec{r}_0$, we obtain explicitly $\vec{k}$ conservation for the total multiphonon process. The spectral distribution of the Raman cross section is then obtained by summing the square of the matrix elements of Eq. (6) over all multiphonon processes for which $\sum_i\vec{k}_i=0$. This calculation is in principle quite complicated and we will not try to carry it out. We shall show, however, how the weighting factors which give scattering by overtones of phonons with $\vec{k}\simeq 0$ derive from Eq. (6) and, moreover, how from Eq. (5) it is possible to obtain an expression for the phenomenological parameter $\Delta$ which is needed for a numerical evaluation of the theory. Let us consider second-order RS. It can be proved that in this case Eq. (6) becomes

$$R^{(2)}(2\Omega(\vec{k}),\omega)$$
$$=\Delta_{\vec{k}}^{2}[\chi(\omega)-2\chi(\omega-\Omega(\vec{k}))+\chi(\omega-2\Omega(\vec{k}))], \qquad (7)$$

where

$$\chi(\omega)=|P_0|^2\sum_{\alpha}\frac{\langle 0|\alpha\rangle\langle\alpha|0\rangle}{E_0+E_\alpha-\omega+i\Gamma} \qquad (8)$$

is the electric susceptibility. Neglecting the $\vec{k}$ dependence of the terms in parentheses in Eq. (7) we obtain

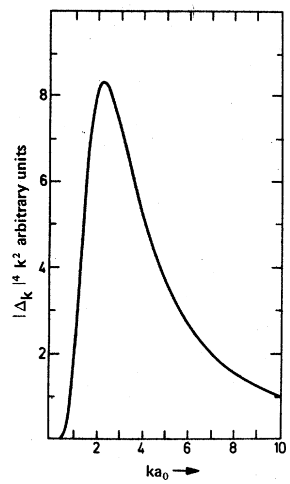

FIG. 4. Plot of $|\Delta_k|^4 k^2$ as a function of $ka_0$. See Eqs. (5) and (9).

$$|R^{(2)}(2\Omega(\vec{k}))|^2 \sim \int |\Delta_{\vec{k}}|^4 k^2 \delta(\Omega - \Omega(\vec{k}))\, dk\,. \tag{9}$$

By substituting Eq. (2) into Eq. (9) we find that the scattering efficiency $|R^{(2)}|$ peaks strongly for phonons with $|\vec{k}| \sim 2a_0^{-1}$ (Fig. 4). It can be shown that these phonons give the largest contribution to the RS cross section for any order. If we take the reduced mass of the exciton to be $m/m_e = 0.2$ (the value in the Eu monochalcogenides ranges from 0.2 to 0.4)[30] we find, with the $\epsilon_0$ and $\epsilon_\infty$ from Table I, $a_0 = 25$ Å. We expect, therefore, that essentially phonons with $k \sim 10^7$ cm$^{-1}$ will participate in the scattering process; the frequency of these phonons should be practically equal to $\Omega_{\text{LO}}(\Gamma)$ as the average radius of the Brillouin zone is ~$10^8$ cm$^{-1}$.

Before considering the general multiphonon case it is worthwhile to make some remarks. First, $\Delta_{\vec{k}}$ is zero for $\vec{k} = 0$, i.e., the effect we discuss depends on the finite wave vector of the phonons. For first-order scattering, the cross section turns out to be proportional to the square of the $\vec{k}$ transfer as in the case of previous interband[19] or exciton calculations.[31] The RS selection rules are contained in Eq. (6) in the term $|P_0|^2$. Let us consider now the general expression, Eq. (6), and assume that the phonon spectrum is dispersionless. We then find

$$R^{(n)}(\omega) = \Delta_{\vec{k}_1} \cdots \Delta_{\vec{k}_n} \sum_{p=0}^{n} \binom{n}{p} (-1)^p \chi(\omega - p\Omega)\, \delta(\vec{k}_1 + \cdots + \vec{k}_n) \tag{10}$$

and

$$\chi(\omega) = |P_0|^2 \sum_{t=0}^{\infty} \frac{1}{t!} \frac{\Delta^{2t}}{(E_0 + \Omega - \omega + i\Gamma)}, \tag{11}$$

where $\Delta^2 = \sum_{\vec{k}} |\Delta_k|^2$. If one inserts Eq. (11) into Eq. (10), an expression for the RS cross section is obtained, which can be written in the convenient form

$$|R^{(n)}(\omega)|^2 = \sum_{\vec{k}_1 \cdots \vec{k}_n} |\Delta_{\vec{k}_1}|^2 \cdots |\Delta_{\vec{k}_n}|^2 \delta(\vec{k}_1 + \cdots + \vec{k}_n) \frac{|P_0|^4}{\Delta^{2n} n!} e^{\Delta^4} \left| \sum_{m'} \frac{\langle n | m' \rangle \langle m' | 0 \rangle}{E_0 - m'\Omega + i\Gamma} \right|^2, \tag{12}$$

where

$$\langle n | m' \rangle = (n!/m'!)^{1/2} \exp(-\tfrac{1}{2}\Delta^2) \Delta^{n-m'} L_{m'}^{n-m'}(\Delta^2)$$

and $L_{m'}^{n-m'}$ is an associated Laguerre polynomial. Equation (12) is almost identical, except for proportionality factors, to the expression one would obtain for the case of a single mode being "displaced" in the excited electronic state.[24,26,27] Actually, this expression is that which has been used in all the cases treated in the framework of the configuration coordinate model.[24,26,27] The effective "displacement" Δ is explicitly given by

$$\Delta^2 = \frac{e^2}{a} \left(\frac{24}{\pi}\right)^{1/3} \frac{(\epsilon_\infty^{-1} - \epsilon_0^{-1})}{\Omega_{\text{LO}}} \frac{1}{w} \int_0^w \frac{x^4 (2 + x^2)^2}{(1 + x^2)^4}\, dx\,, \tag{13}$$

where $w = (3\pi^2)^{1/3} a_0/a$ and $a$ is the lattice parameter. In YbS taking $a = 5.68$ Å,[32] $\epsilon_0$ and $\epsilon_\infty$ from Table I and $a_0 = 25$ Å, we obtain $\Delta = 3.5$. The calculated curves in Fig. 2 have been obtained from Eq. (12) for $\Delta = 1.5$, $E_0 = 2.59$ eV, and $\Gamma = 0.05$ eV ($T = 77$ K) and $\Gamma = 0.1$ eV ($T = 300$ K). It is important to remark that the same set of parameters fits the resonances of 1 LO and 2 LO for a given temperature. In addition, only Γ has been changed in going from 77 to 300 K, i.e., the decrease in intensity with an increase of the temperature is due to *lifetime effects* of the excited electronic state. We consider the agreement between the value for Δ obtained from the fit and that calculated from Eq. (13) to be reasonable. The remaining discrepancy can probably be traced to an overestimate of the electron-phonon interaction near the edge of the Brillouin zone [Eq. (2) is exactly valid only for $k \sim 0$].

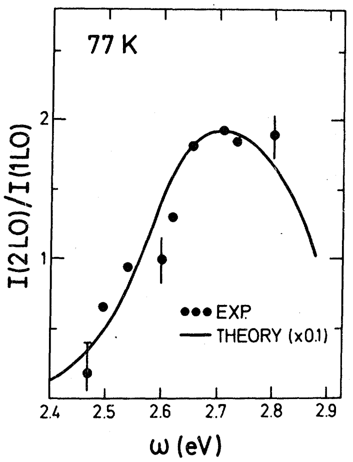

FIG. 5. Dependence of the measured integrated intensity ratio $I(2\ \mathrm{LO})/I(1\ \mathrm{LO})$ on the laser energy compared with the estimates of our model [Eqs. (10) and (11)]. While the model explains the shape of the observed ratio, the absolute value is off by a factor of 10 (see text).

Another test of the theory is given in Fig. 5 where the ratio $I(2\ \mathrm{LO})/I(1\ \mathrm{LO})$ is shown as a function of laser energy. This ratio, as determined from a single measurement, is expected to be less sensitive to the typical geometrical problems presented in a resonant RS measurement. Figure 5 shows that the theory correctly predicts the $\omega$ dependence of this ratio. The discrepancy in the constant term (a factor $\simeq 3$ in the scattering *amplitude*) probably originates also in an overestimate of phonon contributions for $k$ near the edge of the Brillouin zone. It is interesting to remark that the width of the resonant RS curve shown in Fig. 2 is much larger than $\Gamma$ as it is determined by the sum over the many phonon intermediate states. If $\Gamma$ were smaller than $\Omega_{\mathrm{LO}}$, oscillations in the RS cross section would be observed.[27] From the expression for $\chi(\omega)$ [Eq. (11)] we have calculated the theoretical curve in Fig. 3 with the same parameters used to fit the resonant RS curve at 77 K, except for the phonon frequency which was taken as an extra free parameter. Within our configuration-coordinate model the phonon frequency shift must arise from a change of the phonon frequency associated with the excited electronic state. The phonon structure in Fig. 3 is not resolved in Fig. 2 since in the latter the electronic broadening $\Gamma$ appears folded with the phonon frequency $\Omega_{\mathrm{LO}}$. As in other cases of first-order resonant RS, Eq. (10) for $n=1$ can be transformed into the ratio

$$R^{(1)}(\omega) \sim [\epsilon(\omega) - \epsilon(\omega-\Omega)]/\Omega\,. \qquad (14)$$

The measurements of Fig. 3 are related to the first derivative of $\epsilon(\omega)$ with respect to $\omega$. This derivative should exhibit sharper structure than the corresponding finite difference of Eq. (14). We have checked that the calculated structure of Fig. 3 disappears if $\Gamma = 0.05$ eV is replaced by $\Gamma' = 0.08 \simeq 0.05\ \mathrm{eV} + \Omega_{\mathrm{LO}}$. It is also interesting to note that Eq. (14) yields for $\Omega \to 0$, $R \sim d\epsilon/d\omega$ as does the theory of Ref. 19 (bound exciton states). The theory based on free-electron bands or dispersive excitons yields instead $R \sim d^2\epsilon/d\omega^2$.[33] Our model is thus able to account self-consistently for the resonant Raman and the modulated reflectance results, a fact which lends additional support to the interpretation of the structure in the latter as due to LO phonons. In previous works[1,2] a modified version of the cascade model has been invoked in order to account for the origin of the multiphonon processes and an apparent breakdown in $\vec{k}$ conservation in the Yb monochalcogenides. We believe that the reported breakdown in translational symmetry[1,2] is not an intrinsic effect but must be related to impurities since: (a) we did not observe the shift of the first-order peak with exciting energy observed by Vitins[1] in YbS, (b) in rather imperfect samples of YbTe, we observed the broad line positioned between the $\Omega_{\mathrm{TO}}(\Gamma)$ and $\Omega_{\mathrm{LO}}(\Gamma)$ phonon frequency reported by Vitins and Wachter.[1,2] We had, however, difficulties reproducing the spectra from one sample of YbTe to another. This broad line has been invoked as evidence for an intrinsic breakdown of $\vec{k}$ conservation.[1,2] Even if impurities were not the origin of this line, we would find it premature to assign this mode to a first-order process. Nevertheless we think that this line is due to an impurity effect because it shows up in an exciting frequency region where no important electronic transitions in YbTe take place.[1,2,12]

The distinction between RS and hot luminescence (i.e., cascade model[5]) is another aspect of the problem under consideration. Experimental observations in support of a cascade process, following Vitin's paper,[1] are the exponential decrease of the scattering intensity with the order $n$ of the phonon process and the quenching of the Raman intensity with increasing temperature.[1,2] This temperature behavior is shown in Fig. 2. We have shown that such a behavior can be explained in the framework of the configuration model, assuming a temperature dependence of the lifetime of the excited electronic state. On the other hand, we did not observe the exponential decrease of the intensity with the order of the process, as is evident in Fig. 1, where the second-order line is more intense than the first-order peak. We believe that impurity effects are the reason for the discrepancy with Vitins and Wachter's results[1,2]; impurities should enhance the first-order Raman peak more than the second-order one.[21] There is, however, another important point which indicates that the process is not hot luminescence (cascade process), namely, the fact that the phonon frequency is different in the excited and ground electronic states. The latter becomes equal to the LO($\Gamma$) phonon frequency we determined from infrared measurements. For a cascade process one should observe structure at multiples of 235 cm$^{-1}$, i.e., the phonon frequency in the *excited* electronic state. (See Ref. 27 for a discussion of this point).

We mentioned in Sec. I that multiphonon processes are also observed in the magnetic Eu monochalcogenides.[3,4] In the paramagnetic phase of these compounds the first-order peak occurs at a frequency $\Omega_0$, where $\Omega_0 \simeq \Omega_0(L)$.[4] This scattering, which does not conserve $\vec{k}$, is due to spin disorder.[3,4,6-8] In the magnetic saturated phase, on the other hand, the spectra show multiphonon scattering at energy multiples of the $\Omega_{\mathrm{LO}}(\Gamma)$ phonon frequency.[6] The RS spectra in the ordered phase show similar characteristics to the ones we reported here for the diamagnetic YbS.[6] Since the Raman processes in both families of compounds involve the $4f$ levels as initial states in the scattering process we think that our theory should be able to describe the RS experiments in the ordered phase of the Eu monochalcogenides as well. Moreover, RS experiments in the paramagnetic phase of the Eu compounds have already been described in the framework of a configuration-coordinate model.[3,4] It was shown that this model can satisfactorily predict the relative intensities of the overtone spectra.[3,4] No attempt was made, however, in order to explain why $\Omega_0 \simeq \Omega_{\mathrm{LO}}(L)$. It is, interesting then, to show how this fact follows from our theory. Considering Eq. (6) for $n=1$ and neglecting the $\vec{k}$ dependence of $\chi$, it can be proved, for the case of no translational symmetry, that

$$|R^{(1)}(\Omega(\vec{k}))|^2 \sim \int |\Delta_{\vec{k}}|^2 k^2 \delta(\Omega - \Omega(\vec{k}))\, dk\,. \qquad (15)$$

The first-order RS cross section turns out to be a weighted one-phonon density of states. From Eq. (2) we obtain an expression for the weighting factor $|\Delta_{\vec{k}}|^2 k^2$, which is rigorous for $k \sim 0$. In general, because of the symmetry of the electronic state in Eq. (4), this factor weights all modes of dominantly fully symmetric displacement patterns with respect to the Eu ions, giving rise to a large contribution from LO($L$) phonons. A similar situation applies if one considers the interaction of the the phonons with the localized $4f$ holes as discussed in Ref. 8. Thus, we expect that the expression for $\Delta^2$ [Eq. (13)] should correlate the number of overtones observed with the parameters involved in Eq. (13) within the Eu compounds. This correlation is shown in Table II where we also included YbS for comparison. For the radius of the exciton we have taken the expression $a_0 = \epsilon_0 \hbar^2 / m_e e^2$. The values obtained for $\Delta$ are about one order of magnitude larger than the values quoted in Refs. 3 and 4; however, the correlation between $\Delta$ and the number of overtones observed is quite evident.

TABLE II. Calculated values for $\Delta^2$ [Eq. (13)] and number of overtones observed in the Eu monochalcogenides (Ref. 4). The values for $\epsilon_0$, $\epsilon_\infty$, and $\Omega_{\mathrm{LO}}$ have been taken from Ref. 34.

| | Number of observed overtones | $\Delta^2$ |
|---|---|---|
| EuO | 5 | 15.9 |
| EuS | 4 | 10.2 |
| EuSe | 3 | 10.0 |
| EuTe | 1 | 6.2 |
| YbS | 5 | 12.5 |

## V. CONCLUSIONS

We have shown that optical processes in the Yb monochalcogenides involve the participation of a strongly interacting exciton–LO-phonon system. The treatment of this interaction in terms of a simple configuration-coordinate model gives results which are able to explain both the magnitude and shape of the resonance curves for RS and, with the same parameters except for a small phonon frequency renormalization, the detailed structure of the wavelength derivative of the reflectance spectrum. The attempt to explain the magnitude of $\Delta$, while quantitatively unsuccessful due to the inadequacy of the expression taken for the Fröhlich interaction near the zone boundary, nevertheless is capable of explaining the trends observed for the Eu monochalcogenides series.

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