EXPERIMENTAL EVIDENCE FOR THE EXISTENCE OF SECOND ORDER POLARITONS ASSOCIATED WITH VAN HOVE SINGULARITIES AT LARGE WAVE VECTORS

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Light scattering experiments concerning the long wavelength totally symmetric polar transverse modes in GdS have been performed by using an Nd:YAG-laser. Polaritons associated with the A_1 (TO)-phonon at 233 cm^{-1} show resonance couplings with two modes at 204 and 213 cm^{-1}. These modes have been assigned earlier to originate from second order phonon process due to two phonon density of states maxima. The recorded wave vector dependent frequencies and scattering intensities are in good agreement with calculated data.

1. Introduction

The usual macroscopic model to describe polaritons implies dipole coupling between electromagnetic waves and polar transverse phonon modes [1]. It has been realized several years ago that polaritons should exist not only due to photon coupling with zone center polar phonons, but also due to couplings with impurities or two-phonon states [2,3]. As long as crystalline excitations appear in IR-absorption or reflection and thus are associated with an oscillating dipole moment coupling with photons should take place generally. Observation of localized polaritons was reported and discussed earlier [4]. An unambiguous observation of second order polaritons, however, still is missing. One of the few experiments hitherto indicating the existence of these elementary excitations seems to be a weak resonance splitting recorded at the polariton branch associated with the ordinary TO-phonon at 582 cm^{-1} in $LiNbO_3$. The second order mode there was found to be located at 537 cm^{-1} [5]. Other related experiments were able to show the possibility of a direct coupling between first and second order phonons [6,7]. Because $LiNbO_3$ exhibits as many as 9 fundamentals below 582 cm^{-1} it could not be excluded, however, that the observed two-phonon state at 537 cm^{-1} was only due to a combination of zone center modes. The existence of polaritons associated with van Hove singularities at larger wave vectors therefore still was questionable.

In the present paper we discuss polaritons in CdS which has only one single totally symmetric fundamental TO-mode. The cited difficulties with the interpretation appearing in polyatomic crystals as $LiNbO_3$ then are omitted.

2. Results and discussion

CdS has wurtzite structure and belongs to the space group C_{6v}^4 (= C 6_3mc). There are two formula units per primitive cell all atoms having C_{3v}-site symmetry. Factor group analysis predicts $\Gamma(C_{6v}) = 1\,A_1 + 2\,B_1 + 1\,E_1 + 2\,E_2$. The B_1-modes are silent and the E_2-modes only Raman-active. The A_1- and E_1-modes are simultaneously Raman- and infrared-active. Dipole moments of the former are oscillating parallel to the optic axis and those of the latter in the optically isotropic plane. First order polaritons associated both with the A_1(TO)- and E_1(TO)-modes thus are observable by light scattering. At room temperature CdS is optically positive ($n_{eo} > n_o$) for $\lambda > 523.5$ nm and negative ($n_{eo} < n_o$) for $\lambda < 523.5$ nm [8]. The lowest electronic level of the material is located at ~ 500 nm (2.36 eV). When exciting the Raman spectra with lasers in the visible as, for instance, an Ar^+-laser, different types of resonance Raman effects may be recorded. For energies of the incident photons well above 500 nm (λ = 457.9 nm) and enhancement of the zone-center LO-phonon is observed. Further-

more a series of multiples of this mode are recorded [9] in a similar way as for resonance Raman scattering in some gases [10]. No transverse mode scattering is observed in this case. When on the other hand using the green Ar^+-laser line at $\lambda = 514.5$ nm to excite the spectra all first order TO- and LO-phonons and some characteristic second order phonon structures are recorded [11]. LO-scattering processes higher than of second order disappear and the first order TO-scattering intensities become of the same order of magnitude as those of the LO-modes. We point out that the $E_1(TO)$-intensity for Ar^+-laser excitation is larger than the $A_1(TO)$-intensity. Consequently polariton scattering experiments in CdS hitherto were concerned with the two fold degenerate (ordinary) mode only [12]. The laser lines used for excitation in ref. [12] were $\lambda = 514.5$ and $\lambda = 496.5$ nm; both still allowing the observation of transverse E_1-modes.

In our present work we used an Nd:YAG-laser ($\lambda = 1064.8$ nm) to excite the spectra of a "pure" CdS-sample. This means an impurity concentration $n < 10^{16}$ cm^{-3}. The energy of the incident photons then is weak enough to reduce the resonance Raman effects as much as possible and cause predominantly spontaneous scattering. On the other hand the wave number of the laser photons (9391 cm^{-1}) still lies well above the absorption bands in the infrared which

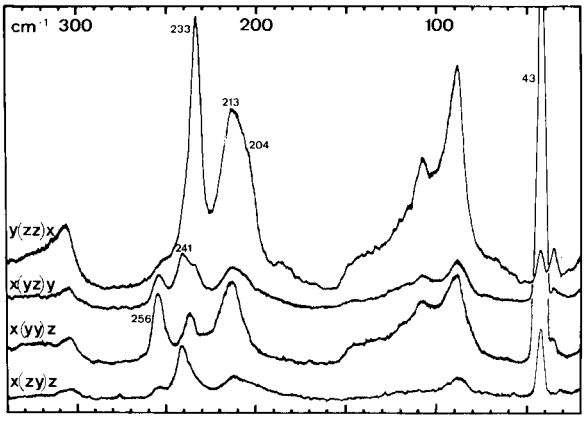

Fig. 1. Survey Raman spectra of CdS. Exciting line $\lambda = 1064.8$ nm, laser output power ~12 W, spectral slit width 4 cm^{-1}. Scattering geometries: a) $y(zz)x$: $A_1(TO)$-mode at 233 cm^{-1}, b) $x(yz)y$: $E_1(TO)$ and $E_1(LO)$-mode at 241 and 305 cm^{-1}, respectively, c) $x(yy)z$: E_2-modes at 254 and 43 cm^{-1} and oblique phonons, d) $x(zy)z$: oblique phonons. All spectra were recorded at room temperature. The $A_1(LO)$-phonon was recorded at ~305 cm^{-1} too.

are located essentially below 1000 cm^{-1}. In fig. 1 four survey phonon spectra for different scattering geometries are reproduced. The upper two traces show pure transverse and longitudinal modes whereas the lower two involve directional dispersion and consequently extraordinary mixed modes [1]. The $A_1(TO)$- and $E_1(TO)$-phonons at 233 and 241 cm^{-1} can be identified easily in the $y(zz)x$- and $x(yz)y$-scans, respectively. We especially draw attention to the inverted intensity ratio $E_1(TO)/A_1(LO)$ relative to the spectra in ref. [11]. Now the totally symmetric TO-phonon appears much stronger than the twofold degenerate mode. Nd:YAG-laser excitation therefore allows also the observation of $A_1(TO)$-polaritons. The broad structure with peaks at ~204 and ~213 cm^{-1} originates from two phonon density of states modes for the combination of two branch frequencies. The recorded Raman spectra agree with corresponding density of states maxima calculated by Nusimovici and Balkanski [13]. These authors report two Raman active coupled modes at 204 and 210 cm^{-1}, respectively, see table 4 in the reference.

A typical polariton spectra series associated with the $A_1(TO)$-phonon at 233 cm^{-1} is reproduced in fig. 2. The positions of the phonon density of states maxima have been indicated by vertical lines for better orientation. When the fundamental polariton mode approaches the higher frequency second order peak the polariton half width as well as its intensity clearly decreases until the intensity becomes weak relative to the second order mode (2.35°-scan). The frequency shift of the latter mode is only small. For further decreasing scattering angles the lower frequency second order mode at 204 cm^{-1} clearly increases in intensity and is shifted towards lower wave numbers. A third resonance coupling finally seems to take place with a weak phonon at ~185 cm^{-1} in the lowest scans.

The undisturbed fundamental $A_1(TO)$-polariton dispersion branch has been calculated and plotted as a dotted line in fig. 3. The full curves include coupling with second order modes. A weak oscillator strength of the 213 cm^{-1}-mode and its position close to the 204 cm^{-1}-mode are responsible for a small frequency shift. The recorded shift of the lower frequency second order mode at 204 cm^{-1}, however, agrees well with the calculated dispersion branch. The oscillator strength of both second order modes were found to be only $S \approx 0.2$. The value for the high frequency di-

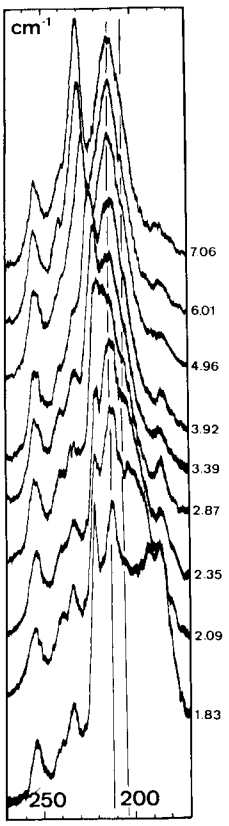

Fig. 2. A_1(TO)-polaritons with wave vectors propagating in the optically isotropic plane. Laser output power ~15 W, spectral slit width 4 cm^{-1}. Internal scattering angles are given to the right in the figure. Resonance coupling with two density of states maxima at ~213 and ~204 cm^{-1} can be recognized. The positions of these modes have been indicated by vertical lines.

electric constant used in our calculations was $\epsilon_{\infty\parallel} = 5.25$. We have omitted the possible third resonance at ~185 cm^{-1} from our calculations because no more reliable experimental data were available here. The refractive indices used when analyzing the spectra were $n_i = 2.336$ and $n_s = 2.334$ for the incident and scattered photons, respectively.

The spectra in fig. 2 demonstrate that an impressive experimental evidence for the couplings also is found with the recorded intensity variations. A comparison of corresponding experimental data with calculated intensities in the polariton region of the A_1(TO)-mode is presented in fig. 4. The formalism used for calculation will be described in more detail together with other experiments [14]. The dashed

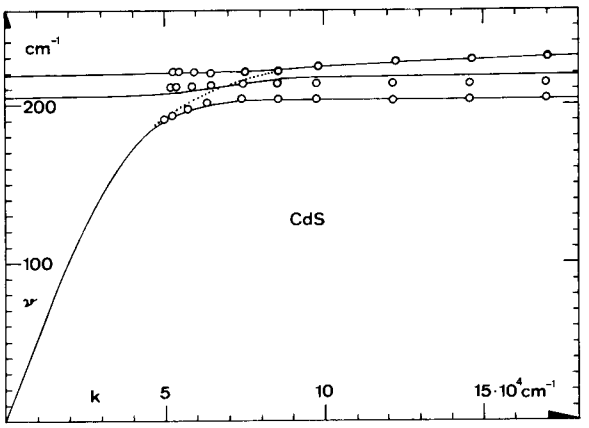

Fig. 3. Calculated A_1(TO)-polariton dispersion curves and experimental data points in the resonance region, see text. The undisturbed dispersion branch is indicated by a dotted curve.

curve corresponds to the expected intensity variation in the absence of second order phonon modes. Full curves again include coupling with the density of states modes. The recorded data are verified by the calculated curves in a quite satisfactory way.

The numerical intensity data were derived from the spectra in the following way.

a) Phonon-spectra: The half widths 2 Γ and peak intensities I_0 of the A_1(TO)-phonon at 233 cm^{-1} and the second order modes at 213, 204 and 185 cm^{-1} were determined by a stepwise procedure. 1) The

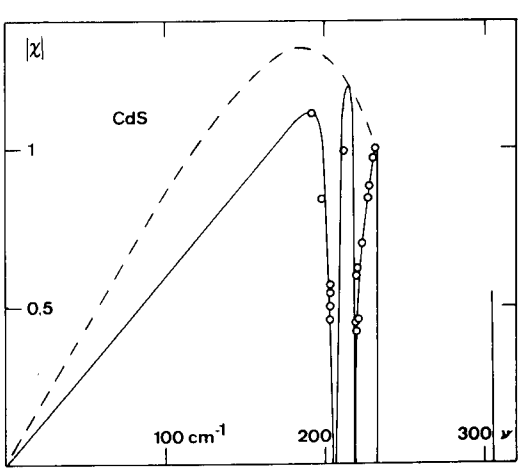

Fig. 4. Calculated A_1(TO)-polariton scattering intensities and experimental data points in the resonance region, see text. The expected intensity variation in the absence of second order resonances is shown by a dashed curve.

background in the region from ~160 to ~180 cm^{-1} was defined as $I \equiv 0$. Density of states vanish here [13]. 2) The half width of the strong fundamental TO-phonon was found to be $2\Gamma(233) = 8\ cm^{-1}$. Its peak intensity was determined. 3) The Lorentz shape of this line was calculated. 4) With this Lorentz shape as background the peak intensity of the mode at 213 cm^{-1} and its half width were derived ($2\Gamma = 14\ cm^{-1}$). 5) The Lorentz shape of this line was determined and the phonon at ~204 cm^{-1} analyzed in the same way, and so on. The experimentally recorded Raman spectrum in the region $160 < \omega < 280\ cm^{-1}$ then can be described analytically correct by

$$I(\omega) = \sum_i \frac{I_0(\omega_i)\Gamma^2(\omega_i)}{(\omega_i - \omega)^2 + \Gamma^2(\omega_i)},$$

$\omega_i = 185, 204, 213, 233, 254\ cm^{-1}$.

b) Polariton spectra: By using the numerical values for $\Gamma(213)$ and $I_0(213)$ derived from the phonon spectra the profile of this mode in the polariton spectra was determined and regarded as constant for all the scans in fig. 2. This approximation appeared to be relatively good when analyzing the spectra in detail. (The frequency shift of the mode was small too!) When taking into account this "Lorentz background" the relative scattering intensities at higher and lower wave numbers relative to the 213 cm^{-1}-mode could be determined by integration and thereafter compared with the calculated values plotted in fig. 4. A quantitative analysis of the present experimental data obviously was not trivial. We therefore decided to describe our method somewhat more in detail.

Finally we want to reproduce also the calculated undisturbed scattering intensities of the ordinary E_1(TO)-polaritons for Nd:YAG laser-excitation, fig. 5. The special choise of sign for the electrooptic tensor element turned out not to influence the shape of the

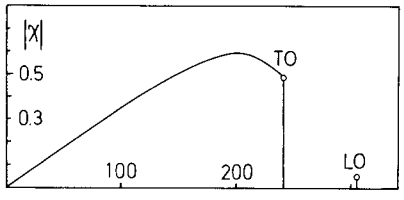

Fig. 5. Calculated susceptibility tensor for the undisturbed ordinary E_1(TO)-polaritons for Nd:YAG-laser excitation with λ = 1064.8 nm.

$|\chi|$-curve remarkably. The E_1-phonon intensity ratio I(TO)/I(LO) is reversed here relative to that reported for Ar^+-laser excitation [11]. Reliable experimental data to verify the calculations unfortunately were not available because of too low scattering intensities of E_1(TO)-polaritons for spontaneous Raman scattering outside the resonance Raman region, see fig. 1.

3. Summary

The experiments reported above show that resonance coupling between first order polaritons and polar second order density of states modes is possible. The coupled modes in our experiments continuously become pure second order polaritons for decreasing frequencies. The dispersion behaviour as well as the spontaneous Raman scattering intensities were found to be in satisfactory agreement with calculated data. Both second order phonon peaks recorded by us have been derived from calculated phonon dispersion curves previously. Their assignment thus seems to be unambiguous.

From the intuitive point of view it may appear somewhat unexpected that a coupling of photons with second order phonons really can take place. In the momentum picture ($\hbar k$), however, this becomes clear immediately when considering that the combination of pairs of phonons with large wave vectors and almost opposite directions easily may combine to second order excitations with small wave vectors ($k < 10^5\ cm^{-1}$). In the wave picture on the other hand the phenomenon can be described correspondingly as an interference of two short wavelength polar modes moving in almost opposite directions. These waves give rise to a long wave beat which becomes of the order of infrared light wavelengths.

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