PHYSICAL REVIEW B VOLUME 10, NUMBER 8 15 OCTOBER 1974

Resonant Raman scattering in GaSe

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(Received 30 May 1974)

The resonant Raman spectrum of GaSe has been investigated using a cw tunable dye laser. A detailed investigation of the wavelength dependence of the scattering efficiency has been carried out in the region just below the energy gap, which for GaSe falls midway in the spectral range of the dye laser. The scattering efficiency was observed to undergo a maximum when the laser energy was equal to the energy of the free exciton. The general wavelength dependence was found to be in good agreement with that predicted by Martin for q-dependent scattering. The observed angular independence of the scattering is, however, in discord with this theory, and for one mode, A_2''(LO), momentum conservation is observed to be broken. The nonpolar modes have been observed to exhibit a strong antiresonant behavior similar to that observed in CdS but the present results cannot be interpreted in terms of the previous empirical models.

I. INTRODUCTION

The first-order Raman spectrum of GaSe has been treated by several authors in recent years.[1-7] In a previous letter,[5] the authors presented an interpretation of the phonon modes at $\vec{k} = 0$ according to the group-theoretical predictions for the ϵ polytype (space group D_{3h}^1). The principal features of this interpretation have recently been corroborated,[4,7] but two aspects remain at variance to the conclusions reached by other authors. Hayek *et al.*[6] have identified a mode at 247 cm^{-1} as one member of a conjugate pair while in our previous work it was contended that such modes should not be observed. In addition, our previous work identified GaSe as a polar crystal in opposition to the contentions of Brebner *et al.*[8] This work, however, presents evidence that identifies the 247-cm^{-1} mode as an A_2''(LO) mode, an identification that is completely consistent with the previous interpretation.[5]

In ionic crystals the Raman spectrum of the polar longitudinal-optical (LO) phonons is dramatically enhanced as the incident light energy approaches the excitonic energy levels of the crystal.[9] An investigation of this resonant enhancement in GaSe constitutes the primary function of the present work. Although the resonant Raman effect has previously been studied extensively for both polar and nonpolar phonons,[9-14] much of the information obtained was somewhat tenuous because the band gaps of most of the compounds of interest did not lie within the spectral range of existing cw tunable dye lasers. The band gap of GaSe at 77 °K, however, lies in the middle of the range of rhodamine 6G tunable dye lasers, and thus one is able to make quantitative comparisons with existing theory over a wide energy range.

In this paper, the results of experiments on the relative scattering efficiency for Raman scattering in GaSe will be presented. Of particular interest is the resonant enhancement of the E'(LO) and A_2''(LO) phonon modes in a geometry where neither is allowed. The former is an example of selection-rule breakdown and the latter is an example of the breaking of Raman inactivity near resonance. Both of these effects have been predicted by Martin[15,16] on the basis of a q-dependent scattering mechanism and the present results thus enable a quantitative comparison to be made with Martin's theory. Although several such comparisons[13,16,17] have been carried out in the past the results are again somewhat sketchy for the reasons given above. More importantly, the crucial aspect of the angular dependence has been investigated in only one instance, with negative results. The present work discusses a similar investigation of the angular dependence in GaSe, with identical results.

The resonance behavior of the nonpolar modes in GaSe has also been investigated. These modes exhibit a pronounced antiresonance as the light frequency approaches the band edge. This behavior is similar to that observed previously in CdS (Refs. 11, 12), where an empirical model was introduced in an attempt to explain the data. An effort has been made to describe the results presented here in terms of this model.

II. EXPERIMENTAL

A. Crystals

The crystals used in this experiment were grown by the Bridgeman technique.[18] In order to obtain spectra where the incident polarization would be along the c axis of the crystal and where right-angle scattering could be employed, a 2-mm-thick crystal was x-ray oriented and cut with edges normal to the x and y crystal axes. To obtain forward scattering with $\hat{\epsilon}_i \parallel \hat{c}$, a slice approximately 0.8 mm thick was taken from the x edge of the same crystal.

B. Method

The spectra were obtained with the use of a Spectra Physics model 370 tunable dye laser and with a 50-mW He-Ne laser. All spectra were obtained at (81 ± 1) °K in a cold-finger Dewar. It was found that at lower temperatures sample luminescence obscured the Raman spectrum.

The Raman signal was calibrated against the 466-cm^{-1} Raman line of an oriented quartz crystal which was mounted immediately prior to the GaSe crystal in the light path. Both crystals are thus imaged on the slit of the spectrometer. Slit widths of approximately 5 cm^{-1} were used in this work. This is somewhat greater than the actual line widths (3 cm^{-1}) and the peak heights should thus represent the intensities of the lines of interest. The spectra were analyzed with conventional photon counting techniques.

C. Absorption corrections

The scattering efficiency relative to the 466-cm^{-1} quartz line was calculated for grazing incidence (with transmission through the quartz reference) according to the procedure of Callender *et al.*[10] The result obtained for the grazing geometry is identical to Eq. (4) of Callender *et al.*[10] except that the incident laser energy at the GaSe sample is attenuated by the reflectance of the quartz reference:

$$\frac{S_{\mathrm{GaSe}}}{S_Q} = K\left(\frac{I^s_{\mathrm{GaSe}}}{I_Q}\right) \frac{\alpha_l^{\mathrm{GaSe}} + \alpha_s^{\mathrm{GaSe}}}{1 - \exp[-(\alpha_l^{\mathrm{GaSe}} + \alpha_s^{\mathrm{GaSe}})w]} \times (1 - R_l^{\mathrm{GaSe}})^{-1}(1 - R_s^{\mathrm{GaSe}})^{-1} ,$$

where

$$K = t^Q(1 - R_l^Q)^3\,(1 - R_s^Q)\,(\eta^s_{\mathrm{GaSe}}/\eta^s_Q) .$$

t^Q is the thickness of the quartz sample, $R_{l,s}$ the sample (reference) reflectance at the laser and scattered wavelengths, respectively, $\alpha_{l,s}$ the absorption coefficient at these wavelengths, η the index of refraction, and w the width of the GaSe sample. In order to obtain quantitative results for the scattering efficiency it is necessary to know the absorption coefficient in the region about the exciton. A detailed investigation of the absorption coefficient of GaSe at 77 °K has not been carried out with $\vec{E} \parallel \vec{c}$, however, because of the impossibility of obtaining thin enough samples with the appropriate orientation. However, oblique incidence methods at room temperature have indicated that the absorption strength for $\vec{E} \parallel \vec{c}$ is about 35 times stronger than for $\vec{E} \perp \vec{c}$ near the exciton.[19] A similar conclusion has been reached by Bourdon and Khelladi.[20] Such measurements have also been performed at 4.2 °K for energies below the exciton by Kamimura *et al.*,[21] who found a long, weak absorption tail due to indirect gap transitions. By using this data (shifted in energy by the band-gap shift from 4.2 to 77 °K), and the data for thick samples for $\vec{E} \perp \vec{c}$ at 77 °K[22] (scaled by the factor of 35), a reasonable estimate of the absorption coefficient can be made. The resultant absorption coefficient is shown in Fig. 1. The energy regions covered by the two works[21,22] are shown in the diagram. The fact that the data of Kamimura is taken at 4.2 °K implies that the absorption coefficient indicated in Fig. 1 in the low-energy tail is probably somewhat lower than the true value, since phonon participation in the indirect process would be temperature dependent. On the other hand, an examination of analogous data allows one to argue that this thermal effect will not significantly affect the low-energy tail of the absorption curve between 77 and 4.2 °K. For example, in GaP, which is also an indirect-gap compound, the heights of the absorption steps as the indirect gap is approached do not change significantly over the range 77–1.6 °K.[23] It is also important to note that for $\vec{E} \perp \vec{c}$ in GaSe the sharpness of the exciton line and the shape of its tail do not change from 77 to 1.6 °K.[24] Finally, the fact that the portions of the curve from each set of measured data can be joined fairly smoothly, proves an additional degree of justification for this procedure. It should be noted, however, that it is in this region of juxtaposition, where measurements have not been performed at 77 °K, and where the absorption curve is very steep and quite sensitive to temperature variations, that the uncertainties in the absorption coefficient will be the largest ($\lesssim 30\%$).

The reflectance values employed were obtained from the $\vec{E} \perp \vec{c}$ measurements.[25] The error intro-

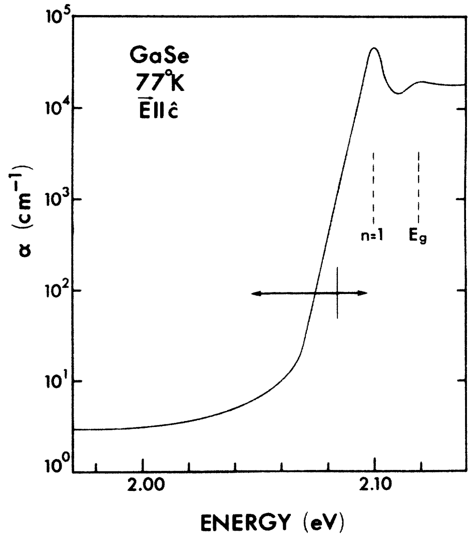

FIG. 1. Estimated absorption coefficient of GaSe for $\vec{E} \parallel \vec{c}$ at 77 °K (after Refs. 19–22 and 24). The curve to the right of the vertical line is taken from data of Ref. 22 and to the left from Ref. 21.

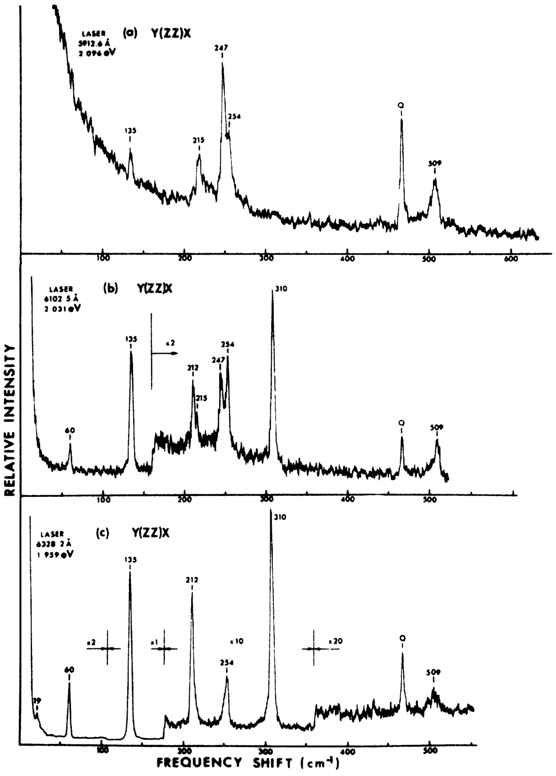

FIG. 2. Resonance Raman spectra of GaSe. The spectra shown correspond to energy shifts, $E_{ex} - \hbar\omega_i$ of (a) 4.2 meV, (b) 69.5 meV, and (c) 141.9 meV. All spectra obtained at 81 °K.

duced by using data obtained in this orientation instead of $\vec{E} \parallel \vec{c}$ will be small compared to the overall experimental error. In conclusion it must be emphasized that in view of the above considerations the values obtained for the scattering efficiency should be regarded as relative rather than absolute efficiencies.

III. RESULTS

A series of spectra recorded with various laser wavelengths is shown in Fig. 2. The notation is the standard one with the incoming and analyzed light in these spectra being $\hat{\epsilon}_i = \hat{\epsilon}_s = \hat{z} \equiv \hat{c}$. Far from resonance [Fig. 2(c)] the spectrum is similar to that obtained previously[5] and a list of the observed modes and their frequencies is given in Table I. The resonant behavior of several of these modes has been studied in detail.

TABLE I. Observed Raman modes in GaSe at 81 °K.

Vibration	Frequency (cm^{-1})
E'	$19.8 \pm .5$
E''	60.0 ± 1.0
A_1'	135.7 ± 1.0
E''	212.3 ± 1.0
E'(TO)	215.6 ± 1.0
A_2''(LO)	247.0 ± 1.0
E'(LO)	254.5 ± 1.0
A_1'	310.8 ± 1.0
$2E'$(LO)	509.7 ± 1.0

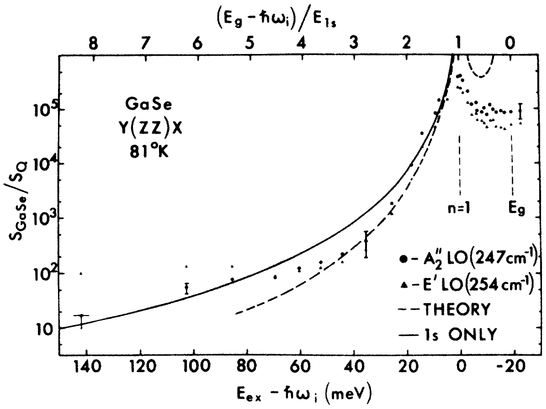

FIG. 3. Relative scattering efficiencies of polar LO phonons of GaSe normalized to the 466-cm^{-1} line of quartz. The theoretical curves are those of Martin (Refs. 16 and 28) (see text). Errors are typically as shown.

A. Polar modes

The most noticeable feature of the spectra presented in Fig. 2 is the resonant behavior of the A_2''(LO) 247-cm^{-1} mode. This mode is normally Raman inactive and as can be seen it is absent far from resonance [Fig. 2(c)]. As the exciting wavelength is decreased, however, this mode appears, grows in intensity, and, in fact, near resonance becomes the dominant feature in *zz* spectra. The E'(LO) mode at 254 cm^{-1}, although Raman active, is also forbidden by selection rules for the *zz* geometry. It can be seen as going from a relatively weak line in the 6328-Å spectrum (possibly due to depolarization) to the second most prominent feature in the GaSe spectrum near resonance. The remaining feature associated with the polar phonons that becomes prominent as the band gap is approached is the $2E'$(LO) mode at 509 cm^{-1}.

The scattering efficiency as a function of excitation energy is plotted in Fig. 3. In this figure the excitation frequency is written both as the energy difference from the exciton line and as a reduced energy parameter $\Delta_i = (E_g - \hbar\omega_i)/E_{1s}$, where E_g is the band-gap energy, ω_i the exciting frequency, and E_{1s} the binding energy of the $n = 1$ free exciton. This notation is used to allow direct comparison with the theory of Martin.[16] At 77 °K the exciton energy has been determined previously to be 2.100 eV in absorption.[26] This result is in good agreement with the value of 2.0984 eV (full width at half-maximum 6.3 meV) that we have obtained in emission at 81 °K, if the band-gap shift of − 0.35 meV/°K is included.[24] From the figure it is obvious that the scattering efficiency of both polar phonons undergoes a distinct maximum at the $n = 1$ free exciton.

B. Nonpolar modes

The A_1' (135 cm^{-1}) and A_1' (310 cm^{-1}) phonons exhibit a much weaker resonant behavior than that of the polar modes. The scattering efficiency of the A_1' (135 cm^{-1}) mode is plotted versus excitation energy in Fig. 4. As can be seen this mode exhibits a striking antiresonance behavior and the scattering efficiency passes through a minimum when the excitation energy is approximately 64 meV below the band gap. This behavior is similar to that observed previously for the $E_2(1)$ mode[11,12] in CdS.

C. Angular dependence

The angular dependence of the scattering efficiency for the polar modes has been investigated in a manner similar to that described by Colwell and Klein.[13] Measurements have been performed over a range of excitation energies extending from 140 to 50 meV below the exciton and the ratio of the backward to forward scattering cross sections has been found to have a constant value of ~1.3± 0.2 throughout this energy interval.

IV. DISCUSSION

A. Spectral features

The Raman spectrum of GaSe has been interpreted previously by the present authors.[5] This work was carried out with excitation far from resonance and the 247-cm^{-1} mode was not observed.

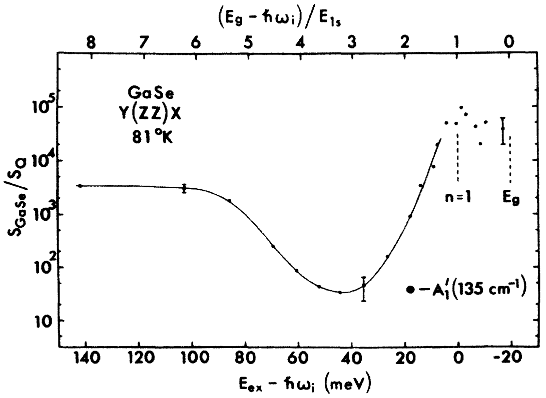

FIG. 4. Relative scattering efficiency of nonpolar A_1' (135 cm^{-1}) phonon. The solid line has been drawn through the experimental points as an aid in visualizing the antiresonant behavior.

A typical nonresonant Raman spectrum is shown in Fig. 2(c). In *zz* oriented spectra only the A_1' (135 cm^{-1}) and A_1' (310 cm^{-1}) modes are allowed. The remaining features appear because of depolarization introduced by the edges of the crystal. This depolarization has a much smaller effect on the relative amplitudes of the modes than do changes in orientation, however, and consequently the selection rules can be clearly verified far from resonance.

Hayek *et al.*,[6] working close to resonance at room temperature, observed the 247-cm^{-1} mode and designated it as the conjugate phonon to the 254-cm^{-1} mode, which they assigned as an E'' phonon. The present experiments, however, show that the 247-cm^{-1} mode appears only as resonance is approached and that it has a distinctly different behavior than that of the 254-cm^{-1} phonon. When a *zx* spectrum at 6102.5 Å (2.0311 eV) is taken, the 247-cm^{-1} peak seen in Fig. 2(b) disappears and the 254-cm^{-1} peak returns approximately to its relative strength of Fig. 2(c). Thus, the resonant mode at 247 cm^{-1} is observed only in *zz* spectra. The resonant behavior of the 247-cm^{-1} mode can easily be reconciled with the predictions of Martin[16] and recent experimental observations[14,17] on forbidden modes. That is, near resonance when *q*-dependent scattering predominates, infrared active modes that are normally Raman forbidden can become Raman active.[14,17] It should be noted that the observation of resonance behavior in only *z*-oriented spectra, that is $\hat{\epsilon}_i \parallel \hat{c}$, is consistent with the theory since the dipole matrix element for both the free-exciton and direct-gap transitions is large only for $\hat{\epsilon} \parallel \hat{c}$.[19,20] The scattering efficiency is proportional to the fourth power of the matrix element and thus the $\hat{\epsilon}_i \parallel \hat{c}$ resonance spectrum should be dominant.

In addition, Leung *et al.*[27] have observed a Reststrahlen band in GaSe with $\vec{E} \parallel \vec{c}$ that terminates at approximately 247 cm^{-1}. This result suggests the identification of the 247-cm^{-1} mode as an LO phonon and in view of this result and the present observations, the 247-cm^{-1} mode has been identified as the Raman-inactive A_2''(LO) mode. A similar identification has also been suggested by Mercier and Voitchovsky.[4] Finally, it should be mentioned that because of the characteristic polar mode behavior of both the 247- and 254-cm^{-1} modes, in conjunction with the previously observed Reststrahlen bands,[2,27] all doubt should be removed as to the polarity of GaSe.

B. Polar modes [E'(LO), 254 cm^{-1}; A_2'' (LO), 247 cm^{-1}]

1. Wavelength dependence

The observed wavelength dependence of the scattering efficiency for the A_2''(LO) and E'(LO) modes

TABLE II. Material parameters of GaSe. Where appropriate, values correspond to right-angle scattering at 5900 Å.

$E_g = 2.120$ eV[a]	$\epsilon_0 = (\epsilon_\perp \epsilon_\parallel)_0^{1/2} = 8.63$[b]
$E_{1s} = 19.6$ meV[a]	$\epsilon_\infty = (\epsilon_\perp \epsilon_\parallel)_0^{1/2} = 7.27$[b]
$\hbar\omega_{LO}(A_2'') = 30.6$ meV[b,c]	$a_0 = a_{\text{Bohr}} R_\infty / \epsilon_0 E_{1s} = 42.5$Å
$\hbar\omega_{LO}(E') = 31.6$ meV[d]	$qa_0 = 0.18$
$n_\parallel \approx 2.8$[e]	
$n_\perp = 2.95$[e]	

[a] Reference 25.
[b] Reference 27.
[c] This work.
[d] References 2 and 4–7.
[e] Reference 19.

is compared to Martin's theory[16,28] in Fig. 3. In this figure the reduced energy parameters $\Delta_i = (E_g - \hbar\omega_i)/E_{1s}$ and $\Delta_0 = \hbar\omega_{LO}/E_{1s}$ are used to plot the curves of the dimensionless scattering efficiency,[16,28] employing the material parameters of Table II. The curves represent the intraband Frohlich interaction (the function H of Ref. 16) for two different cases. The dashed curve is calculated using the states of both discrete excitons and free electrons and holes for the intermediate states in the scattering process. The curve is adjusted to one data point [E'(LO)] at $\Delta_i = 2$ and this point serves as the only constraint. As can be seen from the figure this curve agrees well with the observed scattering when the incident photon energy Δ_i is within 50 meV of the $n = 1$ exciton level. For smaller incident photon energies the calculated values become much smaller than the observed scattering efficiencies. In the case of the E'(LO) phonon this discrepancy can be partially explained as a return to the nonresonant amplitude present in Fig. 2(c). This explanation, however, cannot be invoked in the case of the 247-cm^{-1} phonon which is normally Raman inactive.

The solid curve, on the other hand, represents Martin's results for the intraband Frohlich interaction when only the $n = 1$ state of the free exciton is used as the intermediate state. This curve, that is fixed at the $\Delta_i = 2$ [A_2''(LO)] data point, gives a much better fit in the long-wavelength region, where the absorption corrections are most reliable and the data points therefore most accurate. The agreement is poorest in the energy region approximately 40 meV below the exciton energy, where the measured points fall well below the theoretical curve. As mentioned previously, however, the absorption coefficient of Fig. 1 is expected to be least accurate in this particular region. The fact that the data used to obtain this portion of the curve were obtained at 4.2 °K also means that the absorption coefficient shown in Fig. 1 is almost certainly smaller than the absorption coefficients for the same energies at 77 °K. One would thus expect that the depicted scattering intensities for this and lower incident energies are in turn somewhat small. This would obviously improve the agreement in the 40-meV region and would not seriously affect the agreement at longer wavelengths. It should also be kept in mind that such corrections would worsen the agreement with the dashed curve. In view of these remarks one must conclude that the discrete states of the free exciton are the important intermediate states in the forbidden scattering. It should also be noted in this regard that in the present work any resonance effects at the higher excited states of the exciton, as well as the sharpness of the resonance at the $n = 1$ exciton state, will be muted by thermal effects.

Measurements were also carried out on the polar modes in a 40-meV energy region above the band gap. It was found that the scattering cross section remained essentially constant throughout this region. A small monotonic decrease in the scattering cross section was noted but no distinctive features appeared.

2. *Selection rules*

In GaSe, the E'(LO) phonon has symmetry components $xx - yy$, xy[29] and these selection rules are well obeyed far from resonance.[5] However, as resonance is approached the allowed scattering goes to zero and the "forbidden" diagonal zz scattering becomes predominant. This situation is very similar to that observed in CdS (Ref. 15) for the E_1 (LO) mode. The E'(LO) mode thus represents an example of the type of selection-rule breakdown discussed in detail by Martin.[16]

The A_2''(LO) phonon on the other hand is Raman inactive in GaSe in accord with the absence of this phonon in all spectra taken far from resonance [Fig. 2(c) and Ref. 5]. Thus the A_2''(LO) phonon is an example of a forbidden phonon that becomes active when resonance is approached and q-dependent scattering predominates. Such a selection-rule breakdown has also been predicted by Martin and has been observed previously[14,17] in other compounds. In the present case, however, the phonon propagates in a direction perpendicular to the scattering plane and thus momentum conservation is also lacking. This facet of the scattering is very puzzling and at present the only plausible explanation known to the authors is presented in Sec. IV B3.

As mentioned previously the general behavior of the scattering efficiency of the A_2''(LO) and E'(LO) phonons is qualitatively similar to that observed for the E_1 phonon in Cds.[11] A detailed comparison is, however, impossible because of the approximate degeneracy of the A and E phonons in CdS ($\Delta\nu \simeq 1.8$ cm^{-1})[30] that prevents an investigation of their individual behavior. The occurrence, in CdS, of phenomena similar to those observed here for the A and E phonons cannot be ruled out on the basis of present experimental evidence. In particular, it is possible that near resonance the A phonon contributes to the scattering observed at 305 cm^{-1} in CdS.

3. *Directional dependence*

Martin[16] has pointed out that for q-dependent scattering the scattering efficiency should have an angular dependence proportional to $(\vec{k}_i - \vec{k}_s)^2$ and thus should approach zero in the forward direction. This prediction is in clear disagreement with the present experimental observation of an angularly independent scattering efficiency. An obvious explanation is that the scattering observed here is impurity induced such as that observed in the experiments on CdS by Colwell and Klein.[13] This is not a likely cause here, though, since the scattering efficiency clearly peaks at the free exciton and, in addition, the phonon linewidths are only about 3 cm^{-1} even in resonance. Colwell and Klein,[13] on the other hand, observed a severe (25 cm^{-1}) broadening of the lines due to impurities.

The nonconservation of momentum discussed in Sec. IV B2 and the angular dependence could be explained if some momentum-breaking mechanism existed that was preferentially directed in the crystal.[17,31] Such a mechanism does in fact exist in the present GaSe crystals and consists of the many stacking faults that occur along the z axis of the crystal.[32] These stacking faults modify the crystal periodicity in the z direction and thus destroy momentum conservation along the z direction. If this is so, the angular dependence of the scattering is then proportional to[31] $[\vec{k}_i - \vec{k}_s + (\vec{\Delta} q_z)]^2$ and if $\vec{\Delta} q_z$ predominates the scattering efficiency becomes independent of angle. Thus the existence of stacking faults can be used to explain both the observed angular dependence and lack of momentum conservation.

C. Nonpolar phonons

The observed antiresonant behavior for the 135-cm^{-1} mode is qualitatively similar to that observed for nonpolar modes $[E_2(1)]$ in CdS.[11,12] Ralston *et al.*[11] suggested that the observed minimum in the scattering cross section arose from a cancellation between the resonant and nonresonant components of the scattering tensor.

Their expression for the cross section was later modified by Damen and Scott,[12] who neglected the phonon energy, and obtained

$$\sigma \sim \left(\frac{A\omega_g^2}{(\omega_g - \omega_L)^2} + B\right)^2 ,$$

where ω_g is the gap frequency, ω_L is the laser frequency, and A and B are positive or negative constants. Damen and Scott found that this expression gave a qualitative fit to the limited number of data points that were available for the $E_2(1)$ (43 cm^{-1}) mode of CdS. This relation, however, does not yield even qualitative agreement with the present results. The antiresonances in GaSe occur much closer to the band edge and are much deeper than the antiresonances observed in CdS. As a result the expression of Damen and Scott gives an antiresonance minimum that is much narrower than the observed dip. It is clear that an alternate mechanism will have to be found to explain the present observations. The 308-cm^{-1} mode (A_1') has been observed to exhibit an almost identical behavior to the 135-cm^{-1} mode and is not shown in the figure.

D. Two-phonon resonance

The two-LO-phonon feature at 509 cm^{-1} can also be clearly observed in Fig. 2. Detailed measurements have not been carried out on this mode but a certain similarity with the CdS case can be noted. This involves the fact that only the $2E'$(LO) mode appears and, although the peak is smeared out to a certain extent by anisotropy, the $2A_2''$(LO) is clearly absent. The relative intensity of the $2E'$(LO) mode is, however, much weaker in GaSe than the corresponding 2LO peak in CdS and a large number of multiple-phonon peaks has not been observed in GaSe.

V. CONCLUSIONS

The resonant Raman spectrum of GaSe has been investigated. The results are consistent with a previous interpretation of the Raman spectrum[5] and in addition the 247-cm^{-1} mode is clearly identified as an A_2''(LO) mode in agreement with previous infrared measurements.[27] This identification and the resonant behavior of the A_2''(LO) and E'(LO) modes are a further[2,27] indication of the polar nature of GaSe. The scattering cross section for the polar longitudinal modes exhibits a definite maximum at the $n=1$ free-exciton energy level. This result clearly identifies the free exciton as the intermediate state in the scattering process. The wavelength dependence observed was in satisfactory agreement with the theory of Martin[16] if only the ground state of the free exciton is considered in the calculation of the scattering efficiency. In contradiction to Martin's theory, however, the scattering was found to be independent of scattering angle, and momentum conservation did not hold for the A_2''(LO) phonon. The breakdown of momentum conservation and angular independence were attributed to the existence of stacking faults along the c axis of the crystal.

The nonpolar Raman-active A_1' phonons were observed to undergo a well-defined antiresonance, analogous to that of the $E_2(1)$ (43 cm^{-1}) phonon in CdS.[11,12] The present wavelength dependence, however, could not be reproduced by the empirical model[11,12] used previously. It is hoped that the present work will stimulate a search for an alternate explanation of the antiresonant behavior.

ACKNOWLEDGMENTS

The authors wish to thank Dr. J. L. Brebner for the loan of the GaSe crystals used in this study, and Dr. R. M. Martin for very informative and helpful discussions and for the donation of unpublished calculations. The financial support of the National Research Council of Canada is gratefully acknowledged.

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