Raman Scattering in GaSe

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Received February 27, 1975

Raman spectra have been obtained from both the ϵ and γ polytypes of GaSe. The frequencies of the phonons at the zone center have been obtained for both compounds at 80 K and at 295 K. All modes have been assigned on the basis of their observed polarization dependence to an irreducible representation of the appropriate point group. A comparison of the spectra of the two polytypes has provided further confirmation of previous identifications of the various modes in ϵ-GaSe. Excellent agreement has been obtained between the observed and predicted dependence of the polar mode frequencies with phonon propagation direction. No evidence of conjugate modes has been observed in any of the GaSe spectra.

On a obtenu des spectres Raman des deux polytypes, ϵ et γ, de GaSe. Les fréquences des phonons au centre de zone ont été déterminées pour les deux composés à 80 K et à 295 K. Tous les modes ont été identifiés sur la base de la dépendance entre les polarisations observées et une représentation irréductible du groupe ponctuel approprié. Une comparaison des spectres des deux polytypes à fourni de nouvelles confirmations des identifications faites antérieurement pour les divers modes dans ϵ-GaSe. Il existe un accord excellent entre les observations et les prédictions quant à la variation des fréquences des modes polaires avec la direction de propagation des phonons. On n'a trouvé aucune indication de la présence de modes conjugués dans les spectres de GaSe.

Can. J. Phys., **53**, 1606 (1975)

[Traduit par le journal]

Introduction

GaSe is a semiconducting layer structure compound that is made up of weakly interacting, essentially two dimensional sheets, each of which is four atoms thick. The sheets can be stacked in a variety of ways to give the full three dimensional structure. Three distinct stacking sequences, or polytypes, have been observed for GaSe (Fig. 1, Basinski *et al.* 1969). X-ray investigations of Bridgman and transport grown single crystal platelets (Schubert *et al.* 1955; Terhell and Lieth 1972*a*) have indicated that GaSe crystallizes in the ε polytype (Fig. 1). On the other hand, X-ray powder patterns obtained from similarly grown crystals (Jellinek and Hahn 1961; Wieting and Verble 1972) have indicated that the stacking in such crystals conforms to the β polytype. Finally, when GaSe is grown by the sublimation technique, some crystals are obtained in the form of needles and Terhell and Lieth (1972*b*) have found that the needles crystallize in the γ polytype.

The X-ray patterns obtained from the Bridgman or transport grown crystal platelets have further indicated (Terhell and Lieth 1972*a*, *b*) that such crystals contain many stacking faults and thus the crystals are quite disordered. To account for this disorder it has been suggested (Mooser and Schlüter 1973; Mercier and Voitchovsky 1974) that the platelet crystals actually contain a mixture of the γ and ε polytypes. Terhell and Lieth (1972*a*) have added that the powdering of such crystals would tend to increase the disorder and that the X-ray patterns then obtained from the powder are similar to those that would be obtained for a β polytype. Terhell and Lieth have thus concluded that GaSe usually occurs in only two modifications, namely γ and ε, and the β polytype will occur only as an accident.

Raman scattering and infrared investigations have tended to confirm (Irwin *et al.* 1973; Hayek *et al.* 1973; Yoshida *et al.* 1973; Mercier and Voitchovsky 1974) that GaSe platelet crystals contain the ε modification, but no information has been gained as to the extent to which the γ

modification is present in such crystals. In addition, a number of minor discrepancies concerning the exact identification of certain modes and the appearance of conjugate modes have arisen. It was felt that a Raman scattering investigation of the sublimation grown γ type needles would help to clarify these points as well as providing direct information on the γ polytype itself. This paper presents the results of a Raman scattering investigation of the γ polytype and a comparison of the results with those previously obtained from the ε polytype (Irwin *et al.* 1973).

In the γ polytype all the vibrational modes are Raman active and, thus, a complete picture of the vibrational modes should be obtained from the Raman spectra of the needle crystals. In fact, the present results in combination with a previous infrared measurement (Irwin *et al.* 1973) provide a frequency for all modes having a different intralayer vibration. The present results are consistent with the observation of γ polytypism of Terhell and Lieth (1972*b*). Furthermore, a comparison of the present results with ε polytype spectra has provided confirmation for our earlier interpretation and mode assignments (Irwin *et al.* 1973).

This information has also provided further evidence as to the extent to which GaSe acts as a two dimensional crystal. This evidence is gained by examining the directional dependence of the polar mode frequencies (Loudon 1964). The dispersion of such modes is expected to exhibit two quite different types of behavior. In one case, the electrostatic field associated with the polar modes is the predominant factor in determining the directional dependence of the frequency and in the other case the anisotropy of the short range force constants is expected to dominate the behavior of the frequencies. GaSe, because of its obvious structural anisotropy, might be expected to fall in the latter classification but the results obtained here indicate that the polar modes behave similarly to those in much more isotropic crystals (Arguello *et al.* 1969). This result implies that GaSe has some properties typical of an isotropic crystal. This conclusion is similar to that reached by Ottaviani *et al.* (1974) from investigations of the electronic properties of GaSe.

Crystal Structure and Symmetry

As indicated in Fig. 1 the unit cell of the β polytype spans 2 layers of the crystal and contains 8 atoms. The 24 normal modes of vibration at the center Γ of the Brillouin zone can be represented by the irreducible representations of the D_{6h} point group. At Γ one has:

$$\Gamma \equiv 2A_{1g} \oplus 2A_{2u} \oplus 2B_{1u} \oplus 2B_{2g} \oplus 2E_{1g} \oplus 2E_{1u} \oplus 2E_{2g} \oplus 2E_{2u}$$

of which there are six Raman active modes. Each irreducible representation has been correlated with a set of atomic vibrations by Wieting and Verble (1972). In the ε polytype, the unit cell again spans 2 layers and contains 8 atoms. There are 24 normal modes at the zone center and these can be described by the irreducible representations of the point group D_{3h}:

$$\Gamma \equiv 4A_1' \oplus 4A_2'' \oplus 4E' \oplus 4E''$$

There are now 11 nondegenerate Raman active modes, $4E''$, $4A_1'$, and $3E'$, and 6 infrared active modes, $3A_2''$ and $3E'$. Each of the irreducible representations is assigned to a set of atomic displacements in Fig. 2, in a manner similar to that used previously (Wieting and Verble 1972; Jandl and Brebner[1]). In this figure the bracketed numerals associated with the group representations have no physical significance and are used only as a label. The principal number designates the column and the numerical superscript designates the row in which the mode appears.

The γ polytype has a unit cell spanning 3

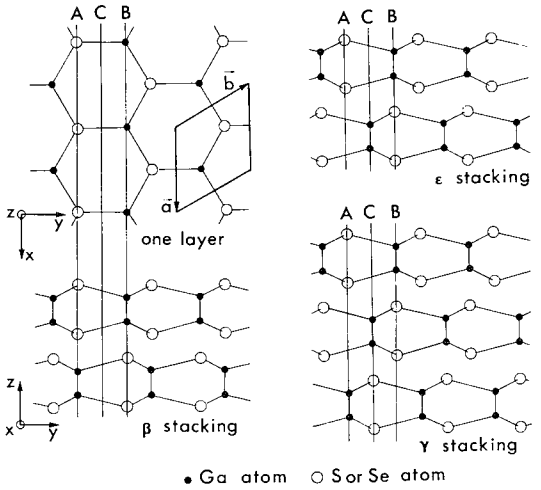

FIG. 1. Stacking sequences for the β, ε, and γ polytypes of GaS and GaSe.

[1]Jandl, S. and Brebner, J. L. 1974. Private communication.

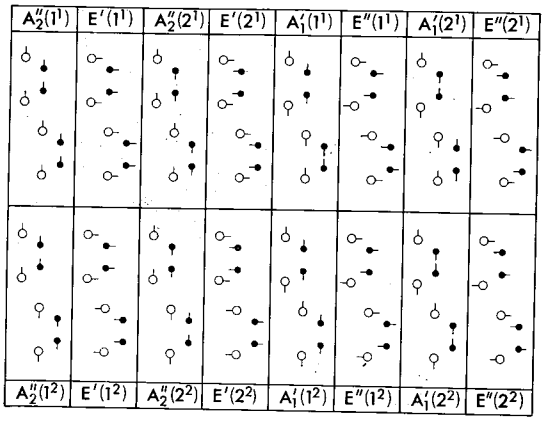

FIG. 2. Normal modes of vibration of the ε polytype.

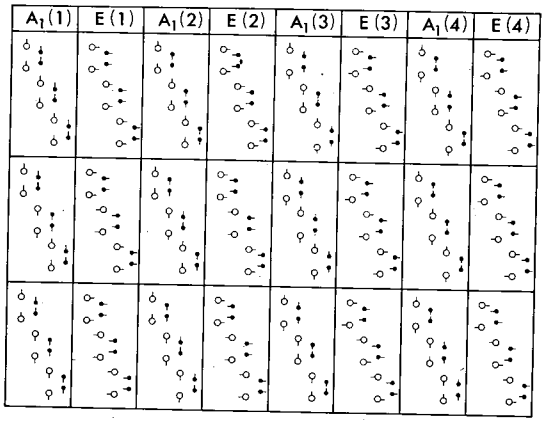

FIG. 3. Normal modes of vibration of the γ polytype.

layers and, thus, 12 atoms. The 36 normal modes of vibration at the zone center are represented by the irreducible representations of the C_{3v} point group:

$$\Gamma \equiv 12A_1 \oplus 12E$$

All the optic modes are now both infrared and Raman active and there should thus be 22 non-degenerate Raman active modes. The assignment of a representation to a set of atomic displacements is shown in Fig. 3. The same notation used in Fig. 2 is used to designate a particular mode of vibration in Fig. 3.

The intralayer vibrations in each column are identical for all three polytypes and only the method of stacking is altered. A one-to-one correspondence can thus be drawn between ε polytype modes and those of the β polytype on the basis of the intralayer vibrations and the results are shown in Table 1. On the same basis, a correspondence can also be drawn between the ε and γ polytypes, but the correspondence is now between columns only. This is also summarized in Table 1.

TABLE 1. Correspondence between modes having identical intralayer vibrations for the β, ε, and γ polytypes

β	ε	γ
A_{2u} B_{2g}	$A_2''(1^1)$ $A_2''(1^2)$	$A_1(1^1)$, $A_1(1^2)$, $A_1(1^3)$
E_{1u} E_{2g}	$E'(1^1)$ $E'(1^2)$	$E(1^1)$, $E(1^2)$, $E(1^3)$
A_{2u} B_{2g}	$A_2''(2^1)$ $A_2''(2^2)$	$A_1(2^1)$, $A_1(2^2)$, $A_1(2^3)$
E_{1u} E_{2g}	$E'(2^1)$ $E'(2^2)$	$E(2^1)$, $E(2^2)$, $E(2^3)$
B_{1u} A_{1g}	$A_1'(1^1)$ $A_1'(1^2)$	$A_1(3^1)$, $A_1(3^2)$, $A_1(3^3)$
E_{2u} E_{1g}	$E''(1^1)$ $E''(1^2)$	$E(3^1)$, $E(3^2)$, $E(3^3)$
B_{1u} A_{1g}	$A_1'(2^1)$ $A_1'(2^2)$	$A_1(4^1)$, $A_1(4^2)$, $A_1(4^3)$
E_{2u} E_{1g}	$E''(2^1)$ $E''(2^2)$	$E(4^1)$, $E(4^2)$, $E(4^3)$

The ε crystals used in this work were grown by the Bridgman technique and were given to us by Dr. J. Brebner. The γ crystals were in the form of needles and were grown by sublimation (Terhell and Lieth 1972*b*).

Results

Raman spectra have been obtained for the γ polytype at both room and liquid nitrogen temperatures. The γ polytype spectra presented in this work were excited with the 632.8 nm line of a He–Ne laser and detected with the apparatus described previously (Irwin *et al.* 1973). As mentioned, the γ polytype crystal was in the form of a needle and the orientation of the faces was determined from X-ray photographs. A diagram of the pertinent section of the needle is shown in Fig. 4. The Raman spectrum of the ε polytype has been investigated and discussed in a previous paper (Irwin *et al.* 1973). However, for the purposes of comparison with the γ polytype, additional ε polytype spectra obtained in the appropriate scattering geometries are presented in this work. These spectra were obtained from the ε

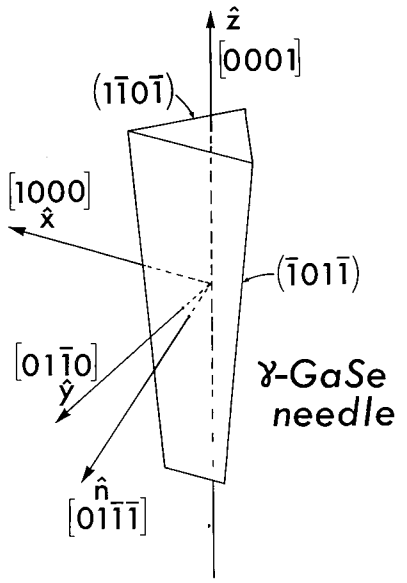

FIG. 4. Diagram of the γ-GaSe needle showing the orientation of the various crystal faces.

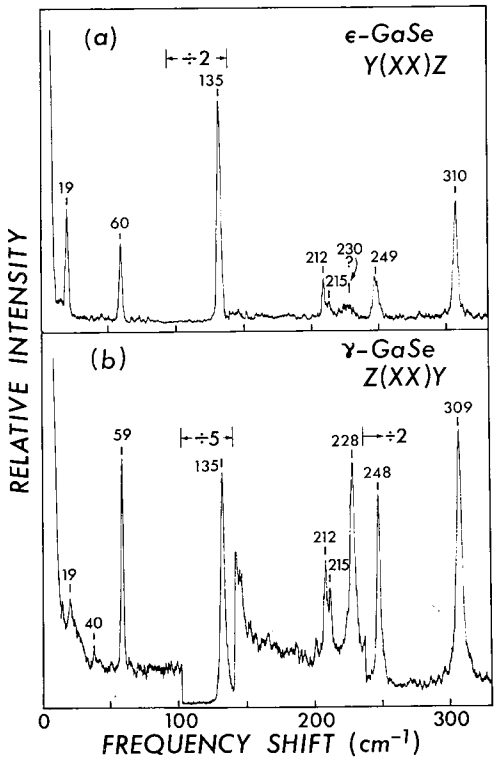

FIG. 5. Raman spectra of ε-GaSe (*a*) from *Y(XX)Z* geometry and γ-GaSe (*b*) from *Z(XX)Y* geometry.

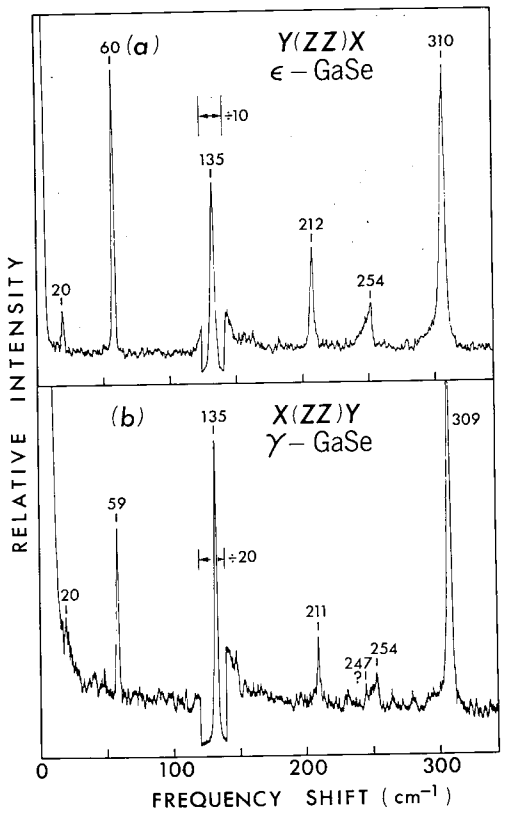

FIG. 6. Raman spectra of ε-GaSe (*a*) from *Y(ZZ)X* geometry and γ-GaSe (*b*) from *X(ZZ)Y* geometry.

polytype crystals described previously (Irwin *et al.* 1973) and the spectral frequencies and interpretation remain unchanged.

Two Raman spectra obtained from a needle of γ-GaSe are compared to two ε polytype spectra in Figs. 5 and 6. In all cases the scattering geometry is defined using standard notation. *X*, *Y*, and *Z* are the axes of the laboratory coordinate system and the crystal is oriented with its X_1 axis along *X*, X_2 along *Y*, and X_3 along *Z*. Here X_1, X_2, and X_3 are the axes defined by Nye (1957) and employed by Loudon (1964). The first and second letters of the designation A(BC)D designate the direction and polarization respectively of the incident light; the third and fourth letters designate the polarization and direction respectively of the scattered light (Damen *et al.* 1966).

In the γ polytype, the *E* modes have symmetry properties $xx - yy$, xy, xz, zy while the *A* modes

TABLE 2. Measured phonon frequencies in ε and γ-GaSe

Frequencies					
ε-GaSe			γ-GaSe		
Mode	$\tilde{\nu}$(77 K)	$\tilde{\nu}$(293 K)	Mode	$\tilde{\nu}$(77 K)	$\tilde{\nu}$(293 K)
$E'(1^2)$	19.8	19.5	$E(1^2)$	20.7 ± 2.0	20.9 ± 2.0
$E''(1^2)$	60.0	60.1	$E(3^2)$	59.4	59.5
$A_1'(1^2)$	135.7	134.3	$A_1(3^2)$	135.0	133.5
$E''(2^2)$	212.3	211.9	$E(4^2)$	211.0	208.7
$E'(2^2)$TO	215.6	214.0 ± 2.0	$E(2)$TO	215.2	213.9
$E'(2^1)$LO	254.5	252.1 ± 2.0	$E(2^1)$LO	255.5	253.2
$A_1'(2^2)$	310.8	308.0	$A_1(4^2)$	309.5	307.4
			$A_1(2^1)$TO	—	235.7
			$A_1(2^1)$LO	247.8	246.5

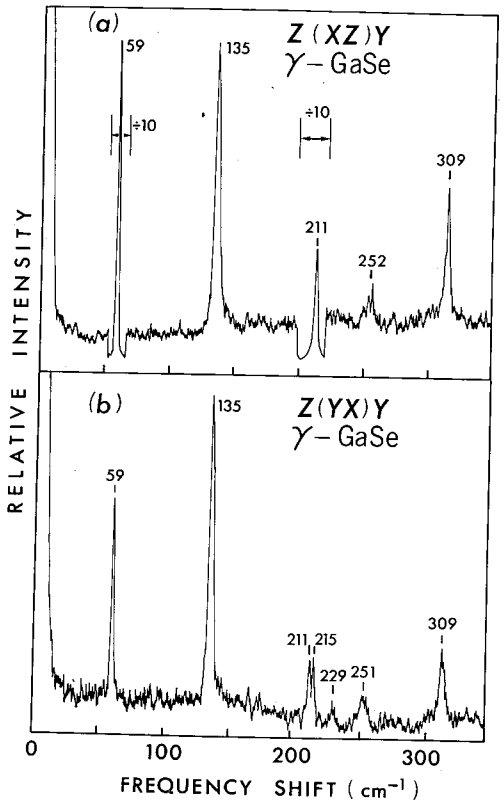

FIG. 7. Raman spectra of γ-GaSe (*a*) from $Z(XZ)Y$ geometry and (*b*) from $Z(YX)Y$ geometry.

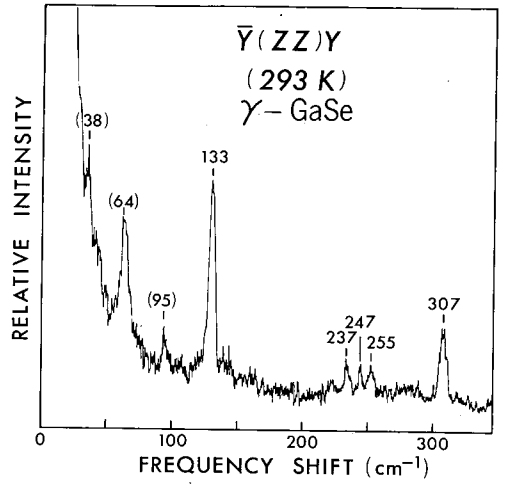

FIG. 8. Raman spectrum of γ-GaSe from $\bar{Y}(ZZ)Y$ geometry.

have only the diagonal elements $xx + yy$, zz (Loudon 1964). Thus, in principle, the two spectra presented for the γ polytype in Figs. 5 and 6 provide sufficient information to distinguish between the two types of modes that are present in the γ polytype. A more complete identification of the modes is enabled, however, if spectra obtained from other scattering geometries are also examined and Figs. 7 and 8 present spectra obtained from the needle in three other scattering geometries. In these figures, those features that are designated by a bracketed number have been found to be due to either neon lines or grating ghosts. A list of the observed frequencies and their mode assignment is contained in Table 2.

Several features in the Raman spectra of both polytypes do not possess a constant frequency as a function of phonon propagation direction. These modes are the polar LO phonons and associated TO phonons. In γ-GaSe it has been possible to measure these frequencies for several different propagation directions and the results are summarized in Fig. 9. In this figure, θ is the angle between the phonon wave vector and the *c* or *Z* axis of the crystal.

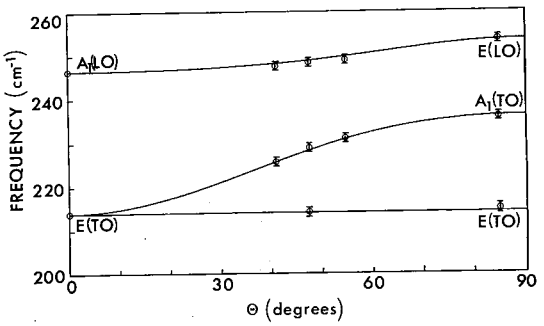

FIG. 9. Frequencies of polar phonons in GaSe for various directions of propagation.

Discussion

A. Comparison of ε and γ Spectra

In the $Z(XX)Y$ spectrum of γ-GaSe (Fig. 5*b*), all phonons are Raman allowed and, thus, should be observable in this spectrum. On the other hand, for the similar $Y(XX)Z$ spectrum of ε-GaSe (Fig. 5*a*), only the A_1 and E' phonons are Raman allowed. As can be seen, however, due to depolarization by the sample edges, the relatively strong E'' phonons at 60 cm^{-1} and 211 cm^{-1} are also observable. Although the corresponding $E(3)$ and $E(4)$ phonons are Raman allowed in the γ spectrum while the E'' phonons are forbidden in the ε spectrum, the relative strengths of the E and A phonons are roughly the same in both Figs. 5*a* and *b*. On this basis, one might conclude that the change in stacking sequence does not appreciably alter the selection rules.

There is a notable difference between the two spectra of Figs. 5*a* and *b*, however. This is the increase in strength of the features at 228 and 248 cm^{-1} in the γ spectrum. It should be noted that the feature identified by 230 (?) in the ε spectrum was very weak and broad and in many cases could not even be observed. A weak feature also appears at approximately 40 cm^{-1} in the γ spectrum. This feature could be assigned to the $A_1(1^2)$ mode, on the basis of its correspondence to $A_2''(1^2)$ which has been observed to lie at 36.6 cm^{-1} (4.2 K) in the ε polytype (Irwin *et al.* 1973). However, experiments carried out on other materials have also produced a peak at this frequency. On this basis and in view of the fact that its frequency is somewhat greater than the expected value of approximately 35 cm^{-1}, this feature has been identified as a ghost. In this regard it should be noted that, because of the large amount of light that was elastically scattered by the small γ crystals, all the low energy features of the γ spectrum were difficult to observe. This was particularly true in backscattering geomtries.

Figures 6*a* and *b* present the $Y(ZZ)X$ spectra of both the ε and γ crystals respectively and for this geometry only the A_1 modes are Raman allowed. Again depolarization permits the observation of relatively strong E'' modes in both spectra. The dominance of the A_1 modes (135 and 309 cm^{-1}) in Fig. 5*b* is obvious, however, and allows their unambiguous identification.

Figures 7*a* and *b* present two further γ-GaSe spectra obtained in the $Z(XZ)Y$ and $Z(YZ)Y$ orientations respectively. Although these spectra are not required for the differentiation between A_1 and E modes, they do provide additional information concerning the effect of stacking. In the ε polytype, the A_1' and E'' modes were the dominant features of the spectra and, as can be seen from these spectra, their counterparts ($A_1(3)$, $A_1(4)$, $E(3)$, and $E(4)$) in the γ crystals retain the same symmetry characteristics. The $Z(YX)Y$ spectrum provides the greatest discrimination against these modes (in ε-GaSe they are forbidden in this geometry) and allows identification of the E(TO) (215 cm^{-1}) mode whose counterpart in ε-GaSe, $E'(2)$, would also be allowed in this orientation. In the $Z(XZ)Y$ γ-GaSe spectrum of Fig. 7*a*, the $E(3)$ and $E(4)$ modes at 60 cm^{-1} and 211 cm^{-1} become dominant, exactly as did their counterparts in the ε-GaSe spectra (Irwin *et al.* 1973).

Given that the frequencies and symmetry characteristics of the most prominent modes are essentially identical in the two crystals, one must conclude that the vibrations are dominated by intralayer forces and that changes in stacking sequence do not greatly influence the properties of the modes. The major change that occurs in going from the ε polytype to the γ polytype is the increase in strength of the features at approximately 230 cm^{-1} and 250 cm^{-1}. These modes are connected with the polar A and E phonons and will be discussed in detail in the following section. The assignments of the observed features to irreducible representations are thus very similar to those made in the ε case (Irwin *et al.* 1973) and the results are summarized in Table 2. The numbers in Table 2 represent averages obtained from several spectra.

B. Polar Optical Phonons

As in ε-GaSe, the modes near 250 cm^{-1} in

the spectra can be attributed to longitudinal optical phonons. In ε-GaSe, however, the A symmetry phonon was of symmetry character A_2'' and was Raman inactive far from resonance (Irwin *et al.* 1973). It did appear near resonance (Hoff and Irwin 1974) and had a measured frequency of 247 cm^{-1}. In γ-GaSe this phonon has A_1 symmetry, is Raman allowed, and as can be seen from the spectra it is present even far from resonance. In ε-GaSe the frequency of the E(LO) phonon was measured to be 254 cm^{-1} and a similar value has been obtained for the corresponding E(LO) phonon from the γ spectra. One must be careful, however, to measure these frequencies only in those cases in which the phonon is propagating along the appropriate crystal symmetry axis. For an arbitrary phonon propagation angle θ from the c axis, the normal mode observed will be a mixture of the A and E modes and will possess an intermediate frequency (Loudon 1964; Arguello *et al.* 1969). In fact, to obtain a complete picture of what actually occurs, one must also consider the associated TO phonons in conjunction with the LO phonons.

An expression for the frequency of these modes for arbitrary propagation directions, θ, from the c axis has been given by Loudon (1964). For $\omega/c \ll k$, one has

$$[1] \qquad \omega = \omega_\perp \text{(ordinary phonon)}$$

and

$$[2] \quad \left(\frac{\omega_\parallel{}^2\varepsilon_\parallel{}^0 - \varepsilon_\parallel{}^\infty\omega^2}{\omega_\parallel{}^2 - \omega^2}\right)\cos^2\theta + \left(\frac{\omega_\perp{}^2\varepsilon_\perp{}^0 - \varepsilon_\perp{}^\infty\omega^2}{\omega_\perp{}^2 - \omega^2}\right)\sin^2\theta = 0 \text{ (extraordinary phonons)}$$

where $\omega_\parallel$, $\omega_\perp$ are the TO phonon frequencies for vibrations parallel (A symmetry) and perpendicular (E symmetry) to the c axis respectively.

One can also define a longitudinal phonon frequency in each direction

$$[3] \qquad \omega_\parallel{}^l = \omega_\parallel \left(\frac{\varepsilon_\parallel{}^0}{\varepsilon_\parallel{}^\infty}\right)^{1/2}$$

$$[4] \qquad \omega_\perp{}^l = \omega_\perp \left(\frac{\varepsilon_\perp{}^0}{\varepsilon_\perp{}^\infty}\right)^{1/2}$$

in analogy with the cubic case.

The measured longitudinal phonon frequency in a polar uniaxial crystal will not necessarily equal these defined frequencies if more than one set of three phonons is infrared active (Loudon 1964). In general, the relations [3] and [4] must be modified to include all the phonons.

In GaSe, however, no evidence has been obtained from the spectra that indicates the existence of any polar modes other than the two mentioned. This is in keeping with other evidence that indicates that the basic behavior possessed by the modes in the ε structure is not greatly modified by the γ stacking. In other words, although all the modes in the γ polytype should be i.r. active, this activity will be very weak for all those modes other than $A_1(2^1)$ and $E(2^1)$. It will also be seen that good agreement is obtained between the measured frequencies and the previously measured dielectric constants (Leung *et al.* 1966). On this basis it is assumed that the dielectric behavior of GaSe is dominated by the $A_1(2^1)$ and $E(2^1)$ modes and the effects of additional polar modes are neglected.

Loudon (1964) had discussed the solution of [2] for the two limiting cases that are applicable to many crystals of experimental interest. The first case considers the limit $(\omega_\parallel - \omega_\perp) \ll (\omega_\parallel{}^l - \omega_\parallel)$ and $(\omega_\perp{}^l - \omega_\perp)$. In this limit the electrostatic forces cause a much greater splitting between modes than is caused by the anisotropy of the force constants. Assuming the above inequalities, one then obtains the approximate solutions for [2],

$$[5] \qquad \omega^2 = \omega_\parallel{}^2\sin^2\theta + \omega_\perp{}^2\cos^2\theta$$

$$[6] \qquad \omega^2 = \omega_\parallel{}^{l2}\cos^2\theta + \omega_\perp{}^{l2}\sin^2\theta$$

That is, the two TO modes mix to give a new mode and similarly a new mode is formed from the mixture of the two LO modes.

The other limiting case discussed by Loudon occurs when the anisotropy of the force constants dominates the behavior of the modes over the electrostatic forces. In this case, one new mode is formed from a combination of E(TO) and E(LO) modes and another results from the combination of the A(TO) and A(LO) modes (Loudon 1964; Arguello *et al.* 1969).

A plot of the angular dispersion of the polar modes according to [1] and [2] is shown in Fig. 9 by the solid lines. The values for $\omega_\parallel{}^l A_1(2^1\text{LO})$, $\omega_\perp{}^l E(2^1\text{LO})$, $\omega_\parallel A_1(2^1\text{TO})$, and $\omega_\perp E(2^1\text{TO})$ have been obtained from Table 2. The dielectric constants have been measured for the ε polytype by Leung *et al.* (1966) and have the values:

$$\varepsilon_{\parallel}^{0} = 7.6; \quad \varepsilon_{\parallel}^{\infty} = 7.1$$
$$\varepsilon_{\perp}^{0} = 9.8; \quad \varepsilon_{\perp}^{\infty} = 7.45$$

As can be seen from Fig. 9 there is excellent agreement between the predicted behavior and the experimental points. The range of angles in which measurements have been made has been limited to an approximately 14° band about 45° because of the large index of refraction of GaSe. Because, however, the measurements made in this region yield values that fall on the most dispersive region of the curve, it is felt that they provide a reliable test of the theoretical predictions.

It should be noted that the dielectric constants of GaSe are such that this crystal should represent a case intermediate between the two limits specified by Loudon (1964). However, as is evident from this figure, the two TO modes mix to produce a new mode as do the two LO modes. This behavior is characteristic of those crystals belonging to the first case mentioned above, that is, characteristic of those crystals in which electrostatic forces dominate over the anisotropy of the force constants. One, thus, arrives at the somewhat surprising conclusion that the polar modes of GaSe, in spite of the highly anisotropic crystal structure, behave similarly to those in polar crystals having a much more isotropic crystal structure (Arguello *et al.* 1969).

C. Conjugate Modes

Hayek *et al.* (1973) have noted the possibility of observing conjugate modes, that is, modes belonging to the same column of Fig. 2, in the Raman spectra of ε-GaSe. As pointed out by Wieting and Verble (1972), these modes should be nearly degenerate in that their frequencies are related by $\omega_2^2 = \omega_1^2 + (\Delta\omega)^2$. Here ω_1 and ω_2 are the frequencies of the modes in the upper and lower rows respectively of Fig. 2 and $\Delta\omega$ is the weak interlayer coupling ($E'(1)$ or $A_2''(1)$). Thus, such conjugate modes would be most easily resolved for the lower frequency vibrations such as $E''(3)$ (60 cm^{-1}). No evidence for such modes was found in the ε spectra (Irwin *et al.* 1973) and this was attributed to the fact that the change in stacking in going from β to ε had little effect on the basic spectral activity of the mode. That is, if it was odd in β and therefore Raman forbidden, its Raman activity remained very small in the ε polytype.

A similar situation occurs in the γ polytype in that, once again, no direct evidence of conjugate modes has been provided by the γ spectra. A weak shoulder on the 135 cm^{-1} line at approximately 141 cm^{-1} has been observed in some of the spectra, in agreement with Hayek *et al.* (1973). Although this feature could be due to the $A_1(3^3)$ mode, it could also arise from second order scattering, impurities, etc. The mode at 150 cm^{-1}, observed in mixed GaS_xSe_{1-x} crystals by Mercier and Voitchovsky (1974), could not be detected in any of the ε or γ spectra obtained here.

We have thus concluded that with the exception of LO polar modes, the dominant features in the spectra arise from modes in the second and center rows of Figs. 2 and 3 respectively.

Conclusions

The Raman spectrum of γ-GaSe has been investigated and interpreted. The spectrum is very similar to that of ε-GaSe in that the frequencies of the major features are identical within experimental error to those measured in ε-GaSe. In addition, the relative intensities and symmetry dependence of the major features were also very similar in the spectra of the two compounds. The main difference between the two spectra was the appearance in the γ spectrum of two strong features corresponding to the combinations of the A(TO) and E(TO) and the A(LO) and E(LO) modes. It will be remembered that the principal difference between the β-GaS and ε-GaSe spectra, aside from the frequencies of the features, was the appearance of additional modes, namely the (LO) mixed modes at approximately 250 cm^{-1} and the weak feature at about 230 cm^{-1}. It has now been found that the major difference between ε and γ is the enhancement of both of these features because of change in activity of the $A_1(2)$ mode in the γ crystals.

Previously, (Irwin *et al.* 1973) it was concluded that, in going from β to ε, the change in stacking had little effect on the spectral activity of the nonpolar features. This conclusion is reinforced by the results of the comparison between the ε and γ polytypes. It must be assumed that the intralayer vibrations determine the basic spectral activity of the modes of vibration.

It has been suggested (Mercier and Voitchovsky 1974) that the Bridgman grown platelet crystals are actually mixtures of the γ and ε polytypes. The present results, however, do not pro-

vide much support for this suggestion. The increase in strength of the mixed TO and LO modes, that is made possible by the $A_2(2)$ mode becoming Raman allowed, is a change that is similar in magnitude to the spectral differences observed (Irwin *et al.* 1973) between the β-GaS and ε-GaSe compounds. On this basis one might infer that the transition between the γ and ε polytypes is equal in sharpness to that between the β and ε polytypes. Certainly the γ content of the ε crystals used in this work must be quite small. In fact, in future works, the relative strengths of the polar mixed modes might be used as a measure of the γ content of a given crystal of GaSe.

The variation in frequency of the mixed TO and LO modes has been studied as a function of phonon propagation direction. The results have led to the somewhat surprising conclusion that the electrostatic forces are the dominant factor, rather than the anisotropy of the force constants, in determining the directional dependence of the frequencies of the mixed polar modes.

In support of this observation Ottaviani *et al.* (1974) have also found that some of the electronic properties of GaSe are very isotropic. The present observation is, thus, surprising only in view of the highly anisotropic crystal structure of GaSe.

Acknowledgments

The authors would like to thank Dr. J. L. Brebner for providing the ε crystal platelets of GaSe that were used in this work. The financial support of the National Research Council of Canada is gratefully acknowledged.

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