Splitting and Coupling of Lattice Modes in the Layer Compounds GaSe, GaS, and GaSe$_x$S$_{1-x}$

M. Hayek[*] and O. Brafman

Department of Physics, Technion-Israel Institute of Technology, Haifa, Israel

R. M. A. Lieth

Chemical Physics Division, Department of Physics, Eindhoven University of Technology, Eindhoven, The Netherlands

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The $\vec{k} \approx 0$ phonon spectra of the layer crystals GaSe, GaS, and their solid solutions are presented. All phonon bands in GaSe (D_{3h} symmetry) and GaS (D_{6h} symmetry) are assigned and good agreement prevails between experimental results and group-theory predictions. It is shown that GaSe behaves approximately like a two-dimensional crystal; judging by the display of its phonons the interaction between layers gives rise to Davydov doublets. It is demonstrated that these splittings in GaSe may be accurately measured. Owing to lack of inversion symmetry both components of some of the doublets are Raman active, and thus the splitting is yielded directly by a single Raman experiment. The largest splitting was found to be about 7 cm^{-1}. A correspondence between GaSe doublets and GaS single Raman bands is proven. A detailed study of $\vec{k} \approx 0$ phonons in GaSe$_x$S$_{1-x}$ solid solutions is presented. It shows that these solid solutions yield an exceptional behavior of the phonon modes; some of the bands are of the one-mode type, while the others are of the two-mode type. In the two GaSe A doublets, mode coupling between the two conjugate lines occurs, and both repulsion and intensity transfer are revealed and discussed.

I. INTRODUCTION

GaSe and GaS are known to be layer crystals, [1-3] which means that the bondings within the layer are considerably larger than those perpendicular to it. The study of such materials is motivated by curiosity as to what extent these compounds may be considered as two-dimensional crystals.

The study of phonons in such materials has recently been conducted on MoS$_2$,[4] As$_2$S$_3$, As$_2$Se$_3$,[5] and GaSe,[6] using Raman and infrared techniques. From symmetry considerations it is concluded that the two techniques are needed to measure the contribution of the interlayer forces. Such experiments were not carried out in GaS, where Raman[7] and infrared[8] measurements were taken separately. The only Raman work performed[7] indicated all six phonon Raman-active bands, but could not yield their assignments. The infrared work[8] is very inaccurate, due to the poor quality of the GaS crystals. In GaSe where the two experiments were performed on the same samples,[6] only partial information was obtained.

In the following we shall show that the full information of the layer interaction in GaSe may be achieved and even more precisely by the use of one method only—Raman spectroscopy. We shall give the assignments of the bands of both GaSe and GaS and discuss the splittings caused by layer interaction in GaSe. The presentation of the study of GaSe-GaS solid solutions serves two purposes: one is to assist the assignments of the GaS phonon branches and the evaluation of the splittings in

GaSe, and the other to achieve a self-contained study of phonon behavior in GaSe$_x$S$_{1-x}$ solid solutions. Finally, we shall show and discuss coupling between modes in GaSe.

II. EXPERIMENTAL

In the present work the single crystals studied are GaSe, GaS, and GaSe$_x$S$_{1-x}$, with different values of x. Crystals were grown by the iodine-transport process[9-11]; GaSe crystals were also available from sublimation and Bridgman processes. All these layer crystals were platelets with dimensions of the order of $10 \times 10 \times 0.1$ mm, with the c axis perpendicular to the plates. The molar fraction x of the mixed crystals was determined by x-ray fluorescence with a precision of $\pm 1\%$.[10]

The Raman set-up is the common one, with a 40-mW He-Ne laser and a 500-mW Ar$^+$ laser. The phonon frequencies were generally determined to ± 1 cm^{-1}, except for very weak and broad bands where a different error range is indicated. The equivalent slit width used was about 2 cm^{-1}. This work was performed mainly at room temperature. Low-temperature measurements were carried out only when better resolution was necessary. High-temperature measurements were taken to obtain near-resonance conditions.

Pressure dependence of both Raman lines and absorption coefficents were taken with an optical hydrostatic-pressure cell up to 10 kbar. The optical cell is described elsewhere.[12] The use of pressure dependence enabled separation of the low-frequency lines from the powerful grating ghost around

20 cm^{-1}.

The scattering geometries employed were right-angle scattering in the xy and xz planes (z is in the c direction) and back scattering in the z direction (perpendicular to the plate).

III. CRYSTAL SYMMETRY AND GROUP THEORY CONSIDERATIONS

The basic structure unit of both GaS and GaSe is the hexagonal unit layer with a point-group symmetry of D_{3h} and two molecules per unit cell. In GaS, only one way of stacking of adjacent layers exists[2] and the crystals have a symmetry of point group D_{6h} with two layers (four molecules) per unit cell.

Three modifications of GaSe have been reported in literature.[1,3] A rhombohedral γ modification with three layers (six molecules) per unit cell and two hexagonal structures β and ϵ. The β-type structure is identical with that of GaS. The ϵ-type structure has a D_{3h} point-group symmetry with two layers (four molecules) per unit cell. In this form, the stacking of the layers does not give rise to an inversion center as it does in the β form.

According to a recent report by Terhell and Lieth[9] β-type GaSe does not seem to exist as a crystal, although powder x-ray pictures of iodine-transport-grown crystals always indicate β-type stacking. The γ-type structure is found in pure form in sublimation-grown needle crystals and is very rare.

In Fig. 1 we see the results of group-theory analysis of the optical activity of vibrational modes in the D_{3h} unit layer, D_{3h} GaSe structure, and D_{6h} GaS symmetry. The unit layer with D_{3h} symmetry and two molecules per unit cell has 12 vibrational modes: four single A modes with vibrations perpendicular to the layer, and four doubly degenerate E modes parallel to the layer. One of the single modes and one of the doubly degenerate modes are acoustic modes, while among the optical modes we have four Raman-active modes, two infrared-active modes, and, since there is no inversion center, one mode that is simultaneously Raman and infrared active.[8]

Since the crystal unit cell (of GaS and ϵ-GaSe is two layers thick, there are twice as many normal modes for the crystal as for the layer, namely, 24 modes. These modes degenerate to the 12 layer modes, in the limit of vanishing interaction between the layers, when the two layers vibrate in phase or out of phase. Details are given in Fig. 1.

IV. RESULTS AND DISCUSSION

Typical Raman spectra of GaSe, GaS, and GaSe$_{0.4}$S$_{0.6}$ crystals are shown in Fig. 2. One can notice that some of the features look alike, while others seem very different. The frequencies of the
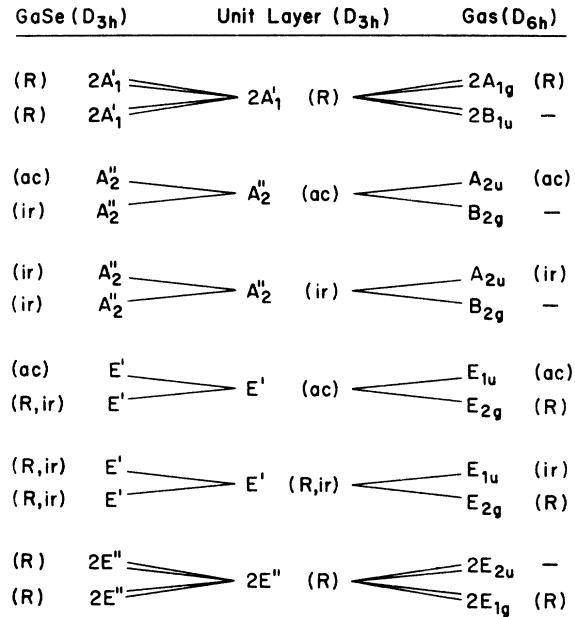

GaSe (D_{3h})	Unit Layer (D_{3h})	GaS (D_{6h})
(R) $2A_1'$ ╲╱	$2A_1'$ (R)	╲ $2A_{1g}$ (R)
(R) $2A_1'$ ╱╲		╱ $2B_{1u}$ —
(ac) A_2'' ╲	A_2'' (ac)	╱ A_{2u} (ac)
(ir) A_2'' ╱		╲ B_{2g} —
(ir) A_2'' ╲	A_2'' (ir)	╱ A_{2u} (ir)
(ir) A_2'' ╱		╲ B_{2g} —
(ac) E' ╲	E' (ac)	╱ E_{1u} (ac)
(R,ir) E' ╱		╲ E_{2g} (R)
(R,ir) E' ╲	E' (R,ir)	╱ E_{1u} (ir)
(R,ir) E' ╱		╲ E_{2g} (R)
(R) $2E''$ ╲╱	$2E''$ (R)	╲ $2E_{2u}$ —
(R) $2E''$ ╱╲		╱ $2E_{1g}$ (R)

FIG. 1. Compatibility diagram showing the relation between the layer vibrations and those of GaSe (D_{3h}) and GaS (D_{6h}). The modes's optical activities are indicated: Raman: R; infrared: ir; acoustical: ac; inactive:—.

zone-center phonons in GaSe$_x$S$_{1-x}$ for $0 \le x \le 1$ are presented in Fig. 3. In Fig. 3 the intensity of the various bands is also indicated, using five-level intensity scale. In pure GaSe the majority of the bands are assigned according to their polarization dependence, one band being assigned on the basis of symmetry and group theory. In GaS only two bands may be assigned according to polarization dependence while the others are readily assigned; the reasoning for this will be discussed below. The main support for these assignments comes from the variation of the $\vec{k} \approx 0$ phonons of GaSe$_x$S$_{1-x}$ as function of the molar fraction x.

A. Phonon-Branches Splitting and Symmetries

As already discussed (Sec. III), GaS and GaSe exhibit layer structure and their layer symmetries are identical.[1,2] We assume that the phonon bands originate from vibrations within the layer, and that owing to the small interaction between layers a small splitting occurs between modes in adjacent layers vibrating in or out of phase. This splitting is called Davydov splitting.[5,13] In the present cases with two layers per unit cell, the splitting yields doublets.

This is true for the two compounds. The main difference may lie in whether or not their crystal symmetry includes inversion. Assuming that GaSe does *not* exhibit the β structure, it does not show inversion symmetry; the opposite is true for GaS (β structure, point group D_{6h}). Having inver-
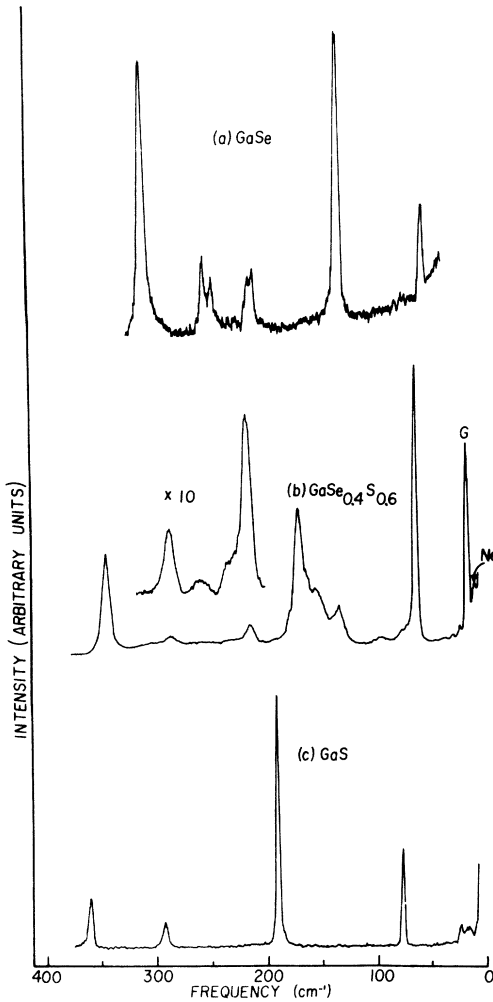
FIG. 2. Typical room-temperature spectra of (a) GaSe, (b) $GaSe_{0.4}S_{0.6}$, and (c) GaS.

sion symmetry, the exclusion principle is obeyed in GaS, and modes that are Raman active will be IR inactive and vice versa. This means that the doublets due to the small interaction between the layers will be such that one member of the doublet will be Raman active, while its conjugate will be infrared active or totally nonactive. In order to measure these doublets one should then perform two different experiments: one in infrared and the other in Raman spectroscopy.[5] However, when inversion symmetry is not present—and this is believed to be the case in GaSe—both components of some of the doublets may be active in Raman. This is exactly what Fig. 3 shows. Two of the doublets are well resolved in pure GaSe(254–247, 214.5–210.5 cm^{-1}). Two are not well resolved and appear as shoulders in the pure compound, but the splitting is enhanced and well resolved when 5 mole% of sulphur is added (307.5 and 135 cm^{-1}).

The band at 58.5 cm^{-1} is a narrow one—it does not split even in the mixed crystals. The low-frequency band at 18 cm^{-1} should be a singlet in Raman, its conjugate being the acoustic E' mode. It means that in GaSe *one* experiment (Raman spectroscopy) is sufficient for measuring the frequency intervals of these Davydov splittings. On the other hand, in Raman scattering from GaS, single bands are observed, their conjugates being Raman inactive due to the D_{6h} symmetry of the crystal.

Table I summarizes the frequencies and the symmetry species of the various bands in GaSe and GaS. Because of the quality of the crystals, better polarization dependences could be obtained with GaSe. From these measurements all but the line at 254 cm^{-1} were properly assigned according to their polarization dependence. Altogether the experimental results are in good agreement with the predictions of group theory. It should be emphasized at this point that we obtained the same spectra from GaSe crystals grown by sublimation, Bridgman technique, or iodine transport. This ensures that in all these different types of crystals
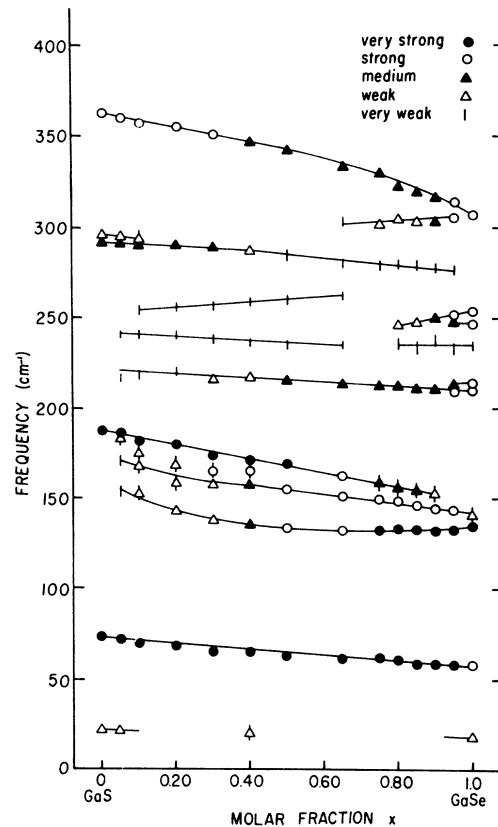

FIG. 3. Phonon frequencies of $GaSe_xS_{1-x}$ vs molar fraction x, $0 \le x \le 1$. Relative band intensities as function of x are indicated. (The intensity ratios between the bands are polarization dependent.)

TABLE I. Frequencies and symmetry species of GaSe and GaS phonons and the frequency relations between the corresponding modes.

GaSe Symmetry species	Frequency (cm^{-1})	GaS Symmetry species	Frequency (cm^{-1})	$\dfrac{\overline{\omega}_{GaSe}}{\omega_{GaS}}$
$E'(\alpha_{xx}-\alpha_{yy},\ \alpha_{xy})$	18	$E_{2g}^{2}(\alpha_{xx}-\alpha_{yy},\ \alpha_{xy})$	22	0.82
$2E''(\alpha_{yz},\ \alpha_{zx})$	58.5	$E_{1g}^{1}(\alpha_{yz},\ \alpha_{zx})$	74	0.79
A_1' $(\alpha_{xx}+\alpha_{yy},\ \alpha_{zz})$	135	$A_{1g}^{1}(\alpha_{xx}+\alpha_{yy},\ \alpha_{zz})$	188	0.73
A_1'	141			
$E'(\alpha_{xx},\ \alpha_{yy})$	210.5	$E_{2g}^{1}(\alpha_{yz},\ \alpha_{zx})$	291.5	0.73
$E'(\alpha_{xy})$	214.5			
E'' $(\alpha_{yz},\ \alpha_{zx})$	247	$E_{1g}^{2}(\alpha_{yz},\ \alpha_{zx})$	296	0.85
E''	254			
$2A_1'(\alpha_{xx}+\alpha_{yy},\ \alpha_{zz})$	307.5[a]	$A_{1g}^{2}(\alpha_{xx}+\alpha_{yy},\ \alpha_{zz})$	363	0.85

[a]Average of the two components of the doublet.

the β structure even if existed had a negligible effect.

In GaS, polarization dependence is sufficient to distinguish between A and E modes only. From the behavior of the phonon lines as a function of the molar fraction x (Fig. 3), the phonon assignments in GaS can be readily determined. From Table I it is clear that also in GaS the agreement between the predictions of group theory and experiment is rather good. The correspondence between GaSe and GaS lines is presented in Table I, but requires additional clarification.

In Sec. IV B we shall deal with one- and two-mode behavior of the mixed-crystal lines. At present we should like to use the phonon behavior in solid solutions (when the molar fraction x is varied) to examine the correlation between the $\vec{k} \approx 0$ phonons in the pure compounds. For one-mode lines, namely, those which start at a GaSe mode and end at a GaS mode, the correspondence is completely clear. This is true for the correspondence of the 18- and 58.5-cm^{-1} GaSe bands with those of 22- and 74-cm^{-1} GaS bands, respectively (Fig. 3). The two-mode behavior of the A_1' doublet 135–141 cm^{-1} in GaSe clearly corresponds to the 188-cm^{-1} band in GaS on the basis of both polarization dependence and frequency relation. The correspondence between the remaining two E'' and E' GaSe doublets around 250 and 212 cm^{-1} and those of 296- and 291.5-cm^{-1} lines, respectively, in GaS is not straightforward but is deduced from the total number of bands predicted by group theory. Moreover, the E' doublet at 212 cm^{-1} originates from vibrations of Ga-Se, [6] while the E'' at 250 cm^{-1} originates from vibrations of Ga-Ga as well as Ga-Se. This is the reason for the latter band being of higher frequency. When selenium is replaced by sulphur the frequency increase of the

212-cm^{-1} mode is thus much more pronounced than for the 250-cm^{-1} band. In GaS the corresponding bands become very close to each other, but are definitely bands belonging to different species. The close frequency values are due to the fact that sulphur is much lighter than gallium or selenium.

We shall now deal with some of the details concerning the assignments and the correlations between GaSe and GaS bands.

(i) In a recent report on GaSe by Wieting and Verble[6] no splittings of the GaSe Raman bands were observed. Those authors analyze their spectra on the basis of the D_{6h} symmetry of the β structure rather than the D_{3h} symmetry of the ϵ structure. Nevertheless their mode assignments, if transformed to D_{3h} symmetry, would match the present assignments. A comparison with the infrared results[6,8] also supports the present assignments of those bands that are both Raman and infrared active; it is to be noted that the infrared resolution is not capable of resolving a 4-cm^{-1} splitting.

On the other hand the present results on GaS cannot be compared to either Raman or infrared earlier works. In the Raman work[7] the six Raman-active lines are reported, but no assignments are given. The infrared results[8] are of limited importance due to the poor quality of the GaS crystals used and the nonuniformity of their thicknesses. The infrared band should be the conjugate of the 291.5-cm^{-1} band, but is reported to be at 310 cm^{-1}. This difference cannot be attributed to the splitting (which should be of the order of 2–3 cm^{-1}) but to experimental inaccuracy.

(ii) It has already been mentioned that the only difficulty among the GaSe assignments occured at the doublet centered at 250 cm^{-1}. This difficulty has two different aspects: When xy is the scatter-

ing plane, the 247-cm^{-1} band does not show a clear polarization dependence. The other line of this doublet, the 254-cm^{-1} band, is more intense in the $x(yx)y$ configuration. On the other hand, when xz is the scattering plane both lines become very much stronger. The two yield the same behavior and may be satisfactorily assigned as E''. Nevertheless, we still base the assignment on group theory, stating that polarization dependence is not well defined.

The second difficulty is the pressure and temperature dependence of the 247-cm^{-1} band. It is the only band for which the intensity is enhanced upon increase of temperature or application of hydrostatic pressure. Both effects cause an increase in the absorption of GaSe, reduce the band gap, and bring it near to resonance conditions with the 6328-Å He-Ne exciting line.[14] This is a known behavior of LO modes.[15] In spite of the fact that according to infrared results an LO mode is expected in this region,[6,8] it is not very likely that the 247-cm^{-1} band is an LO mode. One reason is that with the 5145-Å exciting line this band almost disappears from the Raman spectrum (also in the work by Wieting and Verble[6] it is of very low intensity) and this is not in line with the common behavior of an LO mode.[15] The second reason is that similar behavior is also observed for the 296-cm^{-1} band in GaS. When measurements are taken on GaS with the 4764-Å exciting line, which is close to resonant conditions,[14] the intensity of the 295-cm^{-1} band is enhanced. This is an E_{1g} band and is not supposed to be an LO band because of the GaS D_{6h} symmetry. We conclude that the LO mode is not observed unless it is the weak and broad band around 235 cm^{-1}, which is of unknown origin. Similar behavior of the two bands under near-resonance conditions suggests that the 247-cm^{-1} band of GaSe corresponds to the 296-cm^{-1} band of GaS, while the 254 cm^{-1} band of GaSe should then correspond to a higher-frequency Raman-inactive E_{2u} line of GaS (see Fig. 1). From this it may be concluded that $\omega(E_{2u}) > \omega(E_{1g})$ in GaS.

(iii) Pressure dependence of the phonon frequencies gave two main results: The lowest-frequency band showed the highest-frequency shift with pressure. This was expected, taking into account that its frequency expressed the strength of interaction between the layers, and this interaction increases with pressure. The frequency of this line shifted by about 25% of its zero-pressure frequency when a pressure of 9 kbar was applied. The pressure dependence of the rest of the bands is not as dramatic. The results show a relatively stronger pressure dependence of the A modes.

(iv) In a paper by Zallen et $al.$[5] on As_2S_3 and As_2Se_3, a simple scaling relation is found to connect the phonon frequencies of these two isomorphic compounds. It is correctly indicated there that the existence of such a simple rule is rather surprising in spite of the fact that the structures are intimately related. In the present case, the structures of GaS and GaSe are different. In Sec. IV B we shall discuss the mixed-one and two-mode behavior of GaSe-GaS solid solutions. This behavior indicates that no such relation can be accomplished if based on ratios of the reduced masses alone. The $\omega_{GaSe}/\omega_{GaS}$ values of the various bands are given in Table I. It is true that for the two low-frequency bands that are of one-mode behavior the ratio is almost identical $\omega_{GaSe}/\omega_{GaS} \approx 0.80$, and though the reduced mass relation is $(\mu_{GaS}/\mu_{GaSe})^{1/2} = 0.77$, we choose not to draw any conclusion from this.

There are two main conclusions in this section. The first is that both GaSe and GaS do behave approximately as a two-dimensional solid as regards the phonon branches. The second conclusion is that one observes Davydov splittings in GaSe using Raman spectroscopy alone, and thus the splittings observed can be accurately measured. We believe that the discrepancy for the splitting of the TO mode of GaSe, reported by Wieting and Verble[6] to be~1 cm^{-1} as compared to 4 cm^{-1} in the present work, may have two reasons: (a) Those authors did not observe the doublets in GaSe and they may have measured an average frequency. (b) The accuracy of ir measurements is not that high, and the inaccuracy when the results of two different experiments are compared is even higher. The comparison of three different infrared experiments[6,8,16] gave a much larger discrepancy. In the single Raman measurement the splitting is measured directly. The largest splitting measured in the present work was about 7 cm^{-1}.

B. GaS-GaSe Solid Solutions

The study of phonons in $GaSe_xS_{1-x}$ solid solutions was made not only for the phonon assignments of GaSe and GaS, but is of great interest in itself. In solid solutions two types of behavior of the phonon bands have been reported.[17] One-mode behavior describes the situation in which the $\vec{k} \approx 0$ optic-mode frequencies of the mixed crystal vary continuously with concentration from a frequency characteristic of that of one end-member crystal to that of the other end-member crystal, i.e., in each composition for every allowed mode only one common mode is observed. In two-mode behavior, for each allowed optic mode two bands are observed with frequencies in the vicinity of those of the pure compounds. Several criteria have been developed for predicting whether a given solid solution will show a one- or two-mode behavior. None of the present criteria is capable of explaining all the data on solid solutions.[18] It is expected that a lay-

er-mixed crystal of an approximate two-dimensional behavior will not be a conventional case for any of the criteria[17] because of its extreme anisotropy. For such an example a relation of masses alone cannot be sufficient. If, however, one uses the criterion of Chang and Mitra[19] for $GaSe_xS_{1-x}$ $\mu_{GaSe} > m_S$, one finds that a two-mode behavior is expected. Actually, as can be observed from Fig. 3, both one- and two-mode behavior exist, and for one of the GaSe doublets (307.5 cm^{-1}) the behavior is even more complicated.

When we defined one- and two-mode behavior by the occurrence of one or two modes in the spectra for each mode of the pure compound, we disregarded another important feature: in one-mode behavior the intensity of the band does not vary pronouncedly with the molar fraction. On the other hand a band showing a two-mode behavior (i.e., a characteristic band of each of the pure compounds does exist in the mixture) its intensity should decrease when the concentration of the substitution becomes larger. Both effects are seen in Fig. 3.

There is no doubt that the GaSe bands at 18 and 58.5 cm^{-1} show one-mode behavior, and the doublets centered at 138, 212, and 250 cm^{-1} show typical two-mode behavior. In the high-frequency doublet, matters seem more complicated. The lower-frequency member of this doublet behaves as a two-mode band according to the two criteria. The higher-frequency member should be examined more carefully. The curve describing the mode frequency vs the molar fraction seems to be composed of two curves of different slopes. This may occur also in a one-mode-type band, but then its intensity does not decrease when the solution is diluted, which is the case of this GaSe line. In Fig. 3 it can be seen that the intensity of this line decreases with x starting with pure GaSe or pure GaS. It is thus very likely that also the higher-frequency band is of two-mode type accidentally connected with the GaS band which also shows a two-mode behavior.

This is the only simple ternary solid-solution system (end members being AB binaries), known to us, that shows such a mixed one- and two-mode behavior. Other compounds in which a similar phenomenon was reported, are $Na_{1-x}K_xTaO_3$[20] and $Mg_{1-x}Ni_xF_3$,[21] though those results were not as conclusive as the present ones.

Four of the GaSe bands disappear in the region of $0.60 \leq x \leq 0.90$ (Fig. 3). It is likely that an intensive change of structure takes place in this range of molar fractions. Evidence that this may occur can be found in a report on x-ray unit-cell determination,[10] a study of excitons,[22] and reflection measurements.[23] It seems reasonable that a phase transition from the D_{3h} structure of GaSe to the D_{6h} structure of GaS will not occur at a fixed mixture,

but will take place gradually over a wide range of compositions. Such a process is understood on the basis of the weakness of the interaction between the layers. It is not impossible that crystals having the same molar fraction will yield a different degree of disorder in the stacking of the layers. In addition it should be understood that different kinds of vibrations show different degrees of sensitivity to the substitution of one of the anions by the other one, and thus the lines may disappear at different molar fractions.

Two very weak and very broad bands around 250 cm^{-1} are seen in Fig. 3. These exist in mixed crystals only and are attributed to sulfur-selenium vibrations.

C. Mode Coupling

Each of the two A doublets in GaSe shows coupling between the two modes of the doublet, which have the same symmetry. The phenomenon is more pronounced in the A doublet centered at 138 cm^{-1} and has two aspects: One aspect is the bands repelling each other, and the second is the reversal of the intensity ratio of the bands when the molar fraction is varied. It should be emphasized that this doublet shows a two-mode behavior, and therefore it is appropriate to refer to it as a GaSe doublet also in the mixed crystals.

From Fig. 3 it can be seen that while the frequency of the upper member of the 138-cm^{-1} doublet shifts up almost linearly when the molar fraction x decreases, the frequency of its conjugate first shifts down, and only around $x = 0.70$ starts to shift up again. Had this been the only phenomenon observed in this doublet it would have been interpreted as follows: When the crystal is pure GaSe, the layer structure is an ordered one, and the interaction between the layers is small, namely, the crystal is approximately two dimensional. When sulfur now begins to substitute for the selenium atoms, this layer stacking is probably slightly disturbed, therefore the interaction between the "layers" increases, and the two-dimensional approximation is no longer valid. This is especially true for the largest mixture, where the peak of the disorder occurs. (The degree of the disorder is manifested by the half width of the bands; these are narrowest in the pure compounds and widest for $GaSe_{0.5}S_{0.5}$.) When sulfur now becomes the predominant anion the interaction decreases for the same reason, i.e., a relatively ordered layer structure is now restored.

The second phenomenon observed in this doublet is that the intensity ratio of the two lines is reversed when the χ value is varied (see Fig. 4). This suggests an interaction between the two lines (of the same symmetry) and an intensity transfer between them. Along with that a repulsion between
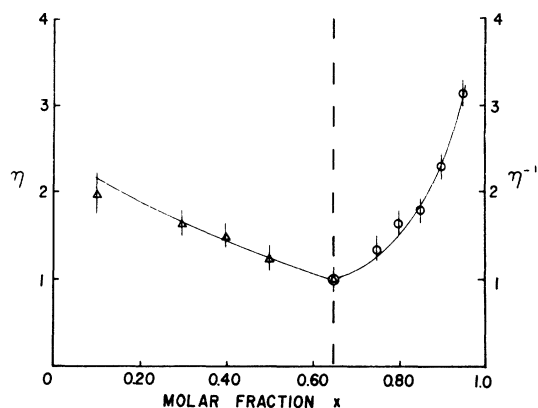
FIG. 4. Intensity ratio of the lines of the 138-cm^{-1} doublet as function of the molar fraction x. $\eta = I(141 \text{ cm}^{-1})/I(135 \text{ cm}^{-1})$.

the two bands occurs. The picture of this doublet in Fig. 3 is therefore a superposition of the inter-action between the layers, and the interaction be-tween the two modes. The way the upper line shifts may be a result of repulsion applied on it from the corresponding 188-cm^{-1} GaS line having the same symmetry. There is an indication of this in Fig. 3.

Because of the two-mode behavior of this doublet the total intensity is reduced when x decreases, and this is obvious from Fig. 3. It should also be mentioned that this line is the most intense one in GaSe and up to $x = 0.70$.

It is now interesting to examine what happens to the counterpart of this line in GaS—the 188-cm^{-1} line. In pure GaS only one line is observed, be-cause of the GaS symmetry. When sulfur is re-placed by selenium the intensity is reduced (again two-mode behavior) and a shoulder starts to ap-pear, which accompanies the main band up to its disappearance. This is expected, in accordance with the reasoning given for the behavior of the GaSe band.

In the other A_1' mode of GaSe (307.5 cm^{-1}) the same phenomenon occurs. The splitting becomes larger when the concentration of sulfur increases and intensity transfer between the two modes takes place. If carefully examined this 307.5-cm^{-1} mode also exhibits a two-mode behavior (Sec. IV B).

Naturally a question arises about the behavior of the rest of the GaSe bands. The other bands have E symmetry, and thus each of the lines is doubly

degenerate; therefore, it is understood why such a repulsion does not necessarily occur. Moreover, in each of these doublets one of the lines disap-pears at $x < 0.95$.

V. CONCLUSIONS

The main conclusions of this work are as fol-lows:

(i) GaSe shows approximately a two-dimension-ality; the lattice vibrations are governed by force constants within the layers, and the small inter-layer interaction gives rise to Davydov doublets. According to the results presented it is obvious that the dominant symmetry of GaSe is different from that of GaS, the main difference being the ab-sence of an inversion center in the first, and its presence in the second. This suggests Raman ac-tivity of both lines in some of the GaSe doublets, and thus the possibility of a direct measurement of the splitting by Raman scattering, as was demon-strated in this work. This is an important im-provement in comparison with other layer crystals in which one line of a doublet must be measured by Raman scattering and its conjugate by infrared measurements. This is unfortunately the case for GaS as well, and the single Raman-active bands there correspond to doublets in GaSe.

(ii) The study of $GaSe_xS_{1-x}$ solid solutions re-veals a behavior of a one-mode type for two of the lines and of a two-mode type for the rest. This is the first case of a relatively simple mixed-crystal system having this mixed type of behavior. This shows that mass ratios alone cannot determine whether a given solid solution will be of a one or a two-mode type.

(iii) The present Raman data of the $GaSe_xS_{1-x}$ solid solutions show evidence of a structural tran-sition that takes place gradually throughout the composition range $0.6 \leq x \leq 0.9$.

(iv) It is shown that coupling exists between modes of the same A symmetry in GaSe and $GaSe_xS_{1-x}$. This coupling causes repulsion between the modes, as well as intensity transfer. This re-pulsion is superposed on the larger interaction be-tween the layers at high degrees of disorder.

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