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LATTICE VIBRATIONS AND THE CRYSTAL STRUCTURE OF GaS AND GaSe

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The infrared-active lattice vibrational modes of GaS and GaSe were studied in the range 50–500 cm^{-1}. The previously observed single reststrahlen band is found to be split into three peaks in the appropriate experimental configurations. The existence of two doubly degenerate infrared-active E modes in both crystals is explained by breaking of symmetry selection rules due to a high number of stacking faults. Based on this conclusion, a new assignment is given to some of the modes and correlation is drawn between the zone-center vibrational frequencies in the two crystals. A simple scaling factor is found to relate most of the modes.

1. INTRODUCTION

THE SEMICONDUCTING crystals GaS and GaSe belong to a group of layered structure compounds. Each layer consists of four sublayers of S(Se)–Ga–Ga–S(Se) which are bound together by strong forces, mostly covalent. The interaction between adjacent layers is much weaker and is believed to be of the van der Waals' type. The layer structure of both GaS and GaSe is well known and has a D_{3h} hexagonal symmetry with two formula units per layer unit cell.[1–3] However, there are several ways of stacking adjacent layers and thus there are several structural modifications of these crystals. GaS was believed to adopt only one of these with space group D_{6h}^4 and two layers (eight atoms) per unit cell.[1] Three modifications are reported for GaSe,[2,3] The β-GaSe is identical to GaS (for the sake of convenience we shall refer to the D_{6h} structure of GaS as β-GaS hereafter). ϵ-GaSe also has two layers per unit cell but has D_{3h} symmetry, while γ-GaSe is a very rare modification with rhombohedral symmetry and three layers per unit cell.

Lattice vibrations of these two crystals have been extensively studied during recent years by means of Raman scattering and far infrared measurements.[4–12] These studies have aimed at answering several questions. The first aim was to elucidate the problem of the real crystal structure of GaSe by assigning the symmetries of the $q = 0$ modes. The second was the nature of the weak interlayer forces, and the third was the extent to which these compounds can be considered to be two-dimensional crystals. However, due to difficulties in crystal growing only thin platelets of single crystals were available. This resulted in some experimental disadvantages. In the far infrared studies no spectra were taken with the electric field of the incident light polarized parallel to the c axis. In the Raman measurements, an unambiguous determination of the mode symmetries is not complete because of

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leakage of scattering intensity into unallowed polarizations. This is especially true for the doubly degenerate E modes for which much controversy persists about the assignment of the modes and their origin. Most of these problems are resolved here by examining the polarized far infrared spectra of large single crystals of GaS and GaSe.[13] This study enabled us to clarify the assignments of all the reported Raman and i.r. modes.

2. SYMMETRY CONSIDERATIONS

The coordination numbers of the gallium and selenium atoms in a single layer are four and three, respectively. The layer unit cell contains four atoms and in the D_{3h} symmetry of the individual layer the division of the 12 long-wavelength normal modes of vibration is:[6]

$$2A_1' + 2A_2'' + 2E' + 2E''$$

of which $A_2'' + E'$ are acoustical modes.

The crystalline structure may give rise to a small splitting of each intralayer frequency into two as a result of the interaction between the two layers in the crystal unit cell.[14] These Davydov doublets are very closely spaced in; for example, the As_2S_3 and As_2Se_3 layer crystals.[14] In the case of the two modifications of GaS(Se) crystals this Davydov splitting occurs in two different ways, as presented schematically in Fig. 1. The symmetries of the 24 vibrational modes of the β-D_{6h} modification at the Brillouin zone-center are:

$$\Gamma = 2A_{1g} + 2A_{2u} + 2B_{1u} + 2B_{2g} + 2E_{1g} + 2E_{1u} + 2E_{2g} + 2E_{2u},$$

(with $A_{2u} + E_{1u}$ as acoustical modes).

For the ϵ-D_{3h} structure the result is simply:

$$\Gamma = 4A_1' + 4A_2'' + 4E' + 4E''$$

where $A_2'' + E'$ are symmetry types of the acoustical modes.

The two structures exhibit a marked difference in the selection rules. The presence of inversion symmetry elements in the D_{6h} structure implies Raman–infrared mutual exclusion. This means that the two crystalline modes that result from the splitting of each E' layer mode show a different behaviour in the

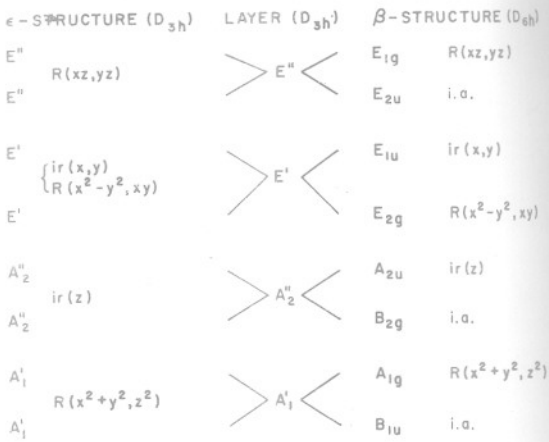

FIG. 1. Symmetry selection rules and the splitting of the layer vibrational modes in different crystal structures of GaS(Se). The polarization selection rules for the Raman (R) and infrared (ir) modes are given in parentheses; i.a.: inactive.

two symmetries. Both are Raman and infrared active in the D_{3h} symmetry whereas one is Raman active and the other infrared active in the D_{6h} structural symmetry. A closer look at the symmetry divisions of the $E'(E_{1u} + E_{2g})$ and $A_2''(A_{2u} + B_{2g})$ normal modes for both structures and their relations to the layer structure reveals that at high energies we expect only one Davydov doublet for each of the A_2'' and the E' layer modes. The resulting additional crystalline A_2'' and E' modes are derived from the layer $A_2'' + E'$ acoustical modes and are rigid layer modes located at very low energies.[15] Thus, the comparison of the Raman and the infrared $E'(E_{1u} + E_{2g})$ modes may serve as a probe for identifying the crystalline structure. In the D_{6h} symmetry we expect to observe in the higher energy (above 50 cm^{-1}) infrared spectrum only one E_{1u} mode (polarized $\perp C$) and one A_{2u} mode (polarized $\parallel C$). In the D_{3h} structure two E' modes ($\perp C$) and two $A_2''(\parallel C)$ are expected. However, in practice the closely spaced Davydov doublets are not expected to be resolved in infrared reflection spectra and both structures should have similar spectra.

3. EXPERIMENTAL

The crystals used in this work were obtained from both Bridgman[12] and iodine transport processes. The iodine transport grown crystals were platelets with

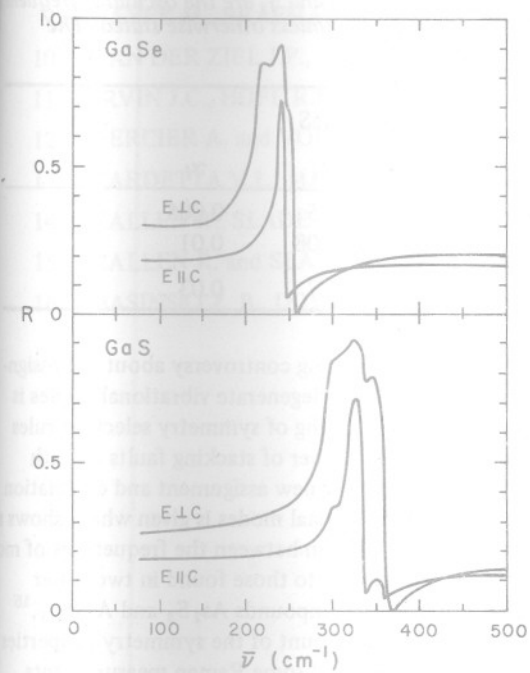

FIG. 2. Reflection spectra of GaS and GaSe crystals for light propagating perpendicular to the c axis.

typical dimensions of 10 × 10 × 0.1 mm with c axis perpendicular to the plates. The Bridgman grown crystals were 8 mm in diameter and 2–3 cm long. The GaS sample was twinned but large enough single crystal pieces could be cut and polished perpendicular to the cleavage planes.

The far infrared reflection spectra in the region 50–500 cm were obtained using a Digilab FTS-14 Fourier spectrometer with 6μ mylar beam splitter. A high resolution of 2 cm^{-1} was chosen despite the reported large width of the reststrahlen bands in both crystals. This was done in an effort to reveal possible fine structure in the wide infrared band.

4. RESULTS AND DISCUSSION

The spectra that were obtained for the experimental configuration with the light propagating in the plane of the layer are given in Fig. 2 for both $E \parallel C$ and $E \perp C$ polarizations. The reststrahlen band of the two crystals splits into three, one mode is observed in the $E \parallel C$ polarization and all three of them in $E \perp C$. The polarization is incomplete in most spectra but this serves to clearly demonstrate the existence of these three modes. The Davydov splitting of the A_2'' layer mode is inaccesible. It might be stated here that the existence of the high energy E mode is also evident in the fine structure of the i.r. spectra of the iodine transport grown platelets. The high resolution spectra of the only available configuration ($E \perp C$) reveal a sharp dip at 336.5 cm^{-1} for GaS and a slope discontinuity at 246 cm^{-1} for GaSe, the latter can be observed also in the data of Wieting and Verble.[7]

A computer oscillator fit program to the $E \perp C$ spectra fails to give satisfactory results as it tends to fit the band to a single oscillator with a transverse frequency of the lower E mode and suppresses the higher two oscillators. The fit was done therefore by trial and error, using the Kramers–Kronig analysis of a spectrum taken with E polarized at 45° to the c axis to obtain initial values for the parameters. This is the reason for the relatively large errors given for some of the parameters in Table.1. The separation of the two E modes in these two crystals is too large to account for by the interlayer splitting.[7,15] Thus, it can be concluded that the weak E mode at 247 cm^{-1} in GaSe (340 cm^{-1} in GaS) is originated from the E'' rigid-layer mode by breaking of symmetry rules due to stacking faults. These faults are known to be severe in both crystals[16] and reduce the local symmetry to C_{3v}. The E modes are allowed in both the Raman and the i.r. in this symmetry. Thus, using in addition to the present measurement the results obtained by Raman scattering,[7–12] we are able to present a complete assignment for the zone center vibrational modes of GaS and GaSe based on their intralayer origin. This is given in Fig. 3 together with the scaling relations of the frequencies. The simple scaling between most of the lines may serve as an additional support to the present assignment.

5. CONCLUSION

The far infrared spectra of GaS and GaSe single crystal has been investigated in the 50–500 cm^{-1} region. This first observation of polarized spectra with the electric field of the incident light polarized parallel to the c axis enabled us to resolve the broad reststrahlen band into three modes. One out of layer and two in-layer doubly degenerate E modes. It was

Table 1. Oscillator parameters for the infrared active modes in GaSe and GaS. ν_i, s_i and γ_i are the oscillator frequency, strength, and damping constant. The estimated error for the frequencies in 2 cm^{-1} unless otherwise stated. The estimated error for s_i and γ_i is 30% for the E modes and 10% for the A_2 modes

Unit layer symmetry	GaSe			GaS		
	ν_i	s_i	γ_i	ν_i	s_i	γ_i
E'	215	2.6	0.02	294	2.5	0.005
E''	247 ± 4	0.05	–	340 ± 4	0.08	0.01
A_2''	236	0.55	0.01	318	0.7	0.03

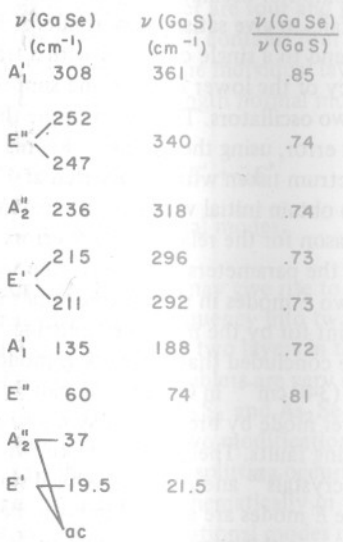

FIG. 3. Frequencies and assignments of zone center phonons of GaSe and GaS. The assignment is based only on layer symmetry. The frequency relations between the corresponding modes is also given.

found that the existing controversy about the assignment of the doubly degenerate vibrational modes is a result of the breaking of symmetry selection rules due to the high number of stacking faults in both crystals. A complete new assignment and correlation between the vibrational modes is given which shows a simple scaling relation between the frequencies of most of the modes similar to those found in two other isomorphic layer compounds As_2S_3 and As_2Se_3.[15] A more detailed account of the symmetry properties and current results of some Raman measurements which are now in progress will be published elsewhere.

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