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LONG WAVELENGTH LATTICE VIBRATIONS IN GaS AND GaSe

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The first order Raman spectra and far infrared absorption spectra of GaS and GaSe have been investigated and interpreted. A correspondence is drawn between the observed vibrational modes of the two crystals and a Raman active polar longitudinal mode has been identified in GaSe. The results are consistent with the existence of GaS in a β-polytype (D_{6h}) and GaSe in an ϵ-polytype (D_{3h}).

INTRODUCTION

THE LONG wavelength lattice vibrations of the semiconducting crystals GaSe and GaS have been the subject of many recent investigations.[1–7] These crystals are members of a family of layer structure compounds and are composed of weakly interacting layers each four atoms thick. GaS is known to crystallize in the so-called β-polytype[3,5–7,12] and its symmetry properties are those of the D_{6h}^4 space group. There are 24 normal modes of vibration at the centre of the Brillouin zone and these can be described by the irreducible representations of the D_{6h} point group.[3]

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

There are six non-degenerate Raman active modes ($2A_{1g}, 2E_{2g}, 2E_{1g}$) and two infrared active modes (E_{1u}, A_{2u}).

On the other hand, the structure of GaSe has been the subject of some controversy. Wieting and Verble,[3] on the basis of X-ray powder patterns, have concluded that GaSe crystallizes in the β-polytype. Jellinek and Hahn[8] had earlier arrived at a similar conclusion, also on the basis of X-ray powder patterns. Other workers,[9–12] on the basis of X-ray photographs obtained from single crystal platelets of GaSe, have suggested that GaSe crystallizes in the ϵ-polytype. In this polytype the intralayer structure is identical to the β-structure but the stacking is altered.[12] The 24 normal modes of vibration of the ϵ-polytype (at Γ) are now given by the irreducible representations of the D_{3h} point group:[5]

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

In this case there are eleven non-degenerate Raman active modes, $4A_1'$, $3E'$, and $4E''$, and there are six non-degenerate infrared active modes, $3A_2''$ and $3E'$.

This paper presents the results of Raman scattering and far infrared investigations on GaS and GaSe. These experiments were undertaken in an effort to investigate the exact symmetry properties of the various modes of vibration and thus arrive at a definitive statement concerning the structure of the crystals. The availability of thick crystals (1–2 mm) and a tunable dye laser has enabled us to obtain clear and well defined spectra that are characteristic of the bulk-material. This in turn has permitted a clear determination of the actual polarization properties of each mode.

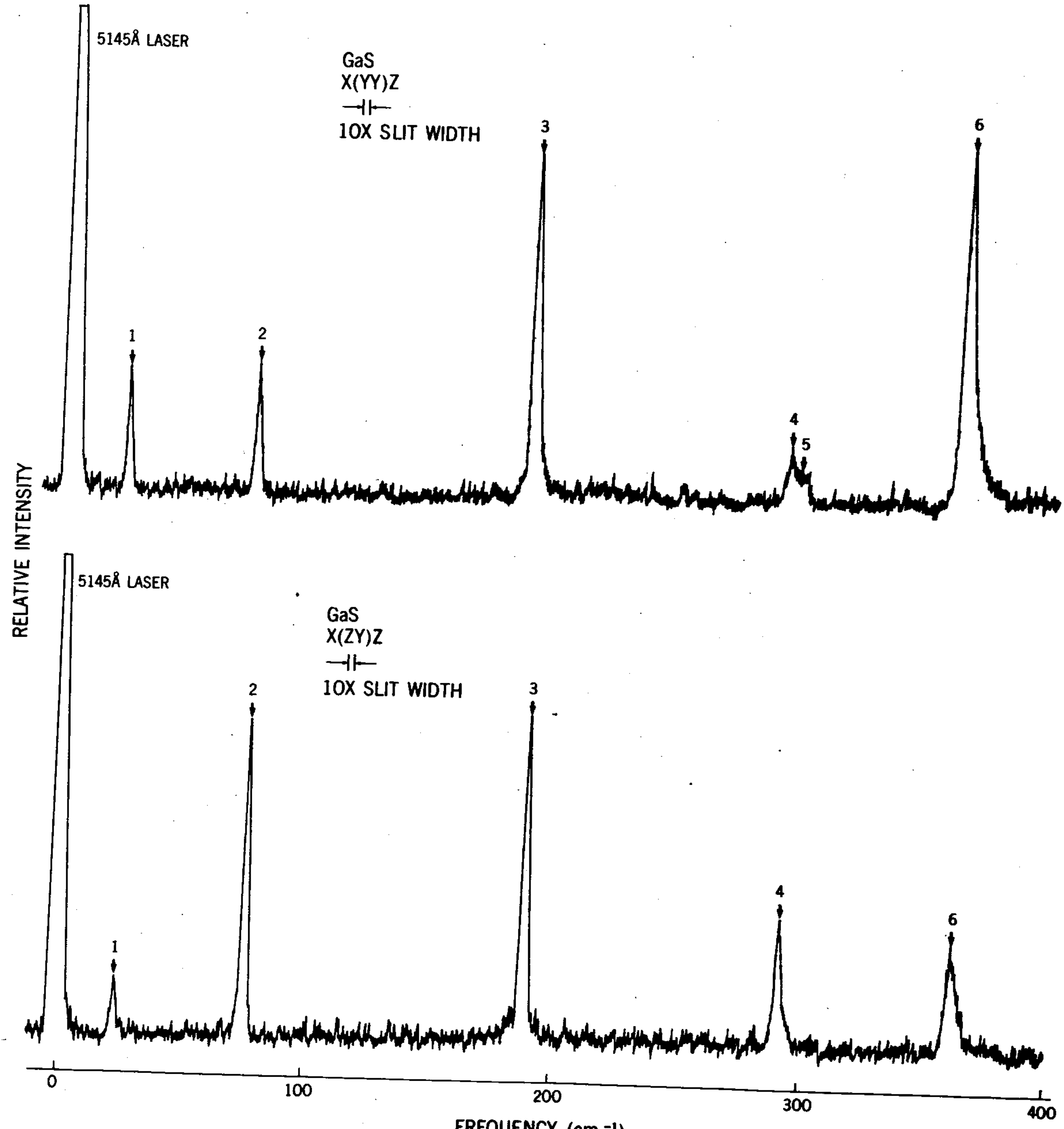

FIG. 1. Raman spectrum of GaS. The spectra were recorded with the crystal at room temperature (293°K).

EXPERIMENTAL

The crystals used in this work were grown by the Bridgeman method. They varied in size but typically were 1 cm square and up to 1–2 mm in thickness. The Raman spectra were analyzed with conventional techniques. The GaS spectra were excited with a single mode of an Argon Ion laser (5145 Å) and an iodine filter was used to discriminate against the Rayleigh line. The GaSe spectra were excited with a He–Ne laser and a Spectra–Physics Model 370 dye laser. The far-infrared spectra were obtained using a He^3-cooled bolometer cryostat. Energy analysis was carried out with a lamellar interferometer (< 80 cm^{-1}).

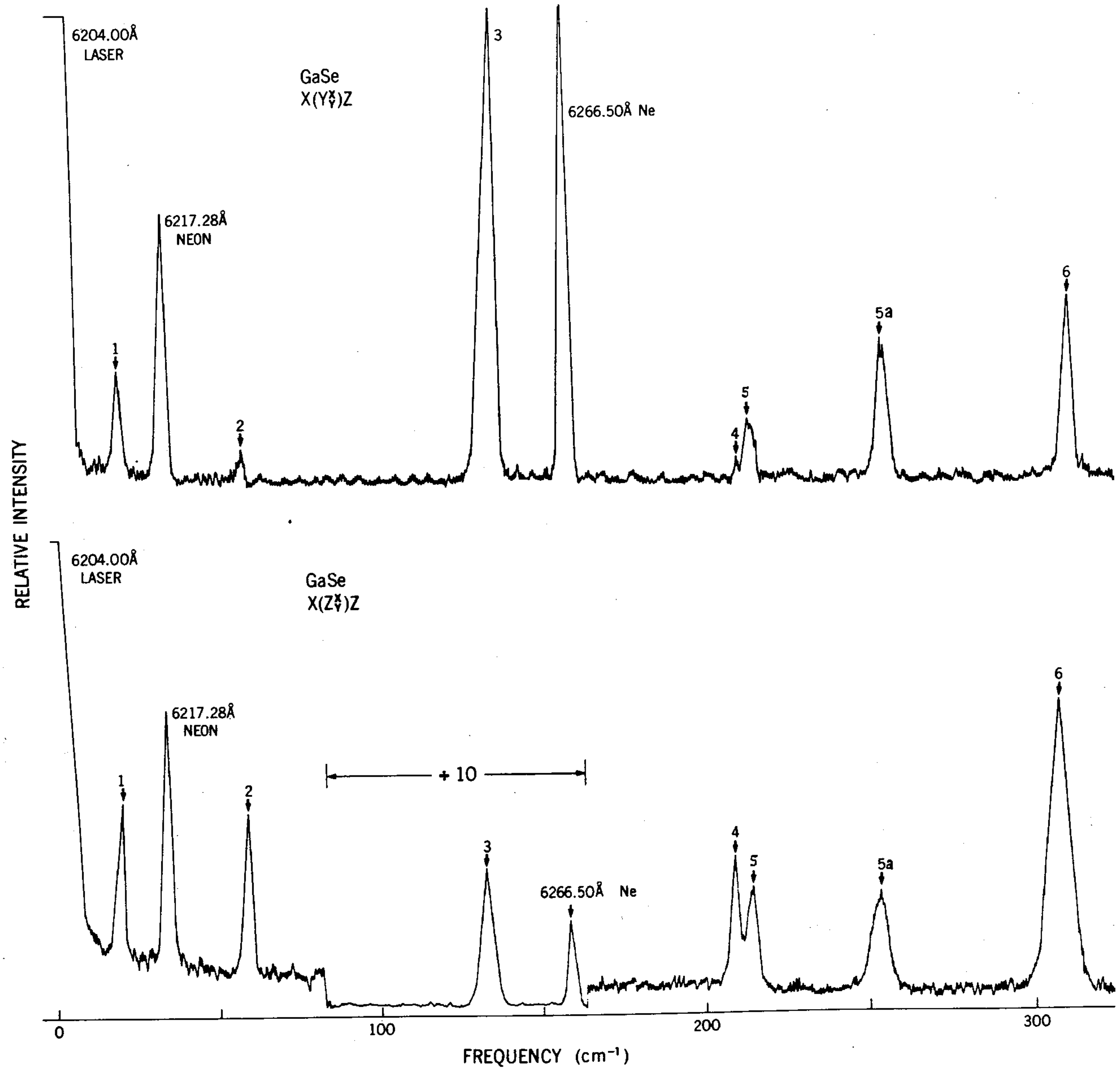

FIG. 2. Raman spectrum of GaSe. The spectra shown were recorded with the crystal at 77°K.

RESULTS

(a) *Raman spectra*

The Raman spectra of GaS and GaSe are shown in Figs 1 and 2 respectively. The scattering geometries shown are described by standard notation and in this notation the z axis is parallel to the c axis of the crystals. The spectra shown are typical of those obtained and were chosen to exhibit the differences between the (xz) or (yz) spectra and the (xx), (yy), or (xy) spectra while at the same time clearly showing the doublet nature of the 211.9 line in GaSe. The measured frequencies are listed in Table 1 beside the irreducible representation having the appropriate polarizability tensor elements. Feature number 5, although not observed by Wieting and Verble, has been observed by Hayek *et al.*[7] The symmetries observed

Table 1. Raman frequencies (293°K) *in* β-GaS *and* β-GaSe. *All values obtained in this work are* ± 1.0 *cm*$^{-1}$ *unless otherwise noted. The values from reference 3 for* GaSe *are listed with the irreducible representation assigned to them in that work*

Feature	Irreducible representation	Polarizability tensor	GaS $\tilde{\nu}$ * (cm^{-1})	GaS $\tilde{\nu}$ † (cm^{-1})	GaSe $\tilde{\nu}$ * (cm^{-1})	GaSe $\tilde{\nu}$ ‡ (cm^{-1})
1	E_{2g}^{2}	$\alpha_{xx} - \alpha_{yy}'\alpha_{xy}$	22.0	22.0	19.5	19.1
2	E_{1g}^{1}	$\alpha_{yz}'\alpha_{zx}$	75.2	74.2	60.1	60.1
3	A_{1g}^{1}	$\alpha_{xx} + \alpha_{yy}'\alpha_{zz}$	187.9	188.0	134.3	134.6
4	E_{1g}^{2}	$\alpha_{yz}'\alpha_{zx}$	290.5	291.4	211.9	249.0
5	E_{2g}^{1}	$\alpha_{xy}'\alpha_{xx} - \alpha_{yy}$	295.0	295.2	215.0 ± 2.0	213.1
6	A_{1g}^{2}	$\alpha_{xx} + \alpha_{yy}'\alpha_{zz}$	360.7	359.9	308.0	307.8
5a	?				252.1	

* This work. † Reference 5. ‡ Reference 3.

here for features 4 and 5(a) differ from those suggested by previous authors,[5,7] and feature number 5(a) remains unassigned.

(b) *Far infrared spectra*

Three lines have been observed in the far infrared absorption spectra of GaSe in the spectral region from 4 cm^{-1} to approximately 260 cm^{-1}. With the light propagating in the plane of the layers and traversing a crystal path length of about 1 cm, lines were observed at 20.1 cm^{-1} ($E \perp c$, 4°K) and at 36.7 cm^{-1} ($E \parallel c$, 4°K). An extremely strong absorption line was observed with the light passing along the c axis ($E \perp c$) through a crystal platelet less than 1 μm thick. The measured frequency of this line was 212.1 ± 1.0 cm^{-1} (293°K) and this value is in good agreement with the frequency of 213.9 cm^{-1} obtained by Wieting and Verble[3] from infrared reflectivity.

No analogous lines were found in the far infrared absorption spectrum of GaS in the spectral region below 260 cm^{-1}. All crystals became opaque to the far-infrared radiation at higher frequencies and the line expected[13] at about 300 cm^{-1} could not be observed.

DISCUSSION

(a) *GaS*

The observed peaks have been assigned to the irreducible representations as shown in Table 1. The assignments were made on the basis of the observed symmetries and agreement is obtained both with the group theoretical predictions and with previous work.[5]

(b) *GaSe*

As will be noted from Table 1, the polarizations observed here have necessitated some changes in the assignments that were proposed by Wieting and Verble.[3] The resulting six assignments made here are consistent with the group theory for a β-polytype, but one feature, number 5(a) (251.1 cm^{-1}), remains unassigned. In an effort to find a consistent correlation between group theory and observations for all seven features a comparison with the group theoretical predictions for the ϵ-polytype was carried out. This comparison however was preceded by some preliminary considerations that are detailed in the following section.

(c) *Comparison of the spectra*

A careful inspection of Figs 1 and 2 reveals a striking similarity between the spectra of GaS and GaSe if feature 5(a) is temporarily ignored. A direct correspondence can be made between the six features of the GaS spectrum and the similarly numbered six features of the GaSe spectrum. A comparison of these features in the two spectra reveals a close correspondence in order of increasing energy, in relative intensity, and in relative frequency separation. This correspondence should perhaps be expected because of the very similar crystal structure and the almost equal bond distances of the two crystals. The

Table 2. Raman active lattice vibrations in ϵ-GaSe (D_{3h}). *The symmetry properties listed for* E′ (*TO*) *and* E′ (*LO*) *are those from the group theoretical tables. The exact selection rules for these modes, however, must be determined using the methods outlined by Loudin.*[14]

Feature	Irreducible representation	Polarizability tensor	$\tilde{\nu}$ (cm^{-1}) (293°K)
1	E'	$\alpha_{xx} - \alpha_{yy}, \alpha_{xy}$	19.5
2	E''	α_{yz}, α_{zx}	60.1
3	A_1'	$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$	134.3
4	E''	α_{yz}, α_{zx}	211.9
5	E'(TO)	$\alpha_{xx} - \alpha_{yy}, \alpha_{xy}$	215.0 ± 2
5a	E'(LO)	$\alpha_{xx} - \alpha_{yy}, \alpha_{xy}$	252.1
6	A_1'	$\alpha_{zz} + \alpha_{yy}, \alpha_{xx}$	308.0

relatively higher frequencies in GaS can be attributed to the relative masses of the sulphur and selenium atoms.

(d) *ϵ-Polytype*

Despite the mode correspondence discussed in the previous section the origin of the 252.1 cm^{-1} line remains unexplained. In order to explain this origin it is assumed that the GaSe used here have crystallized in the ϵ-polytype. In this case there is no centre of inversion in the crystal and the A_1' and E' modes are both Raman active and infrared active. Since GaS and GaSe are polar crystals,[3] the longitudinal (LO) infrared active mode (E_{1u}, E') has a long range electric field associated with it. As is well known,[14] this electric field increases the effective binding and raises the frequency of the LO mode above that of the transverse optic (TO) modes. In GaS this mode (E_{2u}) is Raman inactive but in GaSe the corresponding mode [E'(LO)] is now Raman active and should be observed. Furthemore, the observed symmetry of feature 5(a) (252.1 cm^{-1}) is compatible with the selection rules for an E' (LO) mode in an anisotropic uniaxial crystal with D_{3h} symmetry,[14]

This assignment and those for the other six features observed in GaSe are shown in Table 2 for D_{3h} symmetry. The observed spectral features have all been assigned on the basis of their polarization dependence.

The assignment of the 252.1 cm^{-1} peak as an E' (LO) mode is also suggested by previous observations. Infrared reflectivity work has revealed a Restrahlen band ($E \perp c$) that terminates at approximately 254 cm^{-1}.[1,3] This band edge should correspond to an E' (LO) mode. In addition to these factors the 252.1 cm^{-1} line has been observed to exhibit a resonance behaviour as the wavelength of light approached the absorption edge. This resonance behaviour is characteristic of LO modes.[16]

(e) *Infrared results*

The existence of GaSe and GaS in different polytypes is further indicated by the observation of the 20.1 cm^{-1} (E') and 36.7 cm^{-1} (A_2'') modes in the infrared absorption spectra of GaSe and the absence of any low frequency lines in the spectra of GaS. The observation of the 20.1 cm^{-1} and 36.7 cm^{-1} lines can be attributed to the Raman activity of the E' and A_2'' mode in GaSe whereas the corresponding E_{1g} and B_{2g} modes of GaS are not infrared active.

The fact that these lines are orders of magnitude weaker than the 212.1 cm^{-1} line indicates that the change in the stacking in the ϵ-polytype has a relatively small effect on the activity of the modes. That is, the additional spectral activity of the modes, which is produced by the change from β to ϵ, will be weak compared to the basic activity of the modes of the β-structure.

(f) *Conjugate modes*

Although conjugate modes[3,7,15] should be observed for the E', E'', and A_1' modes in the Raman spectra of the ϵ-polytype, such doublets have not been observed. This is believed to be due to the fact that the change in symmetry from the β-polytype to the ϵ-polytype (e.g. $E_{1u} \rightarrow E'$) results in the corresponding E' mode being very weakly Raman active as discussed previously. This suggestion is reinforced by the infrared observations. In addition the frequency splitting is expected to be small[3] and would thus be difficult to resolve. The splitting should be most easily resolved for the 60.1 cm^{-1} line, and despite a careful search, no evidence of a satellite has been observed in the neighbourhood of this line.

CONCLUSIONS

The first order Raman spectra and far infrared absorption spectra of GaS and GaSe have been investigated. The Raman spectra were performed on thick crystals and with excitation wavelengths for which the crystals were transparent. This allowed a clear determination of the polarization properties of all the observed features. An interpretation of the experimental results has resulted in the identification of GaS as a β-polytype (D_{6h}) and GaSe as an ϵ-polytype (D_{3h}) for the crystals studied here. The choice of an ϵ-polytype for GaSe has entailed assigning the 252.1 cm^{-1} feature to an E'(LO) mode. This assignment was made on the basis of the observed polarization dependence and resonant behaviour of this mode and was reinforced by the previous indications of such a mode in infrared reflectivity experiments. A more detailed account of the symmetry properties and resonance behaviour of the various features will be published elsewhere.

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Raman spektren erster Ordnung und Absorptionsspektren im fernen Infrarot des GaS und GaSe wurden bestimmunt und interpretiert. Die beobachteten Schwingungs moden der beiden Kristalle wurden miteinander verglichen und eine Raman aktive polar longitudinale Mode wurde identifiziert im GaSe. Die Resultate sind vertraglich mit der Existenz des GaS in einer β-Form (D_{6h}) und des GaSe in einer ϵ-Form (D_{3h}).