

Davydov splitting of degenerate lattice modes in the layer compound GaS

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The frequency separation between the essentially degenerate in-plane TO mode and its Davydov conjugate has been observed in the layer compound GaS in a measurement of the Raman and far-infrared spectra. The relative magnitude of the frequencies of the two modes is contrary to what is expected from interlayer Van der Waals forces. Wieting and Verble have observed a similar frequency reversal in the Davydov conjugates in the spectra of MoS₂ and β -GaSe. They have argued that the long-range Coulomb interaction could be responsible for this optical anomaly. Our calculation shows, however, that the effect of such interaction in the deformation-dipole model approximation can not explain the anomaly.

The III-VI compounds, GaS, GaSe, and InSe, form layer-type crystal structures in which a layer consists of four sublayers of S(Se)-Ga(In)-Ga(In)-S(Se). Many of the recent investigators have been interested in the nature of the forces which are responsible for the binding between neighboring layers; such interlayer forces are known to be approximately two orders of magnitude weaker than the intralayer covalent-bond forces.^{1,2} In particular, Wieting and Verble³ have examined the Davydov multiplicity of optical phonons in β -GaSe which has two layers in the primitive unit cell. They have found that the relative frequency magnitude of the Davydov doublet, the $E_{1u}(TO)$ and E_{2g}^1 modes, is contrary to what is expected on the basis of the Van der Waals interlayer interaction. Consequently they have proposed that the frequency reversal is caused by the presence of the long-range Coulomb interaction.

In the present paper we would like to comment that a similar frequency reversal is observed in β -GaS and that such an optical anomaly can *not* be explained in terms of the long-range Coulomb interaction in the deformation-dipole approximation.

It has been well established that GaS crystallizes only in the β polytype which has the hexagonal D_{6h}^4 space symmetry. The lattice has the following 24 phonon normal modes⁴:

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

Among these representations one A_{2u} and one E_{1u} are acoustic modes. The transverse-optic modes, A_{2u} and E_{1u} , are infrared active. The A_{1g} , E_{1g} , and E_{2g} modes are all Raman active, whereas the B_{2g} , B_{1u} and E_{2u} are optically inactive.

Raman-scattering spectra are obtained at 295 K for $Z(XY)Z + Z(XX)Z$ and $X(YZ)\bar{X}$ configurations. Here Z is taken along the c axis. The overall

features of spectra for both configurations are in good quantitative agreement with those obtained by Irwin *et al.*⁵

Far-infrared measurements are performed for the light beam with electric field \vec{E} polarized perpendicular to the c axis at 295 K. Samples are cleaved from the crystal ingot which is also used in the Raman-scattering measurements. Figure 1 shows typical examples of transmission spectra. The reststrahlen band due to the transverse E_{1u} mode and to the associated longitudinal one spreads over the range from 290 to 350 cm⁻¹. These transmission spectra are compatible with the previous ones measured by the present authors⁴ and with the reflection spectrum by Finkman and Rizzo.⁶ Other workers^{5,7} have also attempted to obtain the far-infrared phonon spectrum of GaS. The present data evidently have better experimental accuracy than the previous ones for determining the frequency of the $E_{1u}(TO)$ mode.

The transmission spectrum depends on the dielectric parameters and on the sample thickness, so that the observed spectra are compared with the calculated curves. Since GaS has no other infrared-active mode for $\vec{E} \perp \vec{c}$ polarization, the single-oscillator model⁴ is employed in calculating the transmission spectrum. The best fit to the spectrum of Fig. 1(a) is given by the following parameter values: $\bar{\nu}(TO) = 296 \pm 1$ cm⁻¹, $\epsilon_{10} = 10.6$, $\epsilon_{1\infty} = 7.2$, and $\delta = 6$ cm⁻¹, where $\bar{\nu}(TO)$ is the wave number of the $E_{1u}(TO)$ mode, ϵ_{10} and $\epsilon_{1\infty}$ are the static and optic dielectric constants, respectively, for $\vec{E} \perp \vec{c}$. δ is the damping constant. The choice of these physical-parameter values gives a good fit also to the experimental curve for another sample with different thickness, as shown in Fig. 1(b). Hence, within the experimental accuracy, the Lydane-Sachs-Teller relation gives the wave number of the longitudinal mode associated with the transverse $E_{1u}(TO)$ mode: $\bar{\nu}(LO) = 359 \pm 2$ cm⁻¹.

The wave numbers of phonons obtained from the

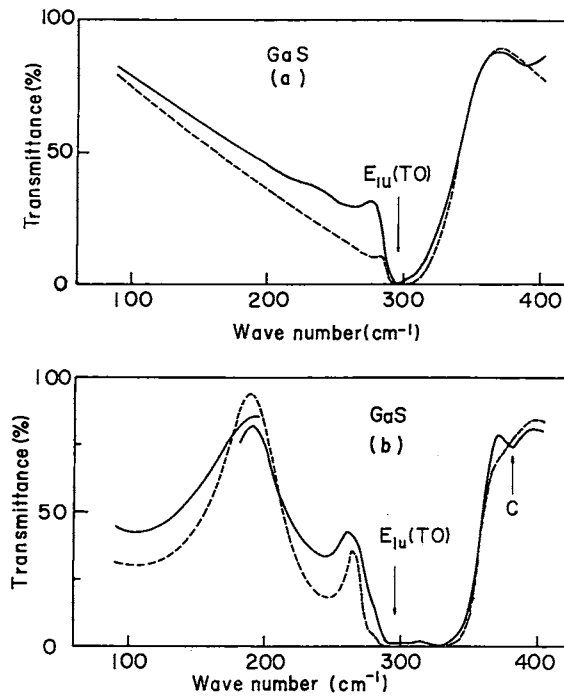


FIG. 1. Far-infrared transmission spectra of GaS. The sample thickness is 1.9 μm (a) or 7.3 μm (b). Broken lines are calculated spectra. The minimum marked as C is attributed to the $E_{1u}(\text{LO}) + E_{2g}^1$ combination band from both energy and symmetry considerations.

present measurement are listed in Table I. Let us pay our attention to the conjugate optical modes $E_{1u}(\text{TO})$ and E_{2g}^1 . According to our results, the frequencies of these modes are $296 \pm 1 \text{ cm}^{-1}$ and $295.0 \pm 0.2 \text{ cm}^{-1}$, respectively; $E_{1u}(\text{TO})$ has a higher frequency by $\sim 1 \text{ cm}^{-1}$ than E_{2g}^1 . These frequency values are in reverse order with respect to what is expected if the Van der Waals force between S atoms is dominant among interlayer forces between various pairs of atoms. According to Wieting and Verble^{3,8} the same kind of relationship exists also in $\beta\text{-GaSe}$ and MoS_2 . Although Brebner *et al.*⁹ have argued against the method used by the former authors to identify the crystal polytype, experimental results of Wieting and Verble seem reasonable in the light of present results.

Figure 2 suggests that little dipole moment is

induced in the rigid-layer mode E_{2g}^2 , which is conjugate with the acoustic E_{1u} mode. Its frequency, therefore, may be determined by the Van der Waals force between S atoms. In $E_{1u}(\text{TO})$ and E_{2g}^1 modes, on the other hand, a finite dipole moment is induced on a Ga-S bond due to its stretching vibration. The dipoles would couple with each other to give rise to the Coulomb force. It follows from Fig. 2 that the *interlayer* force between Ga and S atoms should be larger than the total forces arising from the interlayer S-S and Ga-Ga pairs in order for the resultant Coulomb coupling to cause the frequency of the $E_{1u}(\text{TO})$ mode to be higher than that of E_{2g}^1 .

We have carried out the calculation of the force constants to discuss the above possibility. Since chalcogen atoms are known to have relatively large electronic polarizabilities, we employ the deformation-dipole model developed by Karo and Hardy.¹⁰

S atoms form double hcp lattices with relative displacement of about $\frac{1}{4}\vec{c}$ so that the S sublattice may be regarded to be nearly isotropic. Furthermore, the electronic polarizability of Ga atoms should be considerably smaller than that of S atoms since the valence electron is concentrated near S atoms.¹¹ It follows from these facts that the Lorentz-Lorenz force may be assumed to be isotropic in good approximation. For the dielectric constant $\epsilon_{1u} = 7.2$ obtained above, the Clausius-Mossotti (CM) relation gives $\alpha(\text{Ga}) + \alpha(\text{S}) = 6.9 \times 10^{-24} \text{ esu}$ in GaS, where $\alpha(\text{Ga})$ and $\alpha(\text{S})$ are the electronic polarizabilities of Ga and S atoms, respectively. Taking this estimate into account, we calculate the dynamical matrix with respect to the E modes at the Γ point as a function of electronic polarizabilities and of deformation dipoles. As for the deformation dipole, we take only the covalent Ga-S bond into account. The deformation dipole associated with the metallic Ga-Ga bond is neglected since we are interested in the in-plane transverse modes in which Ga atoms within a unit layer vibrate in the same phase. The dynamical matrix includes a term $(1 - \alpha U H U)^{-1}$, where 1 is the unit matrix, α the polarizability matrix, U the charge matrix, and H Kellermann's Coulomb matrix.¹² Our numerical

TABLE I. Frequencies of normal modes of lattice vibrations in GaS at 295 K. All the frequencies except $E_{1u}(\text{TO})$ and $E_{1u}(\text{LO})$ are obtained from Raman-scattering measurements.

Mode	E_{2g}^2	E_{2g}^1	A_{1g}^1	E_{1g}^2	E_{2g}^1	$E_{1u}(\text{TO})$	$E_{1u}(\text{LO})$	A_{1g}^2
Frequency (cm^{-1})	22.0	74.8	187.9	291.2	295.0	296 ± 1	359 ± 2	360.2

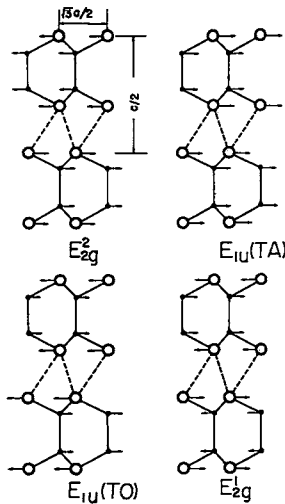


FIG. 2. Interlayer coordination of atoms in GaS. Open circles represent S atoms and black ones Ga atoms. The broken line indicates the interlayer Van der Waals bond between S atoms. The arrow indicates the displacement vector associated with E_{2g}^2 , $E_{1u}(TA)$, $E_{1u}(TO)$, and E_{2g}^1 modes.

calculation shows that several elements of this inverse matrix diverge if $\alpha(\text{Ga}) + \alpha(\text{S}) \approx 9 \times 10^{-24}$ esu. The singularity corresponds to the instability of some phonon modes such as E_{2u}^2 , E_{1g}^2 , and E_{1g}^1 . The above value of $\alpha(\text{Ga}) + \alpha(\text{S})$, however, is considerably larger than the semiempirical one in GaS derived from the CM relationship as mentioned above. The quantitative discrepancy in $\alpha(\text{Ga}) + \alpha(\text{S})$ implies that the frequencies of all phonon modes are real in the GaS crystal, so that the application of the deformation-dipole model may be justified for the present analysis.

In addition to the Coulomb forces, appropriate short-range forces due to the Van der Waals coupling as well as to the Ga-S covalent bond are taken into account in order that the total dynamical matrix gives quantitative consistency with the observed wave numbers of 22.0 and 296 cm^{-1} for E_{2g}^2 and $E_{1u}(TO)$ modes, respectively. The total dynamical matrix thus obtained predicts the frequencies of other modes. The result indicates that, if we compare the effect of the Coulomb forces with that of the short-range ones on the frequency eigenvalues of lattice modes, the Coulomb forces tend to reduce the frequencies of both E_{2g}^1 and $E_{1u}(TO)$ modes, but do not cause the frequency of the $E_{1u}(TO)$ mode to be higher than that of the E_{2g}^1 mode for the relevant value of $\alpha(\text{Ga}) + \alpha(\text{S})$. The calculated value of the frequency separation $\Delta = \bar{\nu}(E_{2g}^1) - \bar{\nu}(TO)$ is found to be in the range from 0.1 to 8 cm^{-1} , depending on the magnitude of the deformation dipole. The presence of the deformation dipole tends to suppress the electronic

polarization of Ga and S atoms¹⁰ so that the value of Δ decreases with the increase in magnitude of the deformation dipole. The effective "deformation" charge γ of $(0.4 \pm 0.1)e^-$ on a S atom gives $\Delta \sim 0.5 \text{ cm}^{-1}$, where $\gamma = dm/dr$ and m is the dipole moment associated with a Ga-S bond with length r .

A similar calculation has been carried out for β -GaSe. The result shows that the essential feature is not different from that of GaS.

Wieting and Verble³ have interpreted their experimental result in β -GaSe in terms of Coulomb forces. The present calculation, however, shows that the Coulomb force can not explain the experimental results in the nearest-neighbor approximation with respect to the deformation dipole.

In the preceding discussion, we implicitly assume a perfect crystal. This assumption may not be valid for our crystal. It is well known that a layer-compound crystal contains a comparatively large density of stacking faults.¹³ The small value of $|\Delta|$ observed in these three layer compounds suggests that such a crystal imperfection affects the close competition between different causes of the interlayer force. In fact Raman measurements by many workers show a scatter in frequencies of the E_{2g}^1 mode in GaS and of the compatible E' mode in GaSe. Their values are found to be in the range from 294.5 to 296.0 cm^{-1} ,^{5,7,14-16} and from 211.0 to 214.5 cm^{-1} ,^{3,5,14,15} respectively, at room temperature. The uncertainty in phonon frequencies could partly be due to the stacking faults and/or the crystal polytypism. We would like to point out that a systematic investigation is required with respect to the effect of the quality of the crystal before we proceed to the theoretical analysis involving higher-order corrections or employing a different model.

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