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Institute of Semiconductors, Academy of Sciences of the Ukrainian SSR, Kiev[1]

Interlayer Interaction in Phonon Spectra of ε-GaSe Crystals

By

V.V. ARTAMONOV, M.YA. VALAKH, and M.P. LISITSA

The distinctive interatomic forces in numerous crystals with layer or chain structures manifest themselves in typical features of the phonon spectra. They result in a weak dispersion of phonon branches for some directions in the Brillouin zone and in low-frequency rigid layer modes. These last-mentioned occur in crystals with at least two layers or chains in the elementary unit cell. In this case a small splitting occurs between modes in adjacent layers (chains) due to the small interaction between layers (chains). The number of components is given by the number of layers per unit cell. The optical activity of each components in absorption or Raman scattering (RS) spectra is determined by selection rules. This behaviour of the long wavelength optical phonons is qualitatively similar to the known Davydov splitting in molecular crystals /1/ and was observed, for example, in the layer compound As_2S_3 /2 to 4/ and in the chain compounds ZnP_2 and CdP_2 /5, 6/. However, As_2S_3 and most of the other crystals being studied have a center of inversion between layers. As a result the exclusion principle is obeyed and the doublets resulting from a small interaction between layers are such that one component is Raman active, while its conjugate is infrared active or totally inactive.

ε-GaSe is, however, one of few layer crystals in which both components of some of the Davydov doublets are Raman allowed due to the lack of inversion symmetry. Therefore the observation of the Davydov splitting in ε-GaSe is of principal significance. Up to now it is still subject of discussion in spite of numerous investigations (see, for example /7/ and references cited therein).

In this paper we present experimental evidence of the Davydov splitting in ε-GaSe and discuss peculiarities of RS spectra caused by weak interlayer interactions.

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[1] Prospekt Nauki 115, Kiev-28, USSR.

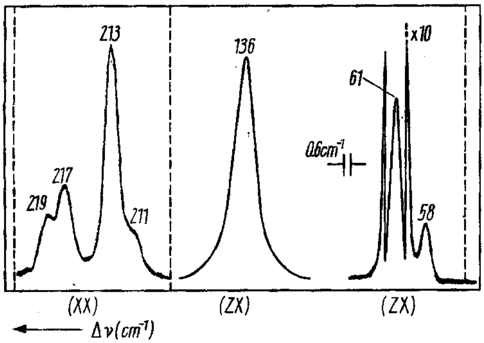

Fig. 1. Davydov splitting in the Raman spectrum of ε-GaSe at T = 80 K

The crystals were grown by the Bridgman technique. Right-angle RS spectra at T = 80 K were recorded using the 632.8 nm line of a He-Ne laser with a double DFS-24 monochromator and a photon counting system.

Comparison of line intensities for various polarisations supports the interpretation given in /8/. In particular the bands at 213 and 217 cm^{-1} which were considered /9/ as Davydov components of the mode E' as a matter of fact show different polarisation properties and hence have to be assigned to different modes. In addition, in spite of sufficiently high resolution (0.6 cm^{-1}) we did not reveal the splitting of the band 136 cm^{-1}, in contrast to the results of /9/. This fact also is consistent with /8/. At the same time, unlike /8/, we resolved with high reliability the doublets $\nu(E'') = 58$ and $\nu(E'') = 61$, $\nu(E'') = 211$ and $\nu(E'') = 213$, $\nu(E') = 217$ and $\nu(E') = 219\ cm^{-1}$ (see Fig. 1). We should mention that evidence for the doublet 58 - 61 cm^{-1} already was reported in /10/.

The value $\Delta\nu_i$ of the Davydov splitting of the mode ν_i may be estimated /11/ as

$$\Delta\nu_i = \frac{\nu_{RL}^2}{2\nu_i}\ , \qquad (1)$$

where ν_{RL} is the frequency of a rigid layer mode (for GaSe $\nu_{RL}(E') = 19.8\ cm^{-1}$).

According to (1) doublets would be most easily resolved for the lower frequency vibrations such as $\nu(E'') = 60\ cm^{-1}$. In this case we obtain from (1) $\Delta\nu \approx 3\ cm^{-1}$. This estimation fits our experimental data. However, according to (1) the mode $\nu(A_1) = 136\ cm^{-1}$ should be resolved with confidence, too ($\Delta\nu \approx 1.5\ cm^{-1}$). This splitting is not found. For the higher frequency vibrations $\nu(E'') = 213$ and $\nu(E') = 217\ cm^{-1}$ the measured splitting is larger than the value predicted by (1).[2] This is not surprising in view of approximate character of (1), derived from the linear chain model.

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[2] The last one corresponds to the most intensitive IR absorption band.

The magnitude of the Davydov splitting is determined by the matrix element describing a resonance intermolecular (interlayer) interaction. In the dipole approximation it is proportional to the square of the dipole moment of the intramolecular (intralayer) excitation. If the dipole moment equals zero then the quadrupole interaction should be taken into account. In other words one would expect the maximum splitting for vibrations with strong oscillator strength /1/. This is well known for molecular excitons /1/. In our case it explains the qualitatively larger splitting of the polar vibration $\nu(E') = 217\ \text{cm}^{-1}$ as compared to that predicted by (1). On the other side, it is likely that this effect results also in the very small ($< 0.6\ \text{cm}^{-1}$) splitting of the strongest Raman-active symmetrical vibration $\nu(A_1) = 136\ \text{cm}^{-1}$.

The significantly different intensities of the components $\nu(E'') = 58$ and $\nu(E'') = 60$, $\nu(E'') = 211$, and $\nu(E'') = 213\ \text{cm}^{-1}$, can be explained as follows. It has been known that for molecular excitations the absorption bands related to Davydov components are determined by the sum and difference of the intramolecular dipole moments (in layer crystals it means intralayer excitations). In ε-GaSe both layers in the unit cell are identical and parallel to each other. Therefore the displacements in conjugate modes are parallel ("sum" component) or opposite ("difference" component). Due to weak interlayer forces the displacements in both layers are not exactly equal and the intralayer dipole moments $\vec{d}_1$ and $\vec{d}_2$ differ somewhat from each other. As a result the band corresponding to $(\vec{d}_1 - \vec{d}_2)$ would not vanish but be essentially weaker than that corresponding to $(\vec{d}_1 + \vec{d}_2)$. The relation between $\vec{d}_1$ and $\vec{d}_2$ must not be identical for different vibrations and therefore the relation between the intensities of corresponding Davydov components could be different from one another. Notice that $\vec{d}_1 = \vec{d}_2$ if inversion symmetry takes place (β-GaSe) (as well as in case of vanishing interlayer forces). In this case one peak of the Davydov doublet could not be seen in the absorption spectra (it may be active in RS spectra).

The qualitative results also hold for RS spectra /10/ which are determined by the differential polarizabilities.

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