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LOW-FREQUENCY LATTICE VIBRATIONS OF δ-GaSe COMPARED TO ε- AND γ-POLYTYPES

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Raman spectra of the new polytype δ-GaSe are given in the low-frequency region ($\omega < 60\ cm^{-1}$) and their relation to lattice vibrations of the simpler polytypes γ, ε is discussed. A simple lattice dynamical model is used to describe the phonon modes in all 3 modifications. First observation of Davydov splitting in ε-GaSe is reported. Particular weakness of one component of this doublet is shown to be a consequence of the specific "molecular" nature of layer crystal.

1. INTRODUCTION

GALLIUM SELENIDE (GaSe) crystallizes under several modifications. Four of them have been proposed so far [1] and designated as β (space group D^4_{6h}), γ (C^5_{3v}), ε (D^1_{3h}) and δ (C^4_{6v}). The existence of the β-structure, which is well ascertained for GaS, is still doubtful in GaSe. Raman spectra of β-GaS and of γ-, ε-GaSe have been published.[2]

In this paper, Raman spectra of δ-GaSe are given and related to those of simpler (γ, ε) polytypes. Davydov doublets in ε-GaSe are discussed. This investigation is limited to the low-frequency region of non-polar modes. Solid lines in Fig. 1 represent phonon dispersion curves for γ-GaSe (one layer/cell) in the z-direction ($\bar{c}$-axis). ε-GaSe (two layers/cell) is then represented by broken lines, the Brillouin zone being halved, and the γ-GaSe zone boundary modes then appear at the center. Repeating this reasoning, we obtain the dispersion in δ-GaSe (four layers/unit cell), which is shown by dotted lines. For this new polytype[3] the activity of the modes is easily found by group theory: For δ-GaSe, the 48-dimensional representation in Γ has the decomposition

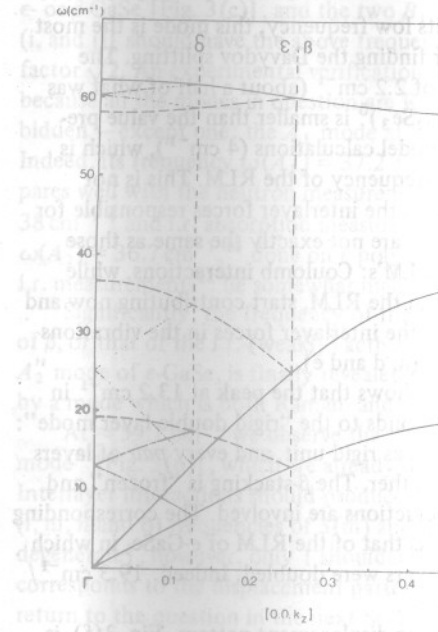

Fig. 1. Dispersion of low-frequency phonons propagating in the z-direction, provided by model calculations for GaSe-polytypes with 1, 2 and 4 layers/unit cell (solid, broken and dotted lines, respectively).

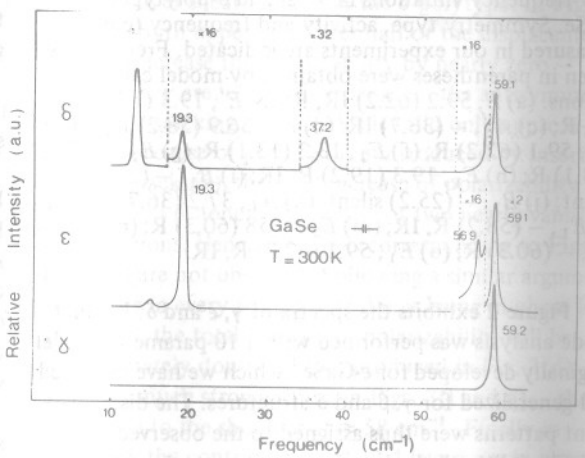

Fig. 2. Low-frequency Raman spectra of γ-, ε- and δ-polytypes of GaSe.

$$\Gamma = 8A_1 \oplus 8B_1 \oplus 8E_1 \oplus 8E_2 .$$

One A_1 and E_1 are acoustic branches. The remaining A_1 and E_1 are Raman allowed as well as E_2; A_1 and E_1 are i.r. allowed, B_1 are silent.

2. EXPERIMENTAL PART

ϵ-type crystals were grown by the Bridgman method; γ- and δ-samples were vapour-grown needles typically a few hundred microns in diameter. Right-angle Stokes scattering spectra were recorded with the red lines of a Kr laser with a triple T 800 Coderg monochromator at a resolution of 0.5 cm^{-1}

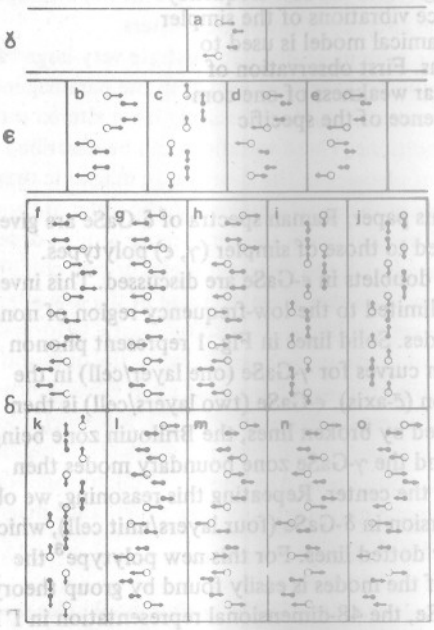

Fig. 3. Normal modes of vibrations corresponding to the low-frequency vibrations in γ-, ϵ- and δ-polytypes of GaSe. Symmetry type, activity and frequency (cm^{-1}) measured in our experiments are indicated. Frequencies given in parentheses were obtained by model calculations. (a) E, 59.2 (62.2) IR, R; (b) E', 19.3 (19.2) IR, R; (c) A_2'', – (36.7) IR; (d) E'', 56.9 (58.2) R; (e) E'', 59.1 (62.2) R; (f) E_2, 13.2 (13.1) R; (g) E_2, 13.2 (13.1) R; (h) E_1, 19.3 (19.2) R, IR; (i) B_1, – (25.2) silent; (j) B_1, – (25.2) silent; (k) A_1, 37.2 (36.7) R, IR; (l) E_1, – (58.2) R, IR; (m) E_2, ≈ 58 (60.3) R; (n) E_2, – (60.3) R; (o) E_1, 59.1 (62.2) R, IR.

Figure 2 exhibits the spectra of γ, ϵ and δ. Normal mode analysis was performed with a 10-parameter model originally developed for ϵ-GaSe[4] which we have modified and generalized for γ, β and δ structures. The displacement patterns were thus assigned to the observed peaks and Fig. 3 lists all the low-frequency normal modes ($\omega < 60\ cm^{-1}$). For this group of modes, neglection of Coulomb forces is legitimate. γ- and ϵ-GaSe spectra agree with those of other authors,[2] except for the following points:

(1) In the γ-spectrum, only the "half-layer shear mode" [Fig. 3(a)] at 59.2 cm^{-1} is observed. We recorded no "rigid layer mode" (RLM) in this polytype – because there is not any: The γ-modification has only one layer in the *elementary* unit cell. The one observed in reference 2 was probably due to the admixture of ϵ-modification to the γ-sample. An error or misinterpretation has often occurred on this point in the literature: As the *elementary* unit cell of γ-GaSe is not hexagonal, one sometimes uses a hexagonal *non-elementary* unit cell, with 3 layers/cell. Both representations are equivalent and the hexagonal one may be even more convenient for some applications – but not for counting the phonon branches or number of rigid layer modes, where only the *elementary* unit cell has to be referred to.

(2) In the ϵ-polytype, besides the RLM at 19.3 cm^{-1}, a weak peak occurs at about ≈ 15 cm^{-1}. It does not belong to the ϵ-polytype and is probably due to stacking faults.

(3) In the ϵ-polytype, besides the strong peak at 59.1 cm^{-1} already observed,[2] we found a new weak peak at 56.9 cm^{-1}. Figures 3(d, e) show that this should be a doublet; the displacement pattern of the "half-layer shear mode" of γ [Fig. 3(a)] is repeated in both layers of ϵ: in one case, the layers vibrate against each other [Fig. 3(d)], in the other, they are in phase [Fig. 3(e)].

Owing to its low frequency, this mode is the most appropriate for finding the Davydov splitting. The measured split of 2.2 cm^{-1} (about a half of what was found e.g. in As_2Se_3)[5] is smaller than the value predicted by our model calculations (4 cm^{-1}), which is implied by the frequency of the RLM. This is not surprising because the interlayer forces responsible for the Davydov split are not exactly the same as those generating the RLM's: Coulomb interactions, while playing no role in the RLM, start contributing now and they may soften the interlayer forces in the vibrations shown in Figs. 3(a, d and e).

Figure 3(g) shows that the peak at 13.2 cm^{-1} in Fig. 2(δ) corresponds to the "rigid double-layer mode": Each layer moves as rigid unit, and every *pair* of layers keeps firmly together. The β-stacking is "frozen" and only ϵ-type interactions are involved. The corresponding eigenfrequency is that of the RLM of ϵ-GaSe, in which the masses of layers were doubled. Indeed: 19.3 $cm^{-1}/\sqrt{2} = 13.65\ cm^{-1}$.

The preceding displacement pattern, Fig. 3(f), is similar: ϵ-stacking is frozen and only the β-forces are involved. No other peak was found close to 13.2 cm^{-1} and this peak must be due to two (exactly or nearly)

degenerate phonons: The frequency of the shear mode in the (hypothetical) β-GaSe would be the same as in ε: 19.3 cm^{-1}. This conclusion is immediately confirmed by the next shear mode at 19.3 cm^{-1} [Fig. 3(h)] which has the same frequency as the shear mode in ε-GaSe, although both "ε-type" and "β-type" effective springs are stretched.

The notion of "effective spring", already used by other authors[6,7] to describe the RLM is indeed no oversimplification. If the interlayer interaction is described by an arbitrary central potential $V(r)$ between the Se–Se (interlayer) neighbours, then the x-, y- and z-vibrations of rigid layers are decoupled and the RLM may be assimilated to the vibrations of a linear chain of masses $2(M_1 + M_2)$ bound together by the effective springs. Although two different springs are needed (shear and compressional), they are both derived from the same interlayer potential. Moreover, the relations connecting the effective springs with the interlayer potential[8] are the same for both ε- and β-stackings.[9]

If the RLM's in δ-polytype suggest an independence of the shear springs on ε- or β-stackings, this implies, via a similar independence of the interlayer potential, that the compressional springs will also be equal in ε- and β-stackings. The series of the three compressional rigid double-layer and rigid-layer modes in δ [Figs. 3(i, j and k)] should therefore exhibit similar properties as the preceding series of the three shear modes: The A_1 mode observed in δ at 37.2 cm^{-1} [Figs. 2(δ) and 3(k)] has to display the same frequency as the compressional RLM in ε- or β-GaSe [Fig. 3(c)], and the two B_1 modes [Fig. 3 (i, and j)] should have the above frequency reduced by a factor $\sqrt{2}$. An experimental verification is not easy, because all the modes in question are Raman forbidden – except one: the A_1 mode at 37.2 cm^{-1} in δ. Indeed, its frequency $\omega(A_1) = 37.2 \pm 0.5$ cm^{-1} compares well with the neutron measurements $\omega(A_2'') \approx 38$ cm^{-1} [4] and i.r. absorption measurements (at $T = 4$ K) $\omega(A_2'') = 36.7$ cm^{-1},[10] done on ε-polytypes. (The older i.r. measurements[11] lie somewhat higher: 40 ± 1 cm^{-1}.)

Significantly, the frequency of the silent B_{2g} mode of β, or that of the i.r.-(weakly) active–Raman-inactive A_2'' mode of ε-GaSe, is finally revealed in the δ-polytype, by a mode which is both Raman- and i.r.-active.

At ≈ 59.1 cm^{-1} we observe the "half-layer shear mode" [Fig. 3(o)], which we already met in ε-polytype. Interlayer interactions should produce a triplet [Fig. 3 (l, m, n and o) frequencies of 3(m) and 3(n) being degenerate], however, only 1 shoulder is resolved. It corresponds to the displacement pattern Fig. 3(m). We return to the question in the next Section.

3. DISCUSSION

ε-GaSe is one of few layer crystals in which both components of the Davydov doublet are Raman-allowed If they appear with different intensities, this can be understood as follows:

In a "perfectly molecular" layer crystal (vanishing interlayer forces) the differential polarizabilities $P_{\alpha\beta,\gamma}(l\kappa)$[12] and the displacements would be equal in both layers. The total increase in polarizability would then be in one case the double of what is produced by single layer [Fig. 3(e)] and zero in the other case [Fig. 3(d)]: One peak would thus be suppressed and the other reinforced. Actually, the interlayer forces are not vanishing but only weak, therefore neither the displacements nor the differential polarizabilities are exactly equal in both layers. Consequently, the Raman cross-section for the "antisymmetric mode" is only approximately vanishing and the corresponding peak is therefore nonzero (Raman allowed), but weak. This is what we observe at ≈ 60 cm^{-1}.

Note that the symmetry of $P_{\alpha\beta,\gamma}(l\kappa)$ or $u_\gamma(l\kappa)$ used above is *not* a consequence of space group symmetry. There exists neither an inversion center in ε-GaSe, nor any other symmetry operation which would transfer one layer into another. We have used only the fact that (1) there are two identical structural units repeated in the crystal's unit cell and (2) the interlayer interactions are weak. These two properties are a specific feature of layer crystals and may be viewed as an additional symmetry which complements, in a layer crystal of this kind, the space group symmetry. In other crystals, one layer *can* be derived from another, e.g. by an inversion (β-GaS) or rotation (PbI_2). This substantially modifies the selection rules and the intensities in the Davydov doublet; in none of the last two cases, however, the specific "molecular" nature of a layer crystal plays any role.

Knowing that the symmetry of β-stacking implies the total change of polarizability to be zero in a mode like Fig. 3d, it is possible to understand the complex of "half-layer shear modes" in the δ-polytype. In Figs. 3 (l and n) both upper and lower half of the displacement patterns increase the polarizability by nearly zero – because they are, each half separately, the antisymmetric mode of β-stacking. Even if this is valid only approximately (because of perturbation introduced by insertion of the ε-stacking), the total increase of polarizability in the unit cell is nonetheless a sum of two nearly vanishing contributions. Hence the peaks corresponding to Figs. 3 (l and n) are not observed. Following a similar argument, the layers in every pair of β-stackings being in phase in Fig. 3(m), the total increase of polarizability will be approximately double of that produced in Fig. 3(d) – anyhow, much stronger than in Figs. 3(l and n) – thus giving rise to the shoulder at ≈ 58 cm^{-1}. Finally in Fig. 3(o), the contributions of all 4 layers are in phase and give rise to the strong peak at 59.1 cm^{-1}.

4. CONCLUSION

Comparing Figs. 2(γ, ϵ and δ), it is clear that Raman measurements in the low-frequency region can be used for characterization of polytypes of GaSe. While the difference between γ, ϵ and δ is read from the frequencies of the RLM's, the distinction between ϵ- and a hypothetical β-GaSe polytype would have to be looked for in the appearance or disappearance of the Davydov doublet at ≈ 60 cm^{-1}. (The *frequencies* of the RLM's are expected to be the same in both modifications.) The i.r. activity or inactivity of the compressional RLM at ≈ 37 cm^{-1} could also be used for this purpose.

REFERENCES

1. KUHN A., CHEVY A., CHEVALIER R., *Phys. Status Solidi* **A31**, 469 (1975).
2. For recent review see e.g. HOFF R.M., IRWIN J.C. & LIETH R.M.A., *Can. J. Phys.* **53**, 1606 (1975).
3. KUHN A., CHEVALIER R. & RIMSKY A., *Acta Cryst.* **B31**, 2841 (1975).
4. JANDL S., BREBNER J.L. & POWELL B.M., *Phys. Rev.* **B13**, 686 (1976).
5. ZALLEN R., SLADE M.L. & WARD A.T., *Phys. Rev.* B3, 4257 (1971).
6. WIETING T.J., *Solid State Commun.* 12, 931 (1973).
7. ZALLEN R. & SLADE M., *Phys. Rev.* B9, 1627 (1974).
8. POLIAN A., KUNC K. & BESSON M. (to be published).
9. These conclusions are limited to the RLM's i.e. to the case when the Coulomb forces are not involved.
10. IRWIN J.C., HOFF R.M., CLAYMAN B.P. & BROMLEY R.A., *Solid State Commun.* 13, 1531 (1973).
11. KURODA N., NISHINA Y. & FUKUROI T., *J. Phys. Soc. Japan* 24, 214 (1968).
12. See e.g. BORN M. & HUANG K., *Dynamical Theory of Crystal Lattices*, equations (23.3), (39.14) and (49.5). Oxford University Press (1954).