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PHONON MODES AND OPTICAL PROPERTIES OF GaS UNDER HIGH PRESSURE

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The frequencies of one- and two-phonon modes in layered GaS have been studied up to 235 kilobars. The variations in linewidth of some of those modes are interpreted by pressure-induced degeneracy with edge-of-the zone densities of states. Optical and Raman data show that a phase transition occurs above 190 kilobars.

I - Experiment

GaS samples, 10 to 20 microns thick are cleaved from vapour-grown needles about 100 μ m in diameter. GaS crystals have the D⁴_{6h} group symetry, and the c-axis is parallel to the length of the needles. The diamond anvil cell setup is identical to that of ref. 1. The 530.2 nm and 647.1 nm lines of a Kr⁺ laser were used in Raman experiments. Transmission measurements were done with a metallographic microscope, with a quartz-iodine lamp as a source. In both sets of experiments, a Coderg T 800 triple monochromator has been used.

The method of pressurization we have used [2] permits to obtain homogeneous stress conditions for pressures as high as 235 kilobars.

II - Results and discussion

1 - Single-phonon modes

On figure 1, are shown the frequencies of one and two-phonon lines versus pressure. The relative pressure coefficients of one-phonon modes, essentially the same as previous by reported data [3 - 5], are shown on the table.



Fig. 1

Raman frequencies versus pressure: One-phonon lines : full circles ; edge-of-the zone overtones : empty circles. Stars indicate the extra frequency observed in the high pressure phase (See text)

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TABLE

	ONE-PHONON MODES						TWO-PHONON MODES	
ROOM PRESSURE WAVENUMBER (CM ⁻¹)	23	74	188	292	296	360	175	215
ASSIGNMENT	E _{2g}	E _{lg}	A _{lg}	E _{lg}	E _{2g}	A _{lg}	2 TA(M)	2 LA(M)
PRESSURE COEFFICIENT (1/y)(dv/dP) in 10 ⁻ BAR ⁻¹	22	1	2,5	2.2	2.2	1.5	-1.	1.2

Pressure coefficients of the Raman-allowed phonons of GaS

The E₂ mode has a very high pressure coefficient (1/v) (dv/dP). It is about one order or magnitude larger than that of the other modes. This is expected since the restoring force for this motion is the weak interlayer interaction which is sensitive to the large variation of the interlayer distance with pressure. This E₂ mode, which has a frequency of 23 cm⁻¹ at atmospheric pressure, was thus shifted to 76 cm⁻¹ at 100 kilobars. This three-fold increase in frequency corresponds to an increase by a factor of 10 in the restoring forces. A lattice dynamical calculation [6] has shown that the intralayer interaction is some 10 times larger than the interlayer one. Then, at 150 kilobars, inter-and intralayer interactions are comparable, and, in that respect, the crystal is quasi-3-dimensionnal above 150 kilobars, although it has retained the same crystal symetry D₆.

The second interesting point on figure 1 is the very low pressure coefficient of the E rigid half-layer shear mode at 74cm⁻¹ (P = 1 bar). This vibration can be seen as an edge-of-the-zone transverse acoustic phonon of GaS molecules on a chain along the c-axis. At high pressure, the inter-and intralayer bonds are of the same order of magnitude, as shown by the frequency of the E R.L.M. In this case, the displacement pattern of the E mode is that of an edge of-the-zone TA phonon with k along the c-axis (in this scheme, the unit cell contains only one GaS molecule, that is a half-layer). In a second step, the difference between inter-and intralayer bonds results in a folding of the Brillouin zone. It brings the TA phonon at the center of the zone, the displacement pattern being the same as in the E g mode of the actual GaS crystal. In this intermediate step, the edge-of-the-zone TA vibration has now a displacement pattern similar to that of the R.L.M. of the actual GaS unit cell (4 GaS molecules). In that model, we expect the frequency of the E g mode and of the R.L.M. to be in a ratio of $\sqrt{2}$. Indeed, at 150 kilobars, we find that (E g)/ (E g) = 66/84 \approx 0.79 instead of the expected value of $\sqrt{2}/2 \approx 0.71$, which is surprisingly close, in view of the approximations.

In conclusion, the displacement pattern of the E $_{\mbox{lg}}$ mode is analogous to that of an edge-of-the-zone TA mode.

Edge of the zone TA phonons, in 3-dimensionnal crystals, are known to exhibit negative Grüneisen parameters [7]. This is because shear distorsions destabilize the ionic system since nearest neighbor distances increase to second order in the strain. The electronic contribution is responsible for the stability of the structure. When pressure is applied the electronic distribution tends to be spread out in most crystals, and this delocalization of the charges decreases the stabilizing electronic contribution, softens the total restoring spring and results in a negative pressure coefficient. This explanation is entirely applicable to the rigid half-layer shear mode (E_{1g}) in GaS : here, an important electronic contribution to the relevant bond (Ga-Ga)^g is due to the overlapping of the d-orbitals on Gallium. It has been shown that, for an isolated layer, these orbitals point inside the layer and are entirely localized within the layer. When interlayer interaction is

switched on the d-orbitals partially point outside (8). High pressure, which increases interlayer interaction in this class of crystals (9) also increases the delocalization of those electrons over the interlayer space and thus brings in a negative contribution to the restoring forces. In the case of ${\rm E}_{1\rm g},$ this contribution is not sufficient, as in the case of TA modes in 3-dimensionnally bonded crystals, to overcome the increase due to other contributions : instead of leading to an absolutely negative coefficient, it results in a weakly positive value.

In summary, we propose to explain the singular value of $1/_{
m V}$ dV/dP for the $74cm^{-1} E_{1\alpha}$ mode as the result of two contributions :

- A positive one coming from the decrease with pressure of the interlayer distances ;

- A negative one coming from the shear motion, and the TA-like character in this modes. The total may be either weakly positive, zero, or negative, but in any case, in algebraic value, much less than for other intralayer modes.

2 -Two-phonon modes

The Raman peaks observed at 175cm^{-1} and 215cm^{-1} fit very well with the 2 TA(M) and 2 LA(M) respectively.

The negative value of the pressure coefficient of the TA mode is similar to those found in 3-D network crystals such as Si, Ge, III-V and II-VI compounds.

It is the first time this behaviour is observed outside crystals with 3dimensionnal molecular units. This tends to confirm that even outside this class of lattices, the negative pressure coefficient of zone-edge phonons is a general property, related to the distortion involved in this type of shear vibrations. On figure 1, it is clear that the A₁₀ mode (188cm⁻¹ at 1 bar) and the 2 LA

On figure 1, it is clear that the A mode ($188cm^{-1}$ at 1 bar) and the 2 LA should cross above 100 kilobars. On figure 2, are shown the full width at half



Fig. 2 Full width at half maximum of Alg phonons versus pressure: 360 and 188 are the original wavenumbers, in cm⁻¹, of these two modes at atmospheric pressure

maximum (F.W.H.M.) of the two Ala modes. The F.W.H.M. of the low - frequency mode increases up to about 140 kilobars, and then decreases again. Comparison between the F.W.H.M. of the two A12 modes indicates that no systematic "spurious" broadening due to stress inhomogeneity disturbs the measurement.

The relative intensity of the two A₁ modes changes by a factor of 10 between 0 and 170 kilobars, the high-frequency mode becoming dominant under high pressure. In low-dimensionnality networks, in particular layer structures, the existence of the highly polarizable electronic distributions of the interlayer bonds results in a very large Raman efficiency with stress. Application of ab initio calculations of Raman cross-sections to the layer compounds, when they become possible, will be a very sensitive test to the calculations.

Optical behaviour and phase transition 3 -

The gap of GaS is 2.55 eV at 300 K and its pressure coefficient is -11X10⁻⁶ eV/bar at zero pressure [4]. At 180 kilobars, due to non-linearity it is still close to 1.8 eV. At this pressure, GaS suddenly changes from dark-red to black, remains opaque both at higher and lower pressure (down to 100 kilobars). when pressure is decreased from 100 to 30 kilobars, the absorption edge shifts again to higher energies, but remains several hundreds of milli eV lower. Fig. 3 shows absorption edges at 30 kilobars upon increase of pressure (curve 1) and after a pressurization to over 200 kilobars (curve 2). This and the occurence of



Fig. 3 Absorption coefficient at 30 kilobars: Increasing pressure curve 1. Decreasing pressure from 235 kilobars down curve 2

an extra Raman mode around 60cm (stars on figure 1) are indications of the modification of the bond pattern. This decrease of the energy gap points to a structural modification where interlayer bonds increase somuch that they compare with intralayer bonds, after a drastic decrease of interlayer spacing. The individual layers, or at least the hexagonal halflayers will undergo little perturbation, whereas the interlayer forces would be of the same order of magnitude as the intralayer Ga-Ga bonds. Then, the crystal would be much closer to 3-dimensionnal first-order binding than in the usual β -type layer modification. The experimental facts which support this proposal can be summed up as follows : 1/ The decrease of the indirect optical edge in the high pressure modification. In this class of semiconductors its decrease under pressure has been observed from the increase of interlayer interaction, due to pressure of the individual layers.

2/ At least, one extra phonon was observed during the decrease of pressure. These extra lines will not be attributed until the high pressure structure is known.

- REFERENCES -

- 1) J.M. BESSON and J.P. PINCEAUX: Rev. Sci. Inst. 50 541 (1979).
- 2) A. POLIAN, J.C. CHERVIN and J.M. BESSON : Phys. Rev. B (in press).
- 3) R.N. TYTE, W. RICHTER and W. RAUTENBERG : Verhandl. D.P.G. VI, <u>10</u>-403 (1975).
- 4) J.M. BESSÓN, R. LE TOULLEC, J.P. PINCEAUX, A. CHEVY and H. FAIR : High
- Temp. High Press. 7 720 (1975).
- 5) A. POLIAN, K. KUNC and A. KUHN : Proc. 13th I.C.P.S., Rome, 1976 (Ed. by S.G. FUMI) p. 392.
- 6) A. POLIAN, K. KUNC, R. LE TOULLEC and B. DORNER : Proc. 14th I.C.P.S.
- Edimburgh (1978). Inst. Phys. Conf. Series. Nº 43, p. 907.
- 7) G. MARTINEZ : In Handbook of Semiconductors, volume 2 (Ed. by M. BALKANSKI). North Holland Publ. Co (1980) p. 181.
- 8) A. BOURDON, A. CHEVY and J.M. BESSON : Ref. 6 p. 1371.
- 9) J.M. BESSON, C.P. JAIN and A. KUHN : Phys. Rev. Lett. <u>32</u>, 936 (1974).