Large increase of the low-frequency dielectric constant of gallium sulfide under hydrostatic pressure

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The pressure dependence of the low-frequency dielectric constant of layered gallium sulfide, parallel to the c axis, is investigated through capacitance measurements. The measured pressure coefficient $\Delta(\ln\epsilon_\parallel)/\Delta P$ is found to be $(80\pm5)\times10^{-3}$ GPa^{-1}. This large and positive pressure coefficient is shown to be coherent with models of charge transfer from the Ga-Ga intralayer bond to the interlayer space under pressure.

I. INTRODUCTION

The pressure dependence of the dielectric constant in most tetrahedrally coordinated semiconductors has been shown to be dominated by the decrease of both the electronic and lattice polarizabilities under pressure, yielding relatively low and negative pressure coefficients.[1] Cadmium sulfide exhibits an anomalous behavior, with a positive increase of the low-frequency dielectric constant, that has been attributed to the occurrence of a phase transition at relatively low pressure.[1] Silicon carbide[2,3] has also been shown to exhibit a small increase of the transverse dynamic effective charge under pressure that should lead to an increase of the lattice contribution to the low-frequency dielectric constant.

However, III-VI layered semiconductors are characterized by a strong crystal anisotropy, affecting both optical and transport properties. Recent measurements in gallium selenide (GaSe) (Ref. 4) and indium selenide (InSe) (Ref. 5) have shown that the binding energy of the exciton strongly decreases under pressure. According to Gauthier *et al.*,[4] this effect is due to an increase of the low-frequency dielectric constant parallel to the c axis,[4] which is explained through a model of charge transfer from intralayer to interlayer bonds, increasing the overall ionicity of the crystal under hydrostatic pressure.

In this paper we report direct measurement of the low-frequency dielectric constant under hydrostatic pressure in a layered compound, gallium sulfide (GaS), closely related to GaSe and InSe.

II. EXPERIMENT

GaS crystals were grown by the Bridgman method, without any purposely added doping agent.[6] Samples for capacitance measurements were cleaved from the ingot with a razor blade and cut into slabs 4–10 μm thick and 1.5×1.5–3×3 mm^2 in size. Gold electrodes were deposited in both faces of each slab, parallel to the c axis, by vacuum evaporation, either as 1.2-mm-diameter circles or 2×2-mm^2 squares. The devices so prepared were mount-

ed in sample holders and soldered to electric leads with silver paste. Electric resistance of these capacitors was higher than 100 MΩ, which corresponds to a resistivity higher than 10^9 Ω cm, in accordance with the semi-insulating character of GaS samples here used.

The capacitance was measured as follows. A 1000-Hz ac voltage is applied to the capacitor and the current is measured with a current sensitive preamplifier and a lock-in amplifier, which gives the complex impedance of the capacitor, from the in-phase and in-quadrature components of the ac current. In order to calibrate the capacitance meter, a series of standard capacitors with capacitances from 2 to 40 pF were measured in the same conditions as the GaS capacitors, i.e., they were mounted on the electric leadthroughs of the pressure obturator and measured inside the pressure cell.

Measurements under pressure were made in a conventional maraging steel vessel, with pentane used as the pressure transmitting fluid. Pressure was measured with a calibrated manganine gauge.

III. RESULTS

Given the geometry of the GaS capacitors studied here, the electric field between the gold electrodes is parallel to the c axis, and with the size being much greater than the thickness, one can neglect the border effects. The capacitance C at a given pressure P is then given by

$$C(P)=\epsilon_\parallel(P)\frac{A(P)}{d(P)} , \qquad (1)$$

where $\epsilon_\parallel$ is the GaS low-frequency dielectric constant, A is the area of gold electrodes, and d is the slab thickness. Even if the aim of this work was not to obtain a precise value of the low-frequency dielectric constant at room pressure, but only its pressure coefficient, we have measured $\epsilon_\parallel$ from the capacitance of several devices at 1 bar. The slab thickness was obtained from the transmission interference fringe pattern in the 500–1000-nm region, by fitting the position of all maxima and minima to the

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refractive index spectrum given by McMath and Irwin.[7] The result of that measured was $\epsilon_\parallel(1 \text{ bar}) = 5.2 \pm 0.3$. This value is in good agreement with the lowest ones reported in the literature (as measured from far-infrared reflectivity experiments) that range from 5.44 to 6.6.[8-11]

$\epsilon_\parallel(P)$ can be obtained from $C(P)$ through Eq. (1), provided one takes into account the pressure dependences of the GaS capacitor area and thickness:

$$A(P) = A(0)(1 - 2\chi_\perp P) ,$$

$$d(P) = d(0)(1 - \chi_\parallel P) ,$$
(2)

where $\chi_\perp = 4.7 \text{ GPa}^{-1}$ and $\chi_\parallel = 23.6 \text{ GPa}^{-1}$ are the GaS compressibilities perpendicular and parallel to the c axis, respectively.[12] Figure 1 gives the GaS low-frequency dielectric constant parallel to the c axis as a function of pressure. From that figure, one can obtain the pressure coefficient $\Delta(\ln\epsilon_\parallel)/\Delta P = (80 \pm 5) \times 10^{-3} \text{ GPa}^{-1}$. By contrast to results reported by Samara,[1] for III-V and II-VI compounds, it is positive and five times higher than the highest one there reported ($-17.3 \times 10^{-3} \text{ GPa}^{-1}$, for GaAs). This result confirms the specificity of chemical bonding in III-VI layered semiconductors, by contrast to tetrahedally coordinated semiconductors.

IV. DISCUSSION

In a polar semiconductor, the low-frequency dielectric constant has both an electronic and a lattice contribution $\epsilon = \epsilon_\infty + \epsilon_l$. Then its pressure dependence can be separated in the following way:[1]

$$\left[\frac{\partial \ln\epsilon}{\partial P} \right]_T = \frac{\epsilon_\infty}{\epsilon} \left[\frac{\partial \ln\epsilon_\infty}{\partial P} \right]_T + \frac{\epsilon_l}{\epsilon} \left[\frac{\partial \ln\epsilon_l}{\partial P} \right]_T .$$
(3)

In the case of III-VI semiconductors, this equation must be written for each polarization condition (perpendicular and parallel to the c axis). The absolute values found in the literature for the electronic and lattice contributions to the GaS low-frequency dielectric constant[8-11] exhibit a small dispersion. Nevertheless, the relative contribution of each mechanism is essentially the same in all references. As our discussion is based in relative contributions and relative changes under pressure, the choice of a set of room pressure values is irrelevant and we use in our discussion those closer to ours in which concern $\epsilon_\parallel$, i.e., those of Refs. 8 and 9: $\epsilon_{\infty\perp} = 6.31$, $\epsilon_{l\perp} = 3.11$, $\epsilon_{\infty\parallel} = 4.95$, and $\epsilon_{l\parallel} = 0.49$.

Let us first discuss the electronic contribution. In that regard, the most complete results in the literature refer to the pressure dependence of the refractive index perpen-
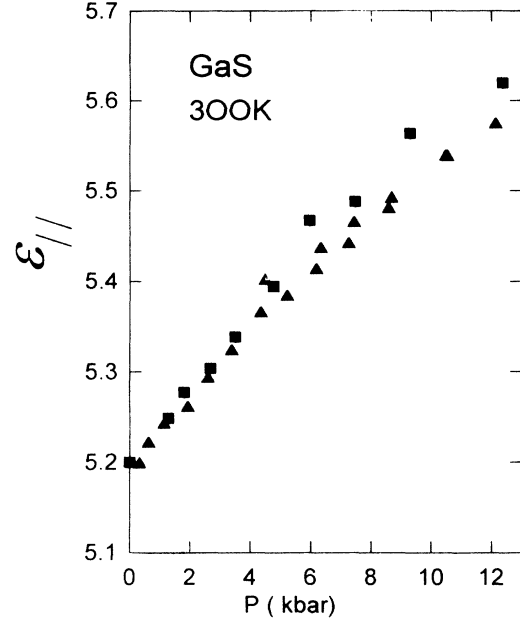

FIG. 1. Pressure dependence of the low-frequency dielectric constant of GaS parallel to the c axis, as obtained from capacitance measurements, with the correction for the echange of capacitor area and thickness under pressure. Experimental points correspond to results from two samples with different contact geometry: 1.2-mm-diameter circle (■) and 2×2-mm² square (▲).

dicular to the c axis. Results for GaSe (Refs. 4 and 14) and GaS (Ref. 15) can be found in the literature. In both cases, the dispersion of the electronic dielectric constant perpendicular to the c axis, can be described through a van Vechten model:[13]

$$\epsilon_\perp(E) = n_\perp^2 = 1 + \frac{E_p^2}{E_{0\perp}^2 - E^2} ,$$
(4)

where E_p/h is the plasma frequency of the valence-band electrons and $E_{0\parallel}$ is the Penn gap of the semiconductor for polarization parallel to the c axis. The pressure coefficient of the electronic dielectric constant is then given by

$$\frac{\partial \ln[\epsilon_\perp(E) - 1]}{\partial P} = \chi - \frac{2E_{0\perp}}{E_{0\perp}^2 - E^2} \frac{\partial E_{0\perp}}{\partial P} ,$$
(5)

where $\chi = \chi_\parallel + 2\chi_\perp$ is the volume compressibility, whose contribution arises from the volume dependence of the plasma frequency. Table I summarizes the results of

TABLE I. van Vechten model parameters for GaSe and GaS, for polarization perpendicular to the c axis, experimental pressure coefficient of the refractive index, and pressure coefficient of the electronic low-frequency dielectric constant, decomposed according to Eq. (5) for $E = 0$.

	E_P (eV)	E_0 (eV)	$\epsilon_{\infty\perp}$	$\frac{\partial \ln n_\perp}{\partial P}$ (10^{-3} GPa^{-1})	$\frac{\partial(\epsilon_{\infty\perp} - 1)}{\partial P} = \chi - \frac{2}{E_{0\perp}} \frac{\partial E_{0\perp}}{\partial P}$ (10^{-3} GPa^{-1})
GaSe	12.27	4.842	7.418	10	$31 = 34.9 - 3.9$
GaS	12.84	5.58	6.31	9	$20 = 33 - 13$

TABLE II. van Vechten model parameters for GaS, for polarization parallel to the c axis, experimental pressure coefficient of the refractive index, and pressure coefficient of the electronic low-frequency dielectric constant, decomposed according to Eq. (5) for $E = 0$.

	E_P (eV)	E_0 (eV)	$\epsilon_{\infty\parallel}$	$\dfrac{\partial \ln n_\parallel}{\partial P}$ $(10^{-3}$ GPa$^{-1})$	$\dfrac{\partial(\epsilon_{\infty\parallel}-1)}{\partial P} = \chi - \dfrac{2}{E_{0\parallel}}\dfrac{\partial E_{0\parallel}}{\partial P}$ $(10^{-3}$ GPa$^{-1})$
GaS	11.8	5.95	4.95	36	$84 = 33 + 51$

Refs. 14 and 15, showing that, for both materials, an increase of the Penn gap must be assumed in order to account for the experimental pressure coefficient of the refractive index. It means that, in layered III-VI semiconductors, the increase of the electronic dielectric constant perpendicular to the c axis is due to the large value of the volume compressibility at low pressure, the electronic polarizability having a negative pressure coefficient like in III-V semiconductors.[1]

As regards the refractive index parallel to the c axis, Polian and co-workers[16,17] have measured the refractive index difference $(n_\perp - n_\parallel)$ in GaS as a function of pressure, through Brillouin effect experiments at $\lambda = 657.1$ nm, yielding $\partial(n_\perp - n_\parallel)/\partial P = -58 \times 10^{-3}$ GPa^{-1}. From this result, along with those of Rannou,[15] one can obtain the pressure coefficient of the refractive index parallel to the c axis, $\partial(\ln n_\parallel)/\partial P = 36 \times 10^{-3}$ GPa^{-1}. According to results of Ref. 7, the dispersion of $n_\parallel$ in the visible region cannot be described through a simple van Vechten model, due to the presence of an allowed direct transition at 3.1 eV. Nevertheless, if one fits the experimental results of Ref. 7 to a model with two gaps (one in the ultraviolet and the other at 3.1 eV), the contribution of the lower-energy transition to the electronic dielectric constant turns out to be lower than 5% and can be neglected. Then we use Eqs. (4) and (5) (for polarization parallel to the c axis) to calculate the electronic contribution to the pressure coefficient of $\epsilon_\parallel$. Table II summarizes the results of this calculation. In that case, the compressibility contribution is not enough to account for the large increase of the electronic dielectric constant and the Penn gap for polarization parallel to the c axis must be assumed to shift to lower energies with a pressure coefficient $\partial E_0/\partial P = -0.152$ eV GPa^{-1}.

With this result, and our experimental result of the previous section, Eq. (3) yields $\partial(\ln\epsilon_{l\parallel})/\partial P = (200\pm50)\times10^{-3}$ GPa^{-1}. This result is also to be compared to those of Samara[1] for III-V semiconductors, in which that pressure coefficient is negative and the largest absolute value occurs for GaAs, $\partial(\ln\epsilon_{l\parallel})/\partial P = -40 \times 10^{-3}$ GPa^{-1}.

In order to give account of that result, let us decompose this pressure coefficient in each of its contributions: The lattice contribution to the dielectric constant can be written

$$\epsilon_{l\parallel} = \frac{N e_{T\parallel}^{*2}}{M\omega_{TO\parallel}^2} , \qquad (6)$$

where N is the number of unit cells per unit volume, $e_{T\parallel}^*$ is the transverse dynamic effective charge, M is the reduced mass of the polar mode, and $\omega_{TO\parallel}$ is the frequency of the

long wavelength transverse-optical mode. The pressure coefficient is then given by

$$\frac{\partial \ln\epsilon_{l\parallel}}{\partial P} = \chi + 2\frac{\partial \ln e_{T\parallel}^*}{\partial P} - 2\frac{\partial \ln\omega_{TO\parallel}}{\partial P} , \qquad (7)$$

the pressure coefficient of $\omega_{TO\parallel}$ is not known. We can assume it to be close to that of polar modes in GaSe, i.e., 20×10^{-3} GPa^{-1}.[4] With that value, the first and third term in the left side of Eq. (7) nearly compensate and the main contribution turns out to be that of the transverse dynamic effective charge, $\partial(\ln e_{T\parallel}^*)/\partial P = (100\pm25)\times10^{-3}$ GPa.$^{-1}$.

Gauthier and co-workers[4,18] have proposed a model in which this large increase of $e_{T\parallel}^*$ in III-VI semiconductors is due to a charge transfer from the Ga-Ga interlayer bond to the interlayer space, as the strength of the interlayer bonds increases under pressure. Along the layers, III-VI semiconductors behave as tetrahedrally coordinated III-VI semiconductors and $e_{T\perp}^*$ has a negative pressure coefficient. In the case of GaSe, the decrease of $e_{T\perp}^*$ has been calculated from the pressure dependence of polar mode frequencies perpendicular to the c axis.[4] These authors have assumed that this decrease is compensated by an equivalent increase of $e_{T\parallel}^*$. With this assumption, they have calculated the pressure coefficient of the low-frequency dielectric constant parallel to the c axis, that turns out to be $\partial(\ln\epsilon_\parallel)/\partial P = 90\times10^{-3}$ GPa^{-1}.[4] Given the similarity between GaSe and GaS, this interpretation is fully compatible with our results.

V. CONCLUSION

From capacitance measurements under hydrostatic pressure, we have shown that the low-frequency dielectric constant of GaS parallel to the c axis strongly increases under pressure. By subtracting the electronic contribution, we have calculated the pressure coefficient of the lattice contribution and have shown that its large positive value can be accounted for by the increase of the transverse dynamic effective charge parallel to the c axis.

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[1]G. A. Samara, Phys. Rev. B **27**, 3494 (1983).

[2]I. V. Aleksandrov, A. F. Goncharov, S. M. Stishov, and E. V. Yakovenko, Pis'ma Zh. Eksp. Teor. Fiz. **50**, 116 (1989) [JETP Lett. **50**, 127 (1989)].

[3]D. Olego, M. Cardona, and P. Vogl, Phys. Rev. B **40**, 3878 (1982).

[4]M. Gauthier, A. Polian, J. M. Besson, and A. Chevy, Phys. Rev. B **40**, 3837 (1989).

[5]A. Goñi, A. Cantarero, U. Schwarz, K. Syassen, and A. Chevy, Phys. Rev. B **45**, 4221 (1992).

[6]A. Khun, A. Chevy, and R. Chevalier, Acta Crystallogr. Sec. B **32**, 983 (1976).

[7]T. A. McMath and J. C. Irwin, Phys. Status Solidi A **38**, 731 (1976).

[8]R. Le Toullec and J. C. Chervin (unpublished).

[9]A. Polian, M. Kunc, R. Le Toullec, and R. Forner, *Proceedings of the 14th International Conference of Physics of Semiconductors, Edinburgh, 1978* (Institute of Physics and Physical Society, London, 1979), p. 907.

[10]V. Riede, H. Neumann, H. X. Nguyen, H. Sobotta, and F. Levy, Physica **100B**, 355 (1980).

[11]K. R. Allakhverdiev, S. S. Babaev, E. Yu. Salaev, and M. M. Tagiev, Phys. Status Solidi B **96**, 177 (1979).

[12]A. Polian, M. Grimsditch, M. Fischer, and M. Gatulle, J. Phys. Lett. **43**, L405 (1982).

[13]J. A. van Vechten, Phys. Rev. **182**, 891 (1969).

[14]N. Kuroda, O. Ueno, and Y. Nishina, Phys. Rev. B **35**, 3860 (1987).

[15]I. Rannou, Thèse de Troisième Cycle, Université de Paris VI, 1987.

[16]A. Polian, Thèse d'Etat, Université de Paris VI, 1982.

[17]A. Polian, J. M. Besson, M. Grimsditch, and H. Vogt, Phys. Rev. B **25**, 2767 (1982).

[18]M. Gauthier, High Press. Res. **9**, 330 (1992).