PHYSICAL REVIEW B VOLUME 45, NUMBER 1 1 JANUARY 1992-I

Raman scattering and x-ray-absorption spectroscopy in gallium nitride under high pressure

Piotr Perlin
Physique des Milieux Condensés, Université Pierre et Marie Curie, T 13-E4, 4 place Jussieu, F-75252 Paris CEDEX 05, France and High Pressure Research Center (UNIPRESS), Polish Academy of Sciences (PAN), Sokołowska 29/37, PL-01-142 Warszawa, Poland

Claude Jauberthie-Carillon, Jean Paul Itie, and Alfonso San Miguel
Physique des Milieux Condensés, Université Pierre et Marie Curie, T 13-E4, 4 place Jussieu, F-75252 Paris CEDEX 05, France

Izabella Grzegory
High Pressure Research Center (UNIPRESS), Polish Academy of Sciences (PAN), Sokołowska 29/37, PL-01-142 Warszawa, Poland

Alain Polian
Physique de Milieux Condensés, Université Pierre et Marie Curie, T 13-E4, 4 place Jussieu, F-75252 Paris CEDEX 05, France

(Received 7 June 1991)

Gallium nitride was studied by Raman scattering and x-ray-absorption spectroscopy up to 60 GPa. A high-pressure structural phase transition was observed in gallium nitride at 47 GPa by means of Raman scattering and x-ray-absorption spectroscopy. We also report the direct determination of the bulk modulus B_0 of this compound (245 GPa). Grüneisen parameters of the four observed phonon modes were established. The transition pressure is compared with existing calculations.

I. INTRODUCTION

The properties of the III-V nitrides are important in both electronics and material science. Due to their small lattice constant [a(BN)=3.6 Å, a_{eff}(AlN)=4.37 Å, a_{eff}(GaN)=4.5 Å]; (AlN and GaN crystallize in the wurtzite structure and we defined $a_{\mathrm{eff}}^3=\sqrt{3}a^2c$), they are very hard large-band-gap semiconductors.

They are or could be used as electroluminescent diodes (GaN is a blue emitter), abrasive powder (BN), or substrates for microelectronics (AlN). As already mentioned, the equilibrium structure of GaN at ambient is the wurtzite one ($B4$) with space group $P6_3/mmc$ (C_{6v}^4, $Z=2$) and a fourfold ion coordination. The lattice parameters are $a=3.190$ Å, $c=5.189$ Å, $u=0.377$, $c/a=1.627$, very close to the ideal values $u=0.375$ and $c/a=1.627$.[1] The main problem occurring for the use of these materials is the difficulty in growing large single crystals. The most used technique is the chemical vapor deposition from GaCl and NH_3 resulting in the deposition of GaN, usually on sapphire[2] which unfortunately has neither the same lattice constant nor the same thermal expansion coefficient, giving rise to strains at the interface.

The single crystals used in the present studies were grown at high pressure ($P\sim 1-2$ GPa) and high temperature ($T\sim 1500-1700$ K).[3] The pressure dependence of the properties of GaN have been only scarcely studied. The absorption coefficient has been studied up to 1 GPa (Ref. 4) and the pressure dependence of the high-frequency E_2 mode up to 16 GPa.[5]

In the present paper, we report on the structural and vibrational properties of gallium nitride up to 50 GPa. The structural properties were studied by x-ray-absorption spectroscopy and the vibrational ones by Raman scattering.

II. EXPERIMENT

A. Crystals and high-pressure technique

The gallium nitride samples studied were single crystals grown at high pressure and high temperature.[3] They were either hexagonal needles grown parallel to the c axis or platelets whose surface is perpendicular to the c axis. Diameter of grown crystals varies from 50 to 700 μm. Crystals of gallium nitride are either nearly colorless or light yellow.

The diamond anvil cells (DAC) used for pressure generation were either a membrane cell[6] or a classical lever arm Mao-Bell construction.[7] Argon or neon, loaded under high pressure, were used as pressure transmitting media and both of them assured quasihydrostatic conditions up to more than 50 GPa. The pressure was measured by determining the shift of ruby luminescence with the use of the power 5 law.[8]

B. Raman scattering

The 514.5-nm line of an argon laser with a power of 25 mW on the diamond surface was used for Raman scattering and for ruby luminescence measurement. The laser beam was focused on the sample with a spot of about 5 μm. Scattered light was collected and analyzed by means of a Dilor XY spectrometer with a photodiodes array. The accuracy was better than 1 cm^{-1}. All spectra were recorded in the backscattering geometry and at room temperature.

C. X-ray-absorption spectroscopy

The x-ray-absorption spectroscopy experiments (XAS) were performed at the energy dispersive station of the LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique) Orsay, France. The main characteristics of the spectrometer have been described elsewhere.[9,10] It uses an elliptically bent crystal (Si[111] in the present case) as a "polychromator" and a diode array as a position-sensitive detector. With this setup, the white beam may be focused down to 500 μm in the horizontal direction (it is only limited by slits in the vertical plane). In the polychromatic focus point, where the sample is placed, the energy distribution has a high degree of homogeneity. The present experiment was performed at the Ga K edge (10 367 eV). An energy range of 400 eV above the edge was accessible. The transmission spectra were measured through the two diamond anvils, and therefore the dispersive scheme is very well suited.[11,12] The sample was finely grained. Silicon oil was used as a pressure transmitting medium. A stainless-steel gasket with a 200-μm-diam hole and an initial thickness of 40 μm was used.

III. RESULTS AND DISCUSSION

A. Raman scattering

Gallium nitride crystallizes in hexagonal wurtzite structure with four atoms in the unit cell and belongs to the C_{6v} space group. The group theory predicts two A_1, two E_1, two E_2, and two B_1 modes. One A_1 and one E_1 are acoustic vibrations. The E_2 modes are Raman active, the A_1 and the E_1 modes are both Raman and infrared active, and the B_1 mode is silent.[13] There are six Raman-active phonons, from which the A_1(TO), E_1(TO), and the two E_2 have already been observed.[14–16] The wurtzite structure is very similar to the zinc-blende (ZB) structure (in fact, they are similar up to the second-neighbor shell), with two atoms in the unit cell in the ZB and four in the wurtzite. Therefore, the dispersion curves for the wurtzite may be deduced from those of the ZB by folding the Brillouin zone along the Λ ([111]) direction. The low- and high-frequency E_2 modes are then analogous, respectively, to the TA(L) and TO(L) of the ZB structure. The experiments were carried out in the backscattering geometry with the k vector of light perpendicular to the c axis on needles and parallel to it on platelets.

TABLE I. Raman selection rules for the configurations used in the present experiments (the c axis is parallel to the z direction).

Sample	P_i	P_s	Allowed modes
Needle	Y	Y	A_1,E_2
	Y	Z	E_1
	Z	Z	A_1
Platelet	X	X	A_1,E_2
	X	Y	E_2
	Y	Y	A_1,E_2

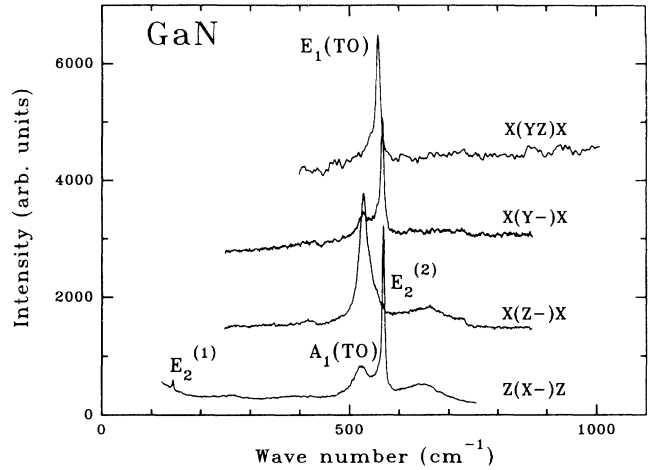

FIG. 1. Raman scattering spectra of GaN at ambient in various geometries.

The selection rules for both configurations are given in Table I.

Figure 1 shows Raman scattering spectra of a needle and a platelet of gallium nitride at ambient pressure for various directions of the polarization of the light. It can be seen that the selection rules listed in Table I are well satisfied. The frequency of all the observed modes is in good agreement with previous observations. Even using high-power laser light and very sensible detection, we were not able to observe the LO modes, in contradiction with a preceding observation.[16] In the high-energy part of spectrum, we can observe a large band with the maximum at 650 cm^{-1}. Polarized measurements prove A_1 character of this band. With no polarization of the light, the four observed modes were followed up to 47 GPa, where the samples suddenly blacken and the Raman signal disappears. The pressure evolution of the Raman

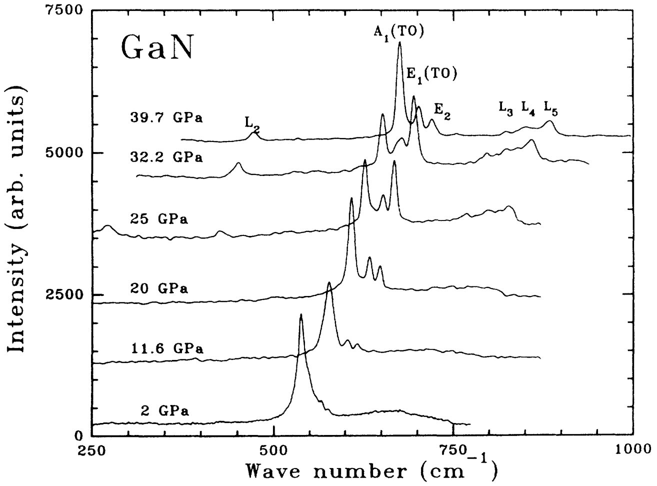

FIG. 2. Raman spectrum of a GaN needle at increasing pressure. L_2–L_5 are lines appearing under pressure (see text). The spectra are shifted upward for clarity,

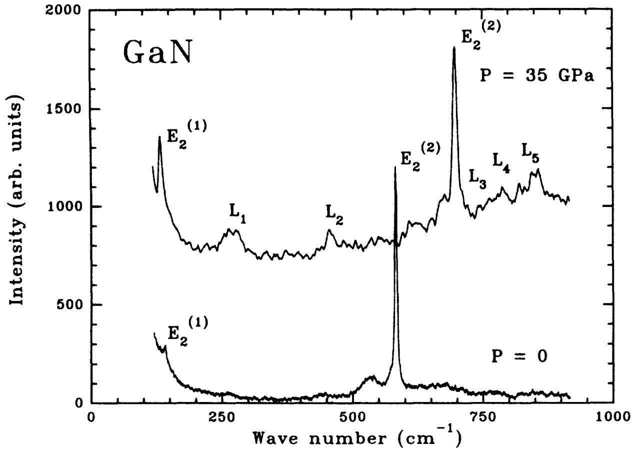

FIG. 3. Raman spectra of a GaN platelet at 0 and 35 GPa.

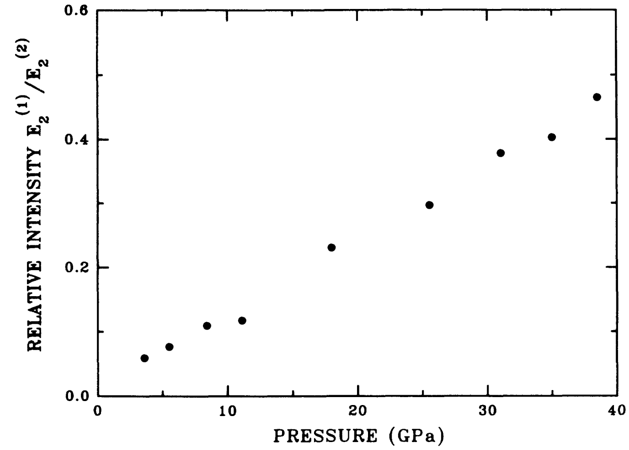

FIG. 5. Intensity ratio of the two E_2 modes as a function of pressure.

spectra of GaN needle and platelet are shown in Figs. 2 and 3, respectively, and the pressure dependence of all observed modes is shown in Fig. 4. The structures described as L_1–L_5 begin to be easily visible at pressure around 25 GPa. The variation of the relative intensity of the two E_2 modes has been determined on a platelet and is shown in Fig. 5. The intensity of the low-frequency mode, $E_2^{(1)}$ increases by 1 order of magnitude, with respect to that of the high frequency $E_2^{(2)}$. Recalling that $E_2^{(1)}$ is analogous to the TA(L) of the zinc-blende structure, this evolution may be well compared to that of the 2 TA(X) in ZnSe (Ref. 17) whose intensity was shown to increase relatively to first-order LO and TO lines.

The pressure dependence of the observed modes (Fig. 4) may be reproduced by the quadratic law

$$\sigma(\mathrm{cm}^{-1})=\sigma_0+\sigma' p+\sigma'' p^2 , \tag{1}$$

where p is in GPa. Table II presents the set of parameters describing all observed modes. Lines L_1–L_5 were fitted by a linear law. γ is the Grüneisen parameter

$$\gamma=\frac{B_0}{\sigma}\frac{d\sigma}{dp} . \tag{2}$$

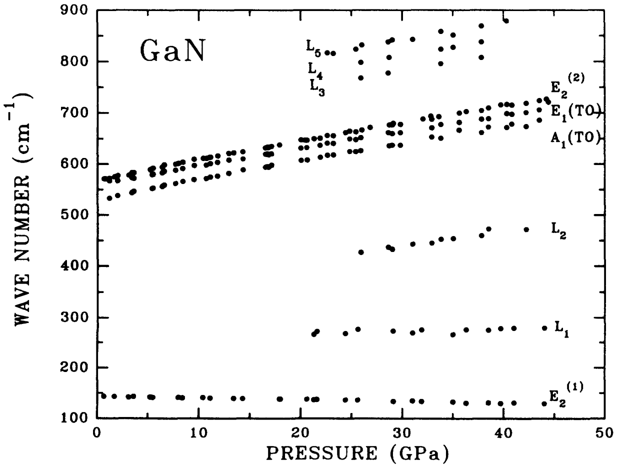

FIG. 4. Pressure dependence of the observed Raman lines.

The values of the Grüneisen parameters of TO and $E_2^{(2)}$ phonons are close to 1.7. This value is typical for the II-VI compounds rather than for III-V compounds, where this value is usually much closer to 1.[18] The pressure coefficient of $E_2^{(2)}$ is in agreement with published data.[5] The Grüneisen parameter of the $E_2^{(1)}$ mode is negative. This uncommon feature of Brillouin-zone center phonons support the analogy between this mode and the edge-of-the-zone TA mode in the zinc-blende structure. The problem of the softening of the TA(L) or TA(X) phonons in the zinc blende was discussed in many papers.[19,20] Similar behavior of the E_2 mode in the wurtzite structure was reported by Mitra *et al.*[21] Following arguments of Weinstein,[19] who found correlation between the Grüneisen parameter of the soft TA modes and the pressure of the phase transition of a given compound, a similar comparison for the $E_2^{(1)}$ mode in the wurtzite structure is possible: the small amount of data only shows that the pressure of transition as a function of the Grüneisen parameter is more than linear.

It is not easy to attribute the L structures to any of the possible multiphonon transition without knowledge of

TABLE II. Fitting parameters used in Eq. (2). γ is the Grüneisen parameter (Eq. 2).

Mode	σ_0	σ'	σ''	γ
A_1 (TO)	531	4.06	−0.0127	1.184
E_1 (TO)	560	3.68	−0.0078	1.609
E_2 (high)	568	4.17	−0.0136	1.798
E_2 (low)	144	−0.25	−0.0017	−0.426
L_1	260	0.40	0	0.377
L_2	339	3.31	0	2.392
L_3	682	3.35	0	1.203
L_4	715	3.21	0	1.100
L_5	732	3.37	0	1.128

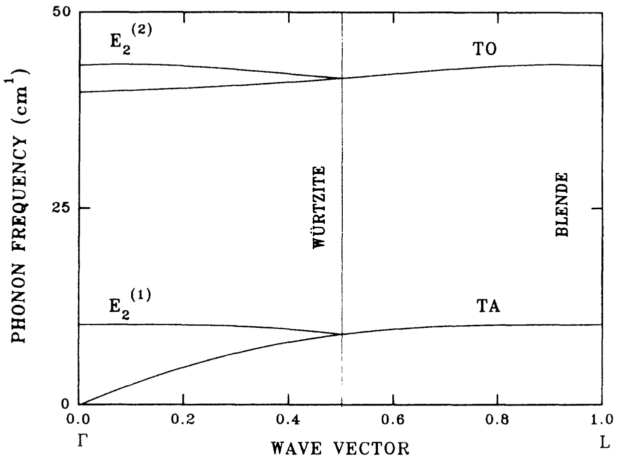

FIG. 6. Correspondence between the Brillouin zone of a zinc-blende and a wurtzite crystal along the [111] direction.

the phonons dispersion curves in this compound. So, we will limit our analysis to the case of the L_1 line, which seems to be the easiest to interpret. The frequency of this line is close to twice the frequency of the $E_2^{(1)}$ mode, and the Grüneisen parameter is unlike other modes close to zero. The simplest assumption is that the L_1 line is related to double-phonon process involving two edges of the Brillouin zone $E_2^{(1)}$ phonons. Having in mind the analogy between the TA(L) (zinc-blende) mode and the $E_2^{(1)}$ (see Fig. 6), we see that the dispersion curve of the $E_2^{(1)}$ phonon has to be flat, and its frequency at the edge of the zone has to be a little smaller than in the zone center. Also, the pressure coefficient of this mode should be very small. All these features are in agreement with observed data. To interpret the other lines, a better knowledge of the lattice dynamics of GaN is necessary.

B. EXAFS

The evolution of extended x-ray-absorption fine-structure (EXAFS) spectra with pressure in the wurtzite phase is shown in Fig. 7. The Fourier transform of the EXAFS oscillations is shown on Fig. 8. The peaks in the Fourier transform are representative of the shells of neighbors. In Fig. 8, the peaks due to the first and second neighbors can be seen, but the main peak corresponds to the second-neighbor shell and therefore the precision obtained in this experiment on the first-neighbor distance is not sufficient, so we will discuss only the second-neighbor distance, i.e., Ga-Ga distance, which is equal to the lattice constant a. The pressure dependence of this parameter is shown in Fig. 9. The pressure dependence of the lattice parameter was fitted by a Murnagham equation:[22]

$$a=a_0\left[1+\frac{B_0'}{B_0}p\right]^{-1/3B_0'} . \qquad (3)$$

Since the precision of the determination of B_0' was not sufficient (±50%), we preferred to impose a value of

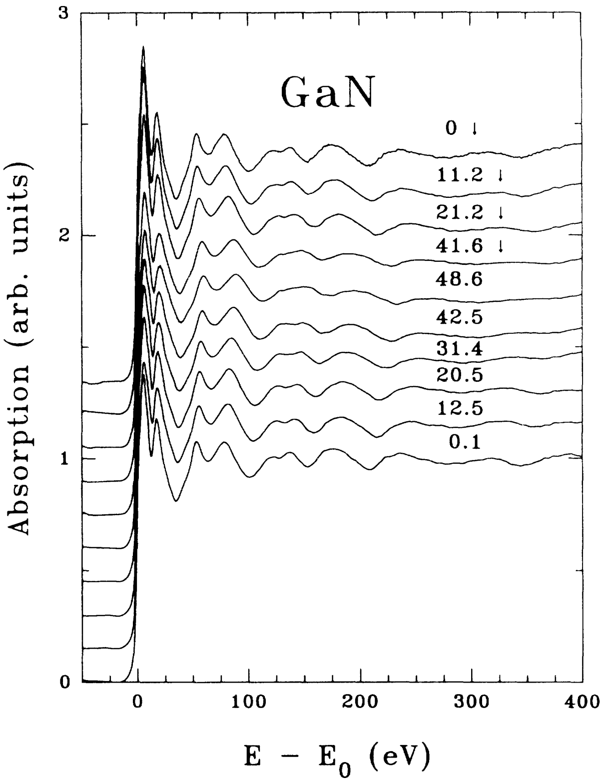

FIG. 7. Absorption spectra of GaN at various pressures in the low-pressure phase. The pressure is increased and then decreased from the bottom to the top.

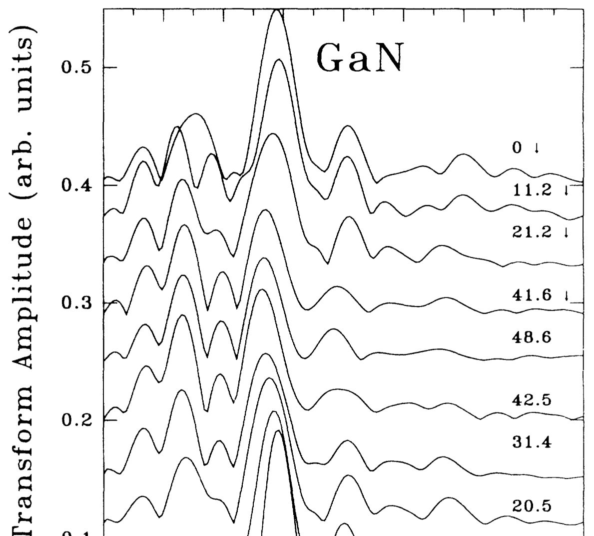

FIG. 8. Fourier transform of the EXAFS oscillations deduced from the spectra shown in Fig. 7. The pressure is increased and then decreased from the bottom to the top.

$B_0'=4$ in agreement with data for BN (Ref. 23) and theoretical prediction of Majewski.[24] The value of the bulk modulus of GaN is deduced from the fit: 245 GPa is somewhat higher than the value calculated on the basis of Van Vechten theory[25] (200 GPa) or obtained from thermal expansion of powdered sample[26] (also 200 GPa).

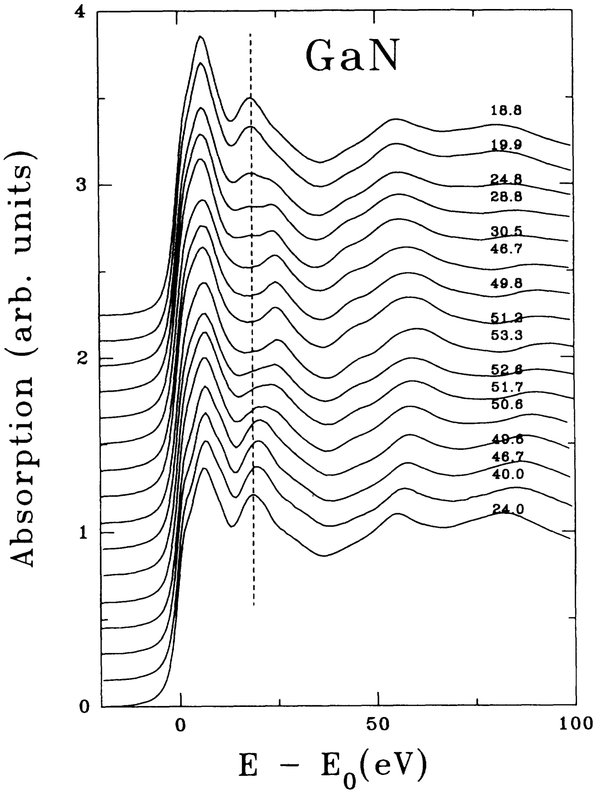

FIG. 10. XANES spectra of GaN at various pressures showing the occurrence of the phase transition around 50 GPa. The signature of the transition lies in the evolution of the first peak above the "white line;" the dotted line is situated at the position of the peak in the low-pressure phase.

C. High-pressure phase transition

When pressurized to 47 GPA, the gallium nitride crystal suddenly blackens and simultaneously the Raman signal disappears. At nearly the same pressure, 48 GPa, there is a sharp decrease of the lattice constant (see Fig. 9). For technical reasons we could not proceed on EXAFS experiment at higher pressures, so only the beginning of the phase transition could be seen. The occurrence of the phase transition was finally observed following the evolution of the XANES (x-ray-absorption near-edge structure) spectra (Fig. 10). XANES represents the part of the XAS spectrum related to the multiscattering of the electron by the number of neighboring atoms, and so is very sensible to local atom arrangement.[27] In Fig. 10, the dotted line is situated on the first peak after the white line in the wurtzite phase. The evolution of this peak with pressure is the signature of the phase transition. It can be seen that the beginning of the phase transition occurs around 50 GPa and the transition is assumed to be complete around 54 GPa. When the pressure is released, the reverse transition begins around 30 GPa and is complete around 20 GPa. It is worth noting here that the XANES spectrum of GaN after a pressure cycle is identical to the initial spectrum, i.e., first the transition is reversible, and second, there is no measurable amorphization. A comparison with other III-V and II-VI compounds shows that, in that sense, GaN is more similar to the II-VI ZnS,[29] ZnSe, or ZnTe (Ref. 30) than to GaAs (Refs. 28 and 31) or GaP.[12] In the II-VI compound, no amorphization was observed, whereas the amorphization of GaP is complete and pressurized GaAs was measured to be 60% amorphous. The reversibility of the transition is confirmed by the reappearance of Raman lines of the wurtzite lattice around 23 GPa, even if these lines are rather broad (Fig. 11). By

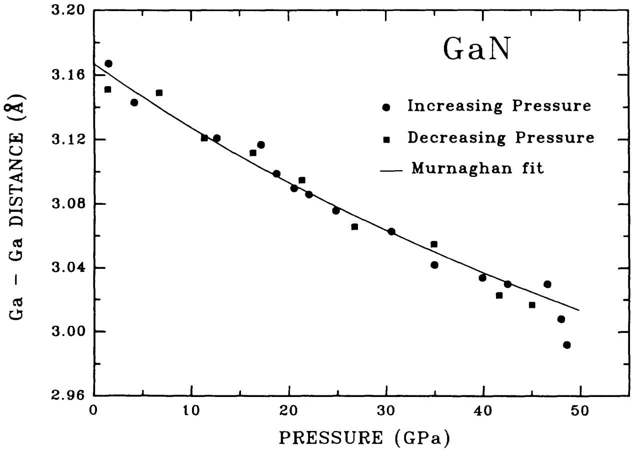

FIG. 9. Pressure dependence of the lattice parameter up to the phase transition. The circles and squares are taken, respectively, at increasing and decreasing pressure; the continuous line is the result of the fit with a Murnaghan equation of state.

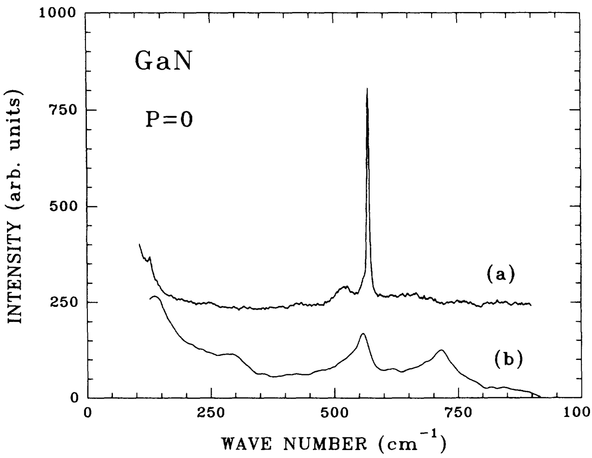

FIG 11. Raman spectra of GaN at ambient conditions. (a) Initial spectrum. (b) Spectrum obtained after a run to 47 GPa.

analogy with a recent result from GaAs,[28] it is possible that these lines are rather related to defect local modes than to be specific to the high-pressure phase. Figure 11 represents the Raman spectra of GaN before and after the phase transition at ambient pressure. We can see that, after the transition, the first-order Raman lines are broadened and have smaller frequency than initially. Appearance of a broad structure in the low- and high-energy regions can be explained, following the arguments of Besson *et al.*,[28] by the suggestion that the effect of the succession of the direct and reverse transition is to transform the original single crystal into nanocrystals. In that case, the actual Raman spectrum is not strictly limited by the law of pseudomomentum conservation, but rather reflects the phonon density of states. Unfortunately, there is no available data about density of states in GaN.

The problem of the structure stability of gallium nitride is seldom considered in the literature. This is due to the nontypical properties of this compound, i.e., short bond length (atomic volume equals 11.4 Å^3: 50% of the atomic volume of GaAs) and relatively high ionicity. In the Philips scale, the ionicity of GaN is 0.5 (Ref. 32) or 0.43 (Ref. 23) and that makes gallium nitride the most ionic from all the III-V compounds. It is known[33] that these two parameters (atomic volume and ionicity) determine, in great part, the character of the phase transition. Almost all discussions of phase transitions of tetrahedrally coordinated compounds consider only the β-tin and NaCl structures as possible high-pressure phases. Although this assumption seems not to be always true [the case of GaAs (Ref. 28)], it is worth seeing if it is possible to predict the value of critical pressure for the transition to one of these structures. In a recent study, Munoz and Kunc[34] have calculated the phase diagram of GaN using the density-functional theory. The calculations of the total energy for various structures (NaCl, NiAs, β-Sn, CsCl) compared with wurtzite show that there should be a phase transition to the rocksalt structure around 55 GPa. Nevertheless, it should be noted that the NiAs phase is very close to the NaCl stability domain, so, within the precision of the calculations, both phases are possible. On the contrary, the β-Sn and the CsCl equations of state lie approximately 1 and 1.2 eV above the NaCl curve, respectively.

IV. CONCLUSION

By Raman scattering and x-ray-absorption spectroscopy, the high-pressure properties of GaN have been studied. The equation of state in the low-pressure phase (wurtzite) deduced from the EXAFS data has been fitted with a Murnaghan equation of state. By fixing B_0' to 4, a value of 245 GPa has been determined for the bulk modulus. A phase transition possibly to a NaCl structure has been found around 48 GPa at increasing pressure, and between 30 and 20 GPa at the downstroke.

ACKNOWLEDGMENTS

Constant interest and very helpful discussions with J. M. Besson and communication of the results of calculations prior to publication by A. Munoz and K. Kunc is acknowledged. Physique des Milieux Condensés is Equipe de Recherche Associée au Centre National de la Recherche Scientifique No. 782.

---

[1] H. Shultz and K. H. Thiemann, Solid State Commun. **23**, 815 (1977).

[2] M. P. Manuska and J. J. Tietjen, Appl. Phys. Lett. **15**, 327 (1969).

[3] S. Porowski, I. Grzegory, and J. Jun, in *High Pressure Chemical Synthesis* (Elsevier Science, Amsterdam, 1989), p. 21.

[4] D. L. Camphausen and G. A. N. Cornell, J. Appl. Phys. **42**, 4438 (1971).

[5] M. I. Eremets, V. V. Struzhkin, A. M. Shirokov, J. Jun, I. Grzegory, and P. Perlin, Acta Physica Pol. A **75**, 875 (1989).

[6] R. Le Toullec, J. P. Pinceaux, and P. Loubeyre, High Pressure Res. **1**, 77 (1988).

[7] H. K. Mao and P. M. Bell, Carnegie Inst. Washington Yearb. **77**, 904 (1978).

[8] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[9] E. Dartyge, C. Depautex, J. M. Dubuisson, A. Fontaine, A. Jucha, and G. Tourillon, Nucl. Instrum. Methods A **246**, 452 (1986).

[10] H. Tolentino, E. Dartyge, A. Fontaine, and G. Tourillon, J. Appl. Cryst. **21**, 15 (1988).

[11] A. Polian, J. P. Itié, E. Dartyge, A. Fontaine, and G. Tourillon, Phys. Rev. B **39**, 3369 (1989).

[12] J. P. Itié, A. Polian, C. Jauberthie-Carillon, E. Dartyge, A. Fontaine, H. Tolentino, and G. Tourillon, Phys. Rev. B **40**, 9709 (1989).

[13] C. A. Argüello, D. L. Rousseau, and S. P. S. Porto, Phys. Rev. **181**, 1351 (1969).

[14] D. D. Manchon, Jr., A. S. Barker, Jr., P. J. Dean, and R. B. Zetterstrom, Solid State Commun. **8**, 1227 (1970).

[15] V. Lemos, C. A. Argüello, and R. C. C. Leite, Solid State Commun. **11**, 1351 (1972).

[16] G. Burns, F. Dacol, J. C. Marinace, and B. A. Scott, Appl. Phys. Lett. **22**, 356 (1973).

[17] G. Weill and J. M. Besson (unpublished).

[18] A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983).

[19] B. A. Weinstein, Solid State Commun. **24**, 595 (1977).

[20] R. Trommer, H. Müller, and M. Cardona, Phys. Rev. B **21**, 4869 (1980).

[21] S. S. Mitra, O. Brafman, W. B. Daniels, and R. K. Crawford, Phys. Rev. **186**, 942 (1969).

[22] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA **30**, 244 (1944).

[23] E. Knittle, R. Wentzkowitch, R. Jeanloz, and M. L. Cohen, Nature **337**, 349 (1989).

[24] J. A. Majewski and P. Vogl, Phys. Rev. B **35**, 9666 (1987).

[25] D. L. Camphausen, G. A. Neville Connell, and W. Paul, Phys. Rev. Lett. **26**, 184 (1971).

[26] V. A. Savastenko and A. U. Sheleg, Phys. Status Solidi A **48**, K135 (1978).

[27] P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid,

Rev. Mod. Phys. **53**, 769 (1981).

[28] J. M. Besson, J. P. Itié, A. Polian, G. Weil, J. L. Mansot, and J. Gonzalez, Phys. Rev. B **44**, 4214 (1991).

[29] J. P. Itié, I. Driques, A. San Miguel, A. Polian, and A. Fontaine (unpublished).

[30] A. San Miguel, J. P. Itié, and A. Polian (unpublished).

[31] Y. K. Vorha, H. Xia, and A. L. Ruoff, Appl. Phys. Lett. **57**, 2666 (1990).

[32] J. A. Van Vechten, Phys. Rev. **182**, 891 (1969).

[33] J. R. Chelikovsky, Phys. Rev. B **35**, 1174 (1987).

[34] A. Munoz and K. Kunc (unpublished).