Bond-bending modes and stability of tetrahedral semiconductors under high pressure: a puzzle of AlN

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Lattice vibrations of the wurtzite-type AlN have been studied by Raman spectroscopy under high pressure up to the structural phase transition at 20 GPa. We have shown that the widely debated bond-bending $E_{2g}$ mode of w-AlN has an abnormal positive pressure shift up to the threshold of the phase transition, whereas in many tetrahedral semiconductors the bond-bending modes soften on compression. This finding disagrees with the results of ab initio calculations, which give a “normal” negative pressure shift. Combination of high dynamical and low thermodynamical stability of AlN breaks the correlation between the mode Gruneisen parameters for the bond-bending modes and the transition pressure, which holds for CdS, InP, ZnO, ZnTe, ZnSe, ZnS, Ge, Si, GaP, GaN, SiC and BeO.

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For the last four decades, a rather curious and at first sight surprising phenomenon of softening of tetrahedral semiconductors under compression has been reported in a number of experimental [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] and theoretical [11, 12, 13, 14, 15, 16, 17, 18] works. Thus, Si, Ge, A$_{IV}$B$_{VI}$ and A$_{II}$B$_{IV}$ semiconductors have pressure-sensitive phonon modes with negative pressure shifts $E_{1u}$, $E_{2u}$, $E_{3u}$, $A_{1g}$ and $E_{2g}$ [19]. Phonon frequency drop, more pronounced for high-Z materials, reaches about 30% at the threshold of the pressure induced phase transitions, when covalent tetrahedral structures lose their stability and transform to more densely packed arrangements.

Earlier, the only known example of a bond-bending mode having a positive, although weak, pressure shift was the “pure bread” bond-bending $E_{2g}$ mode of the low-Z wurtzite-type BeO [14]. This result was being regarded as an exception until recent Raman measurements found a similar behavior for the $E_{2g}$ mode of the wurtzite-type AIN [20]. Ab initio calculations [21] did not catch this feature, giving a “normal” negative pressure shift for the $E_{2g}$ mode of AlN. This discrepancy deserves special attention, since the bond-bending elasticity is one of the most prominent manifestations of directional covalent bonding, and its pressure behavior should be well accounted for. The point to be made here is that AIN represents a complicated case of covalent versus ionic bonding [22]: although its valence charge distribution is highly ionic [23], AlN adopts the tetrahedrally coordinated wurtzite structure under ambient conditions [24]. Aspiring to clarify the question, we have undertaken a complementary high-pressure Raman study of vibrational modes of the wurtzite-type AIN up to its stability limit at about 20 GPa. The pressure dependence of the low-frequency bond-bending $E_{2g}$ mode is traced up to the threshold of the pressure induced phase transition for the first time.

The AlN samples were 20 $\mu$m-thick crystals grown on the sapphire substrate by vapor phase epitaxy. Pressure was produced using the diamond-anvil pressure cell. Compressed helium and methanol-ethanol mixture were used as a pressure-transmitting medium in the first and in the second experimental run, respectively. Pressure was measured in situ by the ruby luminescence technique. The Raman spectra were measured using the THR-1000 triple spectrometer equipped with an OSMA detector (the first run), and the Dilor XY double spectrometer equipped with the CCD detector (the second run). An Ar$^+$ laser ($\lambda = 514.5$ nm) was used as a source of excitation. All spectra were recorded in the backscattering geometry at ambient temperature.

For the hexagonal wurtzite structure with the space group $P6_3$mc ($Z = 2$), a factor-group analysis predicts the following six sets of optical modes at the $k = 0$ [25]:

$$
\Gamma_{op} = A_1 + 2B_1 + E_1 + 2E_2,
$$

where $A_1$, $E_1$ and $E_2$ are Raman active modes, and $B_1$ modes are silent. $A_1$ and $E_1$ are also infrared active, and split into the longitudinal and transverse components (LO and TO). The lowest-frequency $E_2$ mode is a bond-bending mode.

The Raman spectrum of w-AlN has been measured previously under ambient conditions and analyzed in some detail, including the effects of polarization and anisotropy [26, 27, 28]. Our ambient pressure Raman frequencies $\nu_{E_1} = 249$ cm$^{-1}$, $\nu_{A_1,(TO)} = 610$ cm$^{-1}$, $\nu_{E_2} = 657$ cm$^{-1}$, $\nu_{E_1,(TO)} = 669$ cm$^{-1}$, $\nu_{A_1,(LO)} = 890$ cm$^{-1}$, and $\nu_{E_1,(LO)} = 910$ cm$^{-1}$ agree with very reliable data of Ref. [26, 27, 28] within 1%. On increase in pressure, all Raman bands shift continuously to higher phonon energy with no intensity loss to about 18 GPa. Above 18 GPa, the bands weaken and disappear at about 21 GPa in both experimental runs due to the phase transition to the rock salt structure [24, 29]. Representative Raman spectra of w-AlN in the low-energy region as a function of pressure are shown in Fig. 1.
FIG. 1: Raman spectra of AlN as a function of pressure in the low-energy region. The spectral resolution is 0.5 cm$^{-1}$.

FIG. 2: Comparison between the measured and calculated pressure dependence of the Raman frequency for the $E_2^1$ mode. The squares are the first run data, obtained with compressed helium as a pressure transmitting medium. The triangles are the second run data, obtained with ethanol-methanol mixture as a pressure transmitting medium. The solid line 1 is a linear fit of the first run data. The dotted line 2 is guided for the eye. The lines 3 and 4 are calculated dependences obtained in [21] and [20], respectively. The line 5 is the experimental dependence obtained in [20]. All data are shifted along the vertical axis in order to coincide the 1 atm frequencies with the value 249 cm$^{-1}$ obtained in our first experimental run.

Table II compiles the commonly used mode-Gr"uneisen parameters $\gamma_i = -d\ln \nu_i/d\ln V$ obtained for the bond-bending modes $i$ in a series of tetrahedral compounds [33]. Negative value for $\gamma_i$ is observed in each case, except for SiC, BeO and AlN. Although SiC has an essentially zero $\gamma_1$, its quadratic pressure coefficient is negative [31]. Thus, BeO and AlN appear to be the most stable materials with respect to the bond-bending mode on compression.

This bond-bending stability of AlN looks rather surprising, since its wurtzite phase has a rather limited stability range up to 21 GPa. Indeed, experimentally it has been found that the stability of tetrahedral structures with respect to the bond-bending modes correlates with their absolute stability under pressure in such a way that the frequency drop is faster for less stable compounds. Weinstein [4, 6] has discovered that for six diamond and zinc-blende structure semiconductors ZnTe, Ge, Si, ZnSe, 

| Expt. | $E_2^1$ | $A_1$(TO) | $E_2^1$ | $E_1$(TO) | $A_1$(LO) | $E_1$(LO) |
|-------|---------|-----------|---------|-----------|-----------|-----------|
| Run 1 | 0.05(1) | 3.8(2)    | 4.9(2)  | 4.5(1)    | -         | -         |
| Run 2 | 0.05(1) | 4.3(2)    | 4.65(3) | 4.55(6)   | 4.0(1)    | 3.6(7)    |
| Go"ni"a | 0.12(5) | 4.4(1)    | 4.99(3) | 4.55(3)   | -         | 4.61(1)   |
| Calc.  | Gorczyca$^b$ | -0.29    | 4.29    | 4.79      | 4.36      | -         |
|       | Go"ni"a$^a$ | -0.03    | 3.0     | 4.2       | 3.8       | 3.5       | 4.0       |

$^a$Ref. [20]. $^b$Ref. [21].
TABLE II: Mode-Grüneisen parameters for the bond-bending modes.

| Material   | Structure | Bond-bending mode | $\gamma_i$ |
|------------|-----------|-------------------|------------|
| CdS        | wurtzite  | $E_2$             | -2.7\textsuperscript{a} |
| InP        | zinc blende | TA(L)            | -2.0\textsuperscript{a} |
| ZnO        | wurtzite  | $E_2$             | -1.8\textsuperscript{a} |
| GaAs       | zinc blende | TA(L)            | -1.7\textsuperscript{a} |
| ZnTe       | zinc blende | TA(L)            | -1.5\textsuperscript{a} |
| Ge         | diamond   | TA(L)             | -1.52\textsuperscript{b} |
| Si         | diamond   | TA(L)             | -1.3\textsuperscript{c} |
| ZnS        | zinc blende | TA(L)            | -1.8\textsuperscript{a} |
| GaP        | zinc blende | TA(L)            | -0.81\textsuperscript{d} |
| GaN        | wurtzite  | $E_2$             | -0.426\textsuperscript{e} |
| SiC        | hex.(6H)  | $E_2$             | 0.0\textsuperscript{f} |
| BeO        | wurtzite  | $E_2$             | 0.04\textsuperscript{g} |
| AlN        | wurtzite  | $E_2$             | 0.04\textsuperscript{h} |

\textsuperscript{a}Ref. 6.
\textsuperscript{b}Ref. 10.
\textsuperscript{c}Ref. 3.
\textsuperscript{d}Ref. 2.
\textsuperscript{e}Ref. 8.
\textsuperscript{f}Ref. 7.
\textsuperscript{g}Ref. 19.
\textsuperscript{h}This study.

ZnS and GaP there is a remarkable linearity between the mode Grüneisen parameter $\gamma_{TA(X)}$ for the bond-bending TA(X) mode and the transition pressure $P_{tr}$ for these materials. \textit{Ab initio} calculations by Yin and Cohen \textsuperscript{15} have given some insight into the nature of this correlation. They have shown that those individual contributions to the total crystal energy of Si and Ge, which stabilize the bond-bending TA(X) mode, are just the same ones, which preserve the diamond structure from rearrangement to more densely packed structures \textsuperscript{34}. The balance between stabilizing and destabilizing contributions drastically depends on the specific volume, destabilizing contributions becoming stronger under compression.

At present it is possible, following Weinstein and Zallen \textsuperscript{4,6}, to trace the $\gamma_i - P_{tr}$ correlation to much higher pressures, using recent data for w-GaN \textsuperscript{8}, SiC-6H \textsuperscript{7}, \textsuperscript{35} and w-BeO \textsuperscript{36}. The mode Grüneisen parameters determined for the bond-bending TA(L) phonons of InP, GaAs, ZnTe, ZnS, Ge, Si, GaP and for the bond-bending $E_2$ phonons of CdS, ZnO, AlN, GaN, SiC and BeO are plotted in Fig. 3 as a function of the transition pressure $P_{tr}$ ranging to 140 GPa.

Fig. 3 shows that the $\gamma_i$ versus $P_{tr}$ points form a smooth curve deviating from linearity at $P_{tr} > 20$ GPa and approaching to zero at $P_{tr} \approx 100$ GPa. On the basis of this curve one may reasonably expect that materials with $\gamma_i > 0$ should be at least as stable under pressure as SiC does. However, the point for AlN falls far afield from the common curve and tends to continue a linear dependence drawn by high-Z materials.

So, we see that a simple universal correlation between the pretransitional behavior of the bond-bending modes and the stability of tetrahedral semiconductors under high pressure does not exist. To our knowledge, the question why AlN combines a high dynamical and a low thermodynamical stability remains still open, and a detailed microscopic treatment, possibly along the direction indicated by Yin and Cohen \textsuperscript{12}, is required.

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\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{figure3}
  \caption{Correlation between the mode Grüneisen parameter $\gamma_i$ for the bond-bending TA(L) [$E_2$] modes and the transition pressure in a series of tetrahedral semiconductors. Solid and dashed lines are guided for the eye. References are given in Table II and in the text.}
\end{figure}

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[33] The mode-Gruneisen parameters $\gamma_i = -d \ln \nu_i / d \ln V$ are related at zero pressure with the coefficients $\nu_i'$ by the equation $\gamma_i = (B_0 / \nu_0^i) \nu_i'$, where $\nu_i'$ is the mode frequency and $B_0$ is the bulk modulus at ambient pressure.
[34] Namely, the electronic contributions (i.e., the resulting contribution from the electronic kinetic energy, the electron-core interaction energy, the electron-electron Coulomb energy, and the electronic exchange and correlation energy) favor phases with low coordination numbers and stabilize the bond-bending TA(X) mode of the diamond structure, while the core-core Coulomb energy (the Ewald energy) favors phases with high coordination numbers and destabilizes the TA(X) mode.
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