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Pressure-induced transformations of molecular boron hydride

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Abstract

Decaborane, a molecular boron hydride, was compressed to 131 GPa at room temperature to explore possible non-molecular phases in this system and their physical properties. Decaborane changed its colour from transparent yellow to orange/red above 50 GPa and then to black above 100 GPa, suggesting some transformations. Raman scattering and infrared (IR) absorption spectroscopy reveal significant structural changes. Above 100 GPa, B–B skeletal, B–H and B–H–B Raman/IR peaks gradually disappeared, which implies a transformation into a non-molecular phase in which conventional borane-type bonding is lost. The optical band gap of the material at 100 GPa was estimated to be about 1.0 eV.

1. Introduction

Boron hydrides (boranes) are molecular compounds whose structures can be interpreted as fragments of closed boron polyhedra where hydrogen atoms terminate or bridge the boron frameworks (B–H and B–H–B bonds, respectively).

Decaborane (B₁₀H₁₄) is a relatively common borane that forms a molecular crystal at ambient conditions (figure 1) [1, 2]. We have reported its high-*P–T* behaviour up to 35 GPa [3]. Raman spectra of decaborane showed transformation into new phases at 10–35 GPa and above 1000 K and then decomposition to hydrogen and residual boron-rich material at 2500 K.

Some hydrogen-bearing compounds (i.e. hydrogen halides [4] and ice [5, 6]) have been reported to undergo high-pressure transformations to non-molecular phases, and these are possibly accompanied by insulator–metal transitions. In the present study, we explored the behaviour of decaborane up to the 131 GPa using *in situ* optical spectroscopy techniques.

Table 1. Classification of expected fundamental Raman modes [7].

Mode	Number	Frequency (cm ⁻¹)
B–B skeletal bending	3	200–400
B–B skeletal stretching	21	400–1100
B–H bending	20	600–800, 1100–1400
B–H–B bridge	12	1400–2000
B–H stretching	10	2500–2650

2. Experimental details

High-quality, colourless, and transparent crystals of decaborane (purchased from Aldrich Co.), which had flat facets and showed sharp Raman spectra without fluorescence, were selected for the experiments. The decaborane crystals were loaded into diamond anvil cells gasketed with rhenium and compressed to 131 GPa at room temperature. Pressure was measured using the ruby fluorescence method.

Structural changes were observed by Raman scattering and infrared (IR) absorption spectroscopy. The optical band gap of the material was determined from the absorption edge which was calculated from visible transmission spectra.

3. Results and discussion

The decaborane molecule, which has C_{2v} symmetry with 24 atoms, has 66 Raman-active modes, whose rough classification has been reported previously (table 1) [7]. The solid decaborane crystal, which has C_{2h}⁴ (ordered) or C_{2h}¹² (disordered) symmetry with eight molecules in its unit, has 288 Raman-active modes but they have never been identified. Therefore, the present Raman peaks under HP were identified on the basis of molecular Raman-active modes.

In the initial stages of compression, the colourless decaborane changed into a light yellowish form. However, no drastic change was observed in the Raman spectra. With increasing pressure up to 50 GPa, the Raman spectra of decaborane showed peak shifts to higher frequencies without any drastic changes (figure 2).

Above 50 GPa the sample changed colour from transparent yellow to orange/red. As shown in figure 2, the Raman peaks of the B–B skeletal bending/stretching vibrations (below 1100 cm⁻¹) disappeared and a broad peak appeared in the region 800–1200 cm⁻¹, suggesting a change of the skeletal structure of the decaborane molecule. In addition, the B–H–B vibrational peaks shifted discontinuously to lower frequency, which suggests a fundamental change of the B–H–B bridge, one of the unique hydrogen bonding schemes in boranes. However, the character of the remaining of B–H stretching modes indicates the existence of terminal hydrogen atoms in the material, which means that the new phase above 50 GPa is molecular in nature.

Another broad peak also appeared at 2200–2800 cm⁻¹ above 50 GPa. The frequency region, however, overlaps that of the diamond second-order Raman peaks. Moreover, the spectral background becomes higher because of fluorescence from diamond anvils at high pressures of megabars. Therefore, IR spectroscopy was carried out in order to clarify the peak at 2200–2800 cm⁻¹. As shown in figure 3, the IR spectra clearly displayed the existence of the new mode in this frequency region.

Above 100 GPa, the sample became black. The B–B skeletal and B–H–B Raman/IR peaks observed above 50 GPa gradually disappeared (figures 2 and 3). The B–H stretching mode behaved similarly, which implies another transition into a non-molecular phase in which

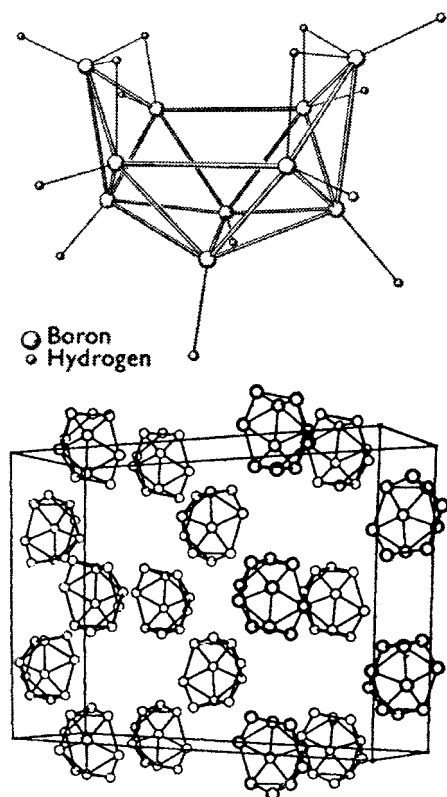


Figure 1. (a) The molecular structure of decaborane (large and small spheres correspond to boron and hydrogen, respectively) and (b) the packing diagram of the unit cell (hydrogen atoms are not included) [1, 2].

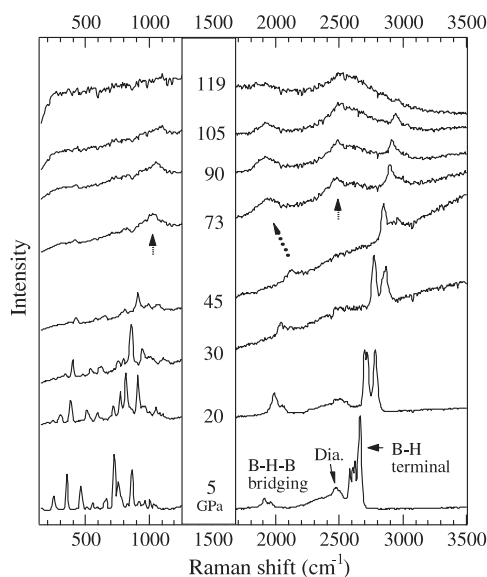


Figure 2. Raman spectra of decaborane at high pressure and room temperature.

conventional borane-type B–H bonding is lost. Peaks in the lower-frequency region (below 1100 cm^{-1}) attributed to lattice vibrations also disappeared.

On the other hand, the broad, new band at $2200\text{--}2800 \text{ cm}^{-1}$ persisted and gradually shifted to higher frequency. In IR spectra the pressure threshold of the transformation is not clear because the IR spectra were obtained from all of the sample area, where a significant pressure distribution exists, while Raman spectra were obtained from a limited area in the centre of the sample. However, the trend of the mode at $2200\text{--}2800 \text{ cm}^{-1}$ is clear in the IR spectra even above 100 GPa.

We wished to examine whether the non-molecular phase above 100 GPa is metallic. The optical band gap of the material, which was estimated from the transmission spectra [5], was decreased with increasing pressure. However, the value of the band gap at 100 GPa was about 1.0 eV, corresponding to a semiconductor. The extrapolation of the pressure dependence of the band gap to higher pressure indicates metallization above 200 GPa (figure 4).

The character of non-molecular borane may be presumed to be intermediate between those of elemental hydrogen and boron. Previous studies have demonstrated that the hydrogen molecule persists to pressures of more than 300 GPa at room temperature (and below), with no sign of metallization under these conditions [8]. On the other hand, Eremets *et al* [9] have reported metallization and superconductivity of elemental boron above 160 GPa, with

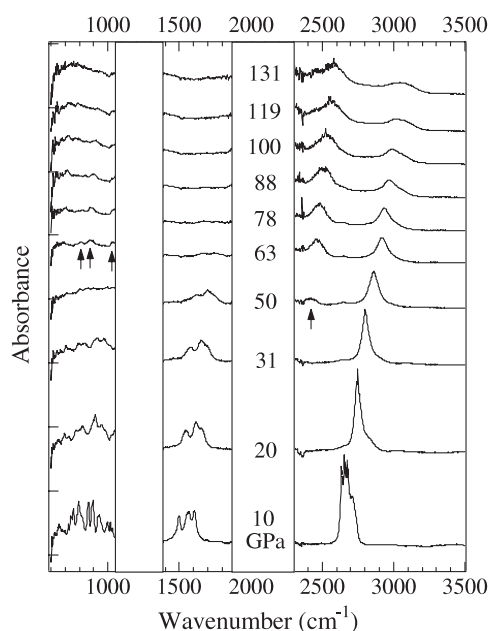


Figure 3. IR spectra of decaborane at high pressures and room temperature.

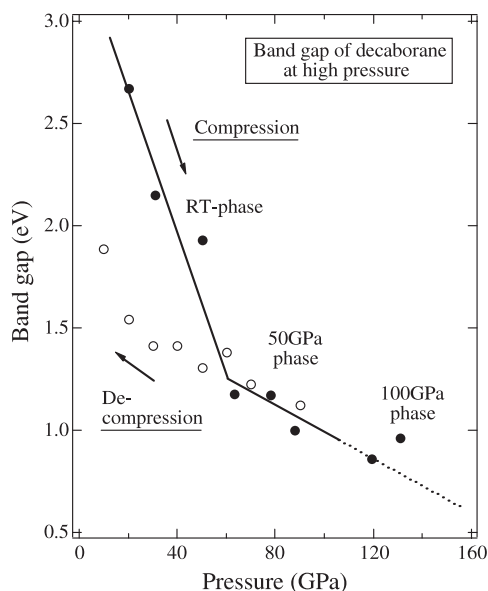


Figure 4. The optical band gap of decaborane at high pressures.

T_c increasing to 11 K at 250 GPa. Thus, the behaviour of possible compounds of boron and hydrogen at these high pressures is of immediate interest.

Acknowledgments

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References

- [1] Kasper J S, Lucht C M and Harker D 1950 *Acta Crystallogr.* **3** 436
- [2] Tippe A and Hamilton W C 1969 *Inorg. Chem.* **8** 464
- [3] Nakano S, Hemley R J, Tschauer O and Mao H-K 2001 *Proc. 8th NIRIM Int. Symp. on Advanced Materials (Tsukuba, Japan)* ed M Akaishi *et al* (Tsukuba: Natl. Inst. Res. Inorg. Mater.) p 49
- [4] Katoh E, Yamawaki H, Fujihisa H, Sakashita M and Aoki K 1999 *Phys. Rev. B* **59** 11 244
- [5] Goncharov A F, Struzhkin V V, Somayazulu M S, Hemley R J and Mao H-K 1996 *Science* **273** 218
- [6] Aoki K, Yamawaki H, Sakashita M and Fujihisa H 1996 *Phys. Rev. B* **54** 15 673
- [7] Keller W E and Johnston H L 1952 *J. Chem. Phys.* **20** 1749
- [8] Mao H K and Hemley R J 1994 *Rev. Mod. Phys.* **66** 671
- [9] Erements M I, Struzhkin V V, Mao H-K and Hemley R J 2001 *Science* **293** 272