Thermal expansion of hexagonal boron nitride

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Hexagonal boron nitride (hBN) is a well known chemically inert, high-melting compound. Its structure is related to that of graphite. Physical and chemical properties of this compound make that it has many applications (for a review of the properties see [1]). The compound distinguishes itself by a strongly anisotropic graphite-like thermal expansion. This behaviour is similar to that of graphite for which the thermal expansion is anisotropic as well [2]. The expansion of hBN in the *a* direction is negative, with the thermal expansion coefficient, TEC, equal -2.9×10^{-6} K^{-1} at 293 K and crossing zero at a high temperature [3]. That in the *c* direction is positive: its absolute value is more than ten times larger, 40.5×10^{-6} K^{-1}, being constant in the range 273-800 K [3]. An equation based mainly on experiments performed at higher pressures [4] indicates somewhat higher absolute TEC values at the room temperature than those given in [3], and an increase of TEC in *c* direction with increasing temperature.

There is a lack of detailed data on thermal expansion at low temperatures. No data on lattice parameters below room temperature could be found in literature. The only existing data on low-temperature expansion [3] include five TEC points experimentally obtained by interferometry (the lowest applied temperature was 82 K). The aim of the present study was a detailed determination of the lattice-parameter values for hBN, in the temperature range from 10 K up to room temperature.

The fine hBN powder studied in the present work was synthesised at Warsaw University of Technology. The measurements were carried out at a powder diffractometer at the B2 beamline. A helium-closed-cycle cryostat with rotating capillary [5] was applied. The instrumental parallel-beam set-up includes a Ge(111) double monochromator, two Soller slits and a NaI scintillation counter. Silicon diode temperature sensor and a PID Controller were used for the temperature control (accuracy of 1 K). The applied wavelength, λ = 1.20720 Å, was determined using least-squares method from five reflection positions of Si NIST 640b diffraction standard (a = 5.43094 Å).

The hBN powder was mounted within a thin-wall capillary of 25 mm length, 1 mm diameter and 0.01 mm wall thickness. The reflection profiles were fitted assuming the gaussian shape. The lattice parameter *a* was determined as an average of values obtained from the positions of 110 and 300 reflections. The lattice parameter *c* was then derived from the *a* value and the position of 114 peak.

The lattice-parameter dependence on temperature is shown in Fig. 1. The obtained room-temperature values are consistent with earlier data. The relative change of *a* and *c* on rising the temperature in the studied range is about -0.06 % and +0.8 %, respectively. The respective increase of the unit cell volume is 0.7 %. The dependencies, especially that for the basal plane where the bonding is of covalent character, are considerably flattened at low temperatures, below about 100 and 50 K, respectively. The property of the lattice parameters to be almost constant at these temperatures illustrates some similarity of hBN to elemental and compound semiconductors which typically exhibit slightly negative thermal expansion at the lowest temperatures. In particular, for the zincblende polymorph of boron nitride, virtually vanishing TEC values have been predicted in [6] (using local density approximation, LDA) to occur in the low temperature range.

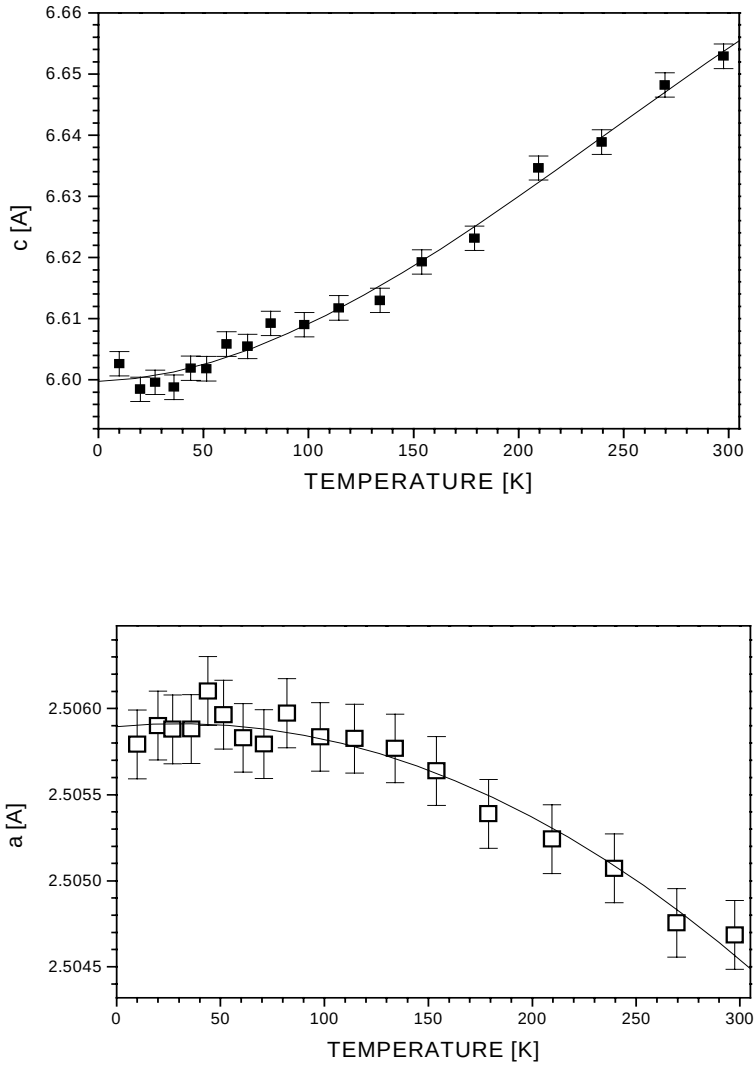

Figure 1: Dependence of lattice parameters, *a* and *c*, on temperature for hexagonal boron nitride (empty squares). The solid lines are a guide to eyes obtained by fitting the experimental powder-diffraction data for *a* and *c* parameters using polynomials of second and third order, respectively.

References

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