Forbidden fivefold symmetry in boron nitride

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A study of the structural changes in boron nitride after neutron bombardment in a fission reactor has revealed the formation of a new crystalline phase. The morphology of the crystallites which form is a five-point star. The diffraction pattern also exhibits a fivefold symmetry.

Pyrolytic boron nitride produced by gas-phase deposition is a highly dispersed textured polycrystalline material with a hexagonal graphite-like lattice. The crystallites, of anisotropic structure, "repeat" the lattice and are thin disks, 5–10 nm thick, or hexahedral prisms with a dimension of 100–300 nm along the α direction. The crystallites are packed with an axial texture axis which coincides with the direction of the gas-phase deposition and the c axis of most of the crystallites.[1] Four polytropic states of BN are known, with sphalerite, wurtzite, rhombohedral, and graphite-like lattices. The stacking faults, which were studied in detail in Ref. 2, play a major role in the transition from a lattice of lower density to one of higher density. Star-shaped crystallites have not been observed previously in boron nitride in any of the phase states or during phase transitions.

In a study of the structural changes in pyrolytic boron nitride after irradiation in a fission reactor (at a thermal-neutron flux of 1.34×10^{20} cm^{-2}) we have observed the formation of crystallites in the form of a five-point star. We studied the material by transmission electron diffraction microscopy (with an electron energy of 125 keV). Samples were prepared for this microscopy by cleavage perpendicular to the texture axis; the electron beam was directed along this axis.

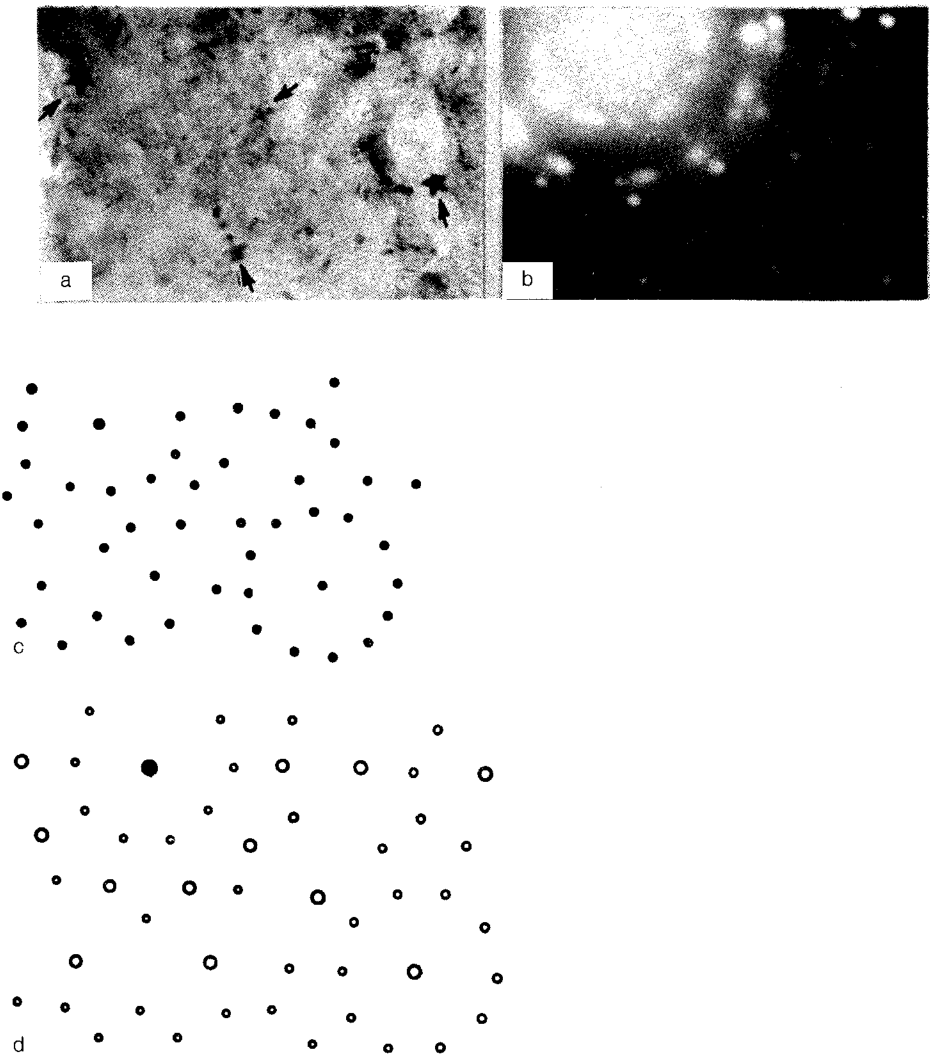

FIG. 1. a—Electron micrograph of the structure of boron nitride (37 000×; bright field; the arrows show star-shaped particles); b—electron microscope diffraction pattern from part of a cleaved section containing the particle which was analyzed; c—schematic diagram of the reflections belonging to the star-shaped particle; d—schematic diagram of an electron diffraction pattern constructed theoretically for a phase which has a fivefold symmetry axis. The sizes of the circles here reflect the relative intensities of the reflections.[3]

The dimensions of the star-shaped crystallites (the distance from the center of a prong to its tip) are 15–20 nm [Fig. 1(a)]. The morphology is a regular five-point star, whose plane is always perpendicular to the texture axis and, correspondingly, the lattice *c* axis. The surface area occupied by the crystallites on the cleaved section is on the order of 1% of the total area. The star-shaped crystallites usually form at the boundaries of prismatic crystallites of the BN matrix. On the electron microscope diffraction patterns from a region of the material containing a particle [Fig. 1(b)], reflections of the matrix are present because of the small size of the particle.

Against the background of the annular reflections of hexagonal BN, we see on these diffraction patterns some Bragg peaks which cannot be assigned to any of the allowed crystal lattice symmetries. In order to identify these reflections, we compared this diffraction pattern with that of the BN matrix, which we obtained in a region which did not contain quasicrystallites. The results of this analysis are shown in Fig. 1(c). A comparison of a schematic diagram of the reflections belonging to the star-shaped particle with the electron diffraction pattern of the crystal lattice of the rapidly cooled alloy Al_6Mn, which has the forbidden fivefold symmetry,[3] reveals that they are approximately the same [Fig. 1(d)]. The differences in the reflections in Figs. 1(c) and 1(d) may stem from both the low quality of our electron diffraction patterns (because the crystallites are small, and errors are introduced during the subtraction of the reflections of the matrix) and the differences between the Al_6Mn and BN lattices. Nevertheless, a fivefold symmetry is the best choice for the star-shaped crystallites.

Schechtman *et al.*[3] and the participants of a debate which their paper started have discussed various possibilities for the existence of this forbidden lattice symmetry, which forms an icosahedral long-range order. Experimentally, however, no one has seen icosahedra. The observed diffraction pattern has been explained either in terms of lattice defects, e.g., a directed multiple twinning of cubic crystals,[4] or particular features of the projection of a six-dimensional crystal lattice.[5] The possibility that this forbidden symmetry would occur was linked in Ref. 6 with an interaction of translational and rotational symmetries.

We know,[2] for example, that graphite-like BN is characterized by several types of stacking faults, which stem from a displacement or rotation of hexagonal networks of molecules with respect to each other. The energy which is released in the course of nuclear reactions, e.g., $^{10}B(n,\alpha)^7Li$, results in the formation of a high concentration of rotational stacking faults. The climb of these faults may lead to the formation of quasicrystallites with the forbidden fivefold symmetry.

[1]K. P. Arefiev *et al.*, Phys. Status Solidi (a) **98**, K27 (1986).

[2]A. V. Kurdyumov and A. N. Pilyankevich, *Phase Transition in Carbon and Boron Nitride*, Nauk. Dumka, Kiev, 1979, p. 188.

[3]D. Shechtman *et al.*, Phys. Rev. Lett. **53**, 1951 (1984).

[4]L. Pauling, Nature **317**, 512 (1985).

[5]P. A. Kalugin, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 119 (1985) [JETP Lett. **41**, 145 (1985)].

[6]G. M. Zaslavskiĭ *et al.*, Usp. Fiz. Nauk **156**, 193 (1988) [Sov. Phys. Usp. **31**, 887 (1988)].

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