JOURNAL OF SOLID STATE CHEMISTRY 1, 150–151 (1970)

The Crystal Structure of the ϕ Phase in the Boron-Sodium System

ROGER NASLAIN† AND JOHN S. KASPER

General Electric Research and Development Center, Schenectady, New York 12301

Received March 24, 1969

The crystal structure of a complex boride, NaB_{15}, has been determined by X-ray diffraction methods using single crystals. The structure consists principally of B_{12} icosahedra arranged in a novel way but with additional boron atoms linking icosahedra together. The sodium atoms occur in large cages that result from the boron arrangement.

Despite much research, the existence of binary alkali borides had been a controversial matter until 1963, when P. Hagenmuller and R. Naslain (*1*) obtained definite evidence with the isolation and characterization of two boron rich sodium borides. One of them, of formula NaB_6, was obtained by the reaction at 1000C, in a sealed tube, of a large excess of sodium with finely divided boron. The other resulted from thermal degradation of NaB_6 at 1000C in an argon atmosphere. This latter phase was designated as ϕ, with the approximate formula NaB_{16}. A later study (*2*, *3*), in which the effects of temperature and vapor pressure of sodium were investigated, allowed a precise definition of the stability ranges for the two phases. Furthermore, this study resulted in the preparation of small single crystals of the ϕ phase which we have used for a full structure determination by X-ray diffraction techniques.

The crystals were prepared at 1200C, at which temperature the equilibrium pressure for Na liq $\rightleftharpoons$ Na vap is 9.5 atm. The chemical composition was $12.6 \pm 0.2\%$ Na; $86.7 + 0.8\%$ B corresponding to the formula $Na_{0.0683}B$. The experimental density was 2.44 g/cm^3.

The Laue and precession photographs, with CuKα and MoKα radiations, defined the symmetry to be orthorhombic with possible space groups Imam(D_{2h}^{28}) or Ima2(C_{2v}^{22}). The lattice parameters were found to be $a = 5.847 \pm 0.005$, $b = 8.415 \pm 0.005$, $c = 10.298 \pm 0.005$ Å.

The number of $Na_{0.0683}B$ units per cell is 60 ± 1, from which it now appears that the most probable formula is NaB_{15} with $z = 4$. The theoretical density for this formulation is 2.426 g/cm^3.

† Permanent address: Service de Chimie Minérale Structurale de la Faculté des Sciences de Bordeaux, associé au CNRS 33, Talence, France.

The intensities for two sets of 306 independent reflections (*hkl* and $\overline{hkl}$) were obtained with the General Electric Company Single Crystal Orienter-Datex Automated System, using CuK$_\alpha$ radiation. The peak height and two background counts were recorded for each reflection.

The approximate structure was obtained readily from the recognition of the similarity in space group and lattice parameters of the ϕ phase to a magnesium–aluminum boride ($a = 10.313$, $b = 8.115$, $c = 5.848$ Å, space group Imam) for which Matkovich and Economy (*4*, 5) have successively attributed the formulae $(MgAl)B_7$ and $MgAlB_{14}$ in two short abstracts. A model for the formulation NaB_{14} and derived from the one proposed by Matkovich and Economy for the magnesium–aluminum boride led after least-squares refinement to an R value of 0.21:

$$R = \frac{\Sigma \| F_o | - | F_c \|}{\Sigma | F_o |} .$$

This model contained B_{12} icosahedra centered at 000, 1/2 1/2 0, 0 0 1/2, 1/2 1/2 1/2, non-icosahedral boron atoms in position (8*h*), *oyz* (with $y = 0.358$, $z = 0.752$), and sodium atoms in 4(*c*), *oy* 3/4 (with $y = 0.344$). The correctness of the model was indicated by the refinement procedure to be approximate, but not complete.

A three-dimensional Fourier synthesis utilizing the signs provided by the trial structure clearly revealed the presence of an additional boron atom in 4(*c*), *oy* 1/4 ($y = 0.25$). Least-squares refinement with the inclusion of the new fifteenth boron atom and with isotropic thermal parameters gave an R value of 0.08 when all 306 measured reflections were used and a value of 0.06 after elimination of all reflections with intensities less than twice the

TABLE I

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR NaB_{15}

Atom	Position	x	y	z	B(Å²)
B_1	16(*j*)	0.2475	0.0364	0.0820	0.89
B_2	16(*j*)	0.1609	0.8343	0.0484	0.81
B_3	8(*h*)	0	0.1529	0.1011	0.98
B_4	8(*h*)	0	−0.0472	0.1641	0.84
B_5	8(*h*)	0	0.3941	0.1450	0.93
B_6	4(*e*)	0	0.2541	1/4	1.57
Na	4(*e*)	0	0.3386	3/4	1.44

standard deviation. A final Fourier synthesis showed no additional significant maxima beyond those corresponding to the 60 boron atoms (all essentially equivalent in electron density) and the four sodium atoms.

The final atomic coordinates and thermal parameters are given in Table I.

The structure of the ϕ phase is characterized by the presence of a boron skeleton constituted principally of B_{12} icosahedra centered at 000, 1/2 1/2 0, 0 0 1/2, 1/2 1/2 1/2 and with a five-fold axis of each icosahedron inclined 13° to the *c* axis in planes parallel to *oyz*. The average intraicosahedral B–B distance is 1.807 Å. The icosahedra are linked either by direct intericosahedral B–B bonds or by intermediary B_5–B_6–B_5 triangles and sodium atoms. The mean length of B–B bonds formed externally by icosahedral boron atoms is 1.746 Å. The B_5–B_6 separation is 1.599 Å and is the shortest distance in the structure; it is essentially the predicted distance for an electron-pair bond and values close to it have been found in various boron and boride structures, as, for example, in the tetragonal *I* structure for the special boron atom (*6*). It would appear that the coordination of atoms B_5 and B_6 is four, but additional weaker bonding may be present since distances of 2.08 and 2.16 Å also occur. These distances are only somewhat larger than those found for the three-center bonding (2.02 Å) in α-boron (*7*).

Sodium occupies the center of a cage formed by 16 boron atoms with full occupancy of sites 4(*c*)-an occupancy factor of 0.998 was determined from least-squares refinement. There are two groups of B–Na distances, one with an average value of 2.798 Å; the other with a mean value of 2.551 Å. The presence of the somewhat short B–Na distances, suggests that sodium bonding to boron is important to the stabilization of the structure.

The formula NaB_{15}, resulting from this structural study, confirms the results of the chemical analysis. A convenient formulation to indicate the number of boron atoms in the basic icosahedral framework is NaB_3B_{12}.

Acknowledgments

We are grateful to J. Etourneau for his collaboration in the chemical study, to L. H. Vogt, Jr. for his advice and assistance with computer programs and to R. E. Hughes for calling to our attention the similarity in structural parameters for the ϕ phase and the magnesium–aluminum boride.

References

1. P. HAGENMULLER AND R. NASLAIN, *Compt. Rend.* **257**, 1294 (1963).
2. P. HAGENMULLER, R. NASLAIN, M. POUCHARD, AND C. CROS, International Symposium on the Alkali Metals, Nottingham (1966). The Chemical Society, SP No. 22, Burlington House, London (1967).
3. R. NASLAIN, Thesis, No. 188, Bordeaux, 1967.
4. V. I. MATKOVICH AND J. ECONOMY, *Abstract* **E12**, *Am. Cryst. Assoc.* Winter Meeting, Atlanta (1967).
5. V. I. MATKOVICH AND J. ECONOMY, *Abstract* **I1**, *Am. Cryst. Assoc.* Summer Meeting, Buffalo (1968).
6. J. L. HOARD, R. E. HUGHES, AND D. E. SANDS, *J. Am. Chem. Soc.* **80**, 4507 (1958).
7. B. F. DECKER AND J. S. KASPER, *Acta Cryst.* **12**, 503 (1959).