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The structure of tetragonal $(B_{12})_4B_2Ti_{1.3-2.0}$. By LINUS PAULING, *Linus Pauling Institute of Science and Medicine, 2700 Sand Hill Road, Menlo Park, California 94025, U.S.A.*

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It is pointed out that the reported values of interatomic distances in the tetragonal crystal investigated by Amberger & Polborn [*Acta Cryst.* (1975), B31, 949–953] are in agreement with the composition $(B_{12})_4B_2Ti_{1.3-2.0}$ and are not in agreement with a structure in which two C atoms are introduced in place of the two nonicosahedral B atoms, as had been suggested by Ploog [*Acta Cryst.* (1976), B32, 981–982].

Amberger & Polborn (1975) investigated tetragonal crystals obtained by the interaction of boron trichloride and titanium tetrachloride at 1150°C, and assigned to them a structure involving B_{12} icosahedra and strings in which Ti atoms and B atoms alternate. It was then suggested by Ploog (1976) that the atoms alternating with the Ti atoms in the strings are not B atoms, but C atoms, picked up by the crystals from the graphite in the apparatus. A principal reason for Ploog's suggestion is that Amberger & Polborn found in a difference Fourier series a value for the electron density in this position somewhat larger than that expected for B. Amberger & Polborn (1976) have replied that the crystals studied by them were taken from a carbon-free region of the boride deposit, and that there are other reasons for concluding that they have B atoms rather than C atoms in the 2(b) position.

A decision between the two structures can, moreover, be made by consideration of the observed values of the bond lengths. From the bond lengths we calculate the bond numbers of various bonds and, by summing these over an atom, obtain a value for the valence of the atom. If there were no electron transfer, the valence 4 would be found for Ti, 3 for B, and 4 for C. Electron transfer might increase or decrease the valences by as much as one unit, but the valence of C cannot increase, so that for C a value between 3 and 4 is expected.

Values of the bond number n for a bond with fractional bond number are given by the following equation (Pauling, 1947):

$$D(n) = D(1) - 0.60 \text{ \AA} \log n. \quad (1)$$

The value of $D(1)$, the length of a single bond between two atoms A and B , is equal to the sum of their single-bond radii minus the Schomaker–Stevenson correction for difference in electronegativity, which is $0.08 \text{ \AA} (x_A - x_B)^2$:

$$D(1) = R_A + R_B - 0.08 \text{ \AA} (x_A - x_B)^2,$$

in which x_A and x_B are the values of the electronegativity of the two atoms (Pauling, 1960). For Ti the value of x is 1.5, for B 2.0, and for C 2.5. The value of the single-bond radius for Ti, obtained from the observed distance in the metal, is 1.324 Å. That for B, obtained from tetragonal B_{12} , is 0.79 Å, and that for C, obtained from diamond, is 0.722 Å.

The atom in position 2(b) has four B neighbors at a distance of 1.670 Å and two Ti neighbors at 2.536 Å. If C atoms occupy the position 2(b), the bond number for the four C–B bonds is 0.57 and that for the two C–Ti bonds is 0.14, leading to the valence 2.56 for C. This value is far too small to be acceptable. Accordingly, if the bond lengths are correct the atoms in position 2(b) are not C atoms.

With B in 2(b) the four B–B bonds have bond number 0.71 and the two B–Ti bonds have bond number 0.17, corresponding to a valence for B of 3.19. This value is accept-

able. By this criterion, then, the atoms in 2(b) are B atoms.

The reported bond lengths for the bonds formed by the Ti atom are 2.255 for eight neighboring B atoms, 2.502 for four, and 2.536 Å for two. These correspond to bond numbers 0.50, 0.18, and 0.17 respectively, giving a valence for Ti of 5.1 (5.0, to within the experimental error). It seems likely, accordingly, that an electron has been transferred to Ti from the surrounding boron atoms. The direction of this electron transfer corresponds to the electronegativity principle, in that Ti is more electropositive than B, and accordingly some of the negative charge, about 0.3 as given by the difference in electronegativity for the five covalent bonds with partial ionic character, is transferred in the reverse direction, leaving the net charge on Ti about -0.8 (Pauling, 1950).

Apparently there has also been some transfer of an electron to the B atoms in 2(b), if the valence 3.19 can be relied upon.

The other bond lengths are in agreement with these considerations. They correspond to an average valence for the remaining B atoms of about 2.95, with a corresponding resultant electric charge $+0.05$.

Ploog makes the statement that the Ti atoms in the 2(a) positions merely fill interstitial holes, his arguments being based on the available bond orbitals. The argument is not valid, however, inasmuch as the bonds formed by the B orbitals in 2(a) with the four B atoms that surround them at the corners of an oblate tetragonal bisphenoid are not single bonds, each requiring an orbital of each of the bonded B atoms, but are instead fractional bonds, requiring only a fractional orbital. Moreover, it is impossible that Ti atoms should occupy interstitial positions, without forming bonds with the surrounding atoms, because the bond energy is required for stabilizing the crystal. The enthalpy of sublimation of Ti is more than 400 kJ mol^{-1} , corresponding to a Ti–Ti single-bond energy greater than 200 kJ mol^{-1} . The energy of a single bond between Ti and B is greater than the average of the Ti–Ti and B–B single bonds, because of the difference in electronegativity. It is this increase in the bond energy, corresponding to the difference in electronegativity, that causes the crystals containing Ti to be stable relative to pure B and pure Ti (Pauling, 1960).

References

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