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Electron deformation density in titanium diboride chemical bonding in TiB_2

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Abstract

Titanium diboride, TiB_2, crystallizes in the AlB_2-type structure, hexagonal $P6/mmm$. The conventional, free atom crystal structure refinement led to $R = 2.23\%$, and including extinction corrections to $R = 1.58\%$. Multipole refinements with multipoles up to order four (hexadecapole) reduced the R value to 1.21%. Difference density maps revealed charge deficiencies on the boron sites and broadbands of charge accumulations between the boron atoms indicating a graphitic B-delocalization of the boron sp^2 hybrid orbitals.

Keywords: Titanium diboride,TiB_2; Chemical bonding; Electron deformation density

1. Introduction

Condensed boron compounds are next to diamond the hardest materials we know. Most have B_{12} icosahedra as the principal building units, like boron carbide, elementary boron and several aluminum borides, like AlB_{10}, AlB_{12} or C_4AlB_{24}. Important exceptions are cubic boron nitride, c-BN, crystallizing in the zincblende structure, the second hardest material we know, but also titanium diboride (TiB_2). Hardness is always attributed to strong covalent bonding between atoms. To understand bonding and hardness, we are looking for redistribution of electrons of the neutral free atoms with charge accumulation between the atoms. This can be studied by accurate single crystal X-ray diffraction followed by extensive calculations based on HO (high order) structure refinements yielding $(X-X)$ deformation density maps and by multipole refinements.

TiB_2 is especially challenging. TiB_2 is characterized by high stability (melting point 3253 K) and extreme hardness. In agreement with the hexagonal symmetry the hardness is extremely anisotropic. The electric conductivity is metallic [1–3], about five times larger than that of Ti. The conductivity is however isotropic [3]. Because of the unfavorable ratio of Ti with 18 electrons to boron with five electrons this investigation poses some specific difficulties. In addition, the presumable metallic conductivity may lead to a delocalization of the bonding electrons into the conduction band rather than into covalent bonding between the atoms.

The crystal structure of TiB_2 is the C32 type of the AlB_2 structure as shown in Fig. 1 [4]. TiB_2 crystallizes hexagonal in space group $P6/mmm$ characterized by alternating hexagonal layers of metal and boron atoms. The extreme hardness together with the unusual graphite-like structure of the boron sublattice suggests that appreciable directional bonding should be present. The metal atoms Ti are sandwiched between infinite hexagonal sheets of the more electronegative boron atoms. From quantum-chemical calculations by Perkins and Sweeny [1], we expect a charge transfer from Ti to the graphite-like boron layers, which are supposed to develop considerable B bonding.

2. Experimental

Single crystals of TiB_2 were kindly provided by Dr. Feurer and Dr. Constant, Toulouse, France [5]. They were grown by chemical vapor transport. Vapor grown material is quite general not stoichiometric, and the

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crystals used in this investigation had the composition $TiB_{1.89}$ (B/Ti = 1.888 ± 0.021, determined by spectrophotometric methods [5]). The crystal chosen for the diffraction experiments was a hexagonal prism 0.12 mm high and 0.20 mm in diameter. For the experiments we tried to grind the crystal to a sphere. Because of the extreme anisotropic hardness we ended up however with an ellipsoid 200 100 m. Measurements were made with Mo- and Ag-$K\alpha$ radiation in the whole sphere in reciprocal space. Because of absorption (Table 1), only the Ag data were further processed. Out of a total of 3089 measured reflections, 182 unique reflections were obtained. This indicates about a 17-fold overdetermination of each reflection, guaranteeing high data accuracy. The internal R-value, R_{int} was 0.059%. The crystal data, experimental data and parameters are compiled in Table 1.

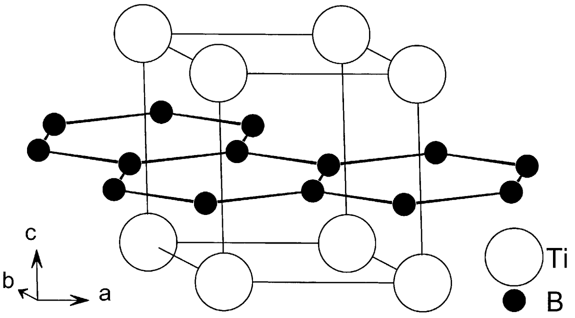

Fig. 1. Crystal structure of TiB_2.

3. Crystal structure refinement and deformation density

Conventional refinement (IAM—independent atom model; on F) of the crystal structure using neutral Hartree–Fock scattering factors with only the scale factor and two thermal parameters u_{11} and u_{33} for each atom resulted in $R = 2.23\%$, weighted $R_w = 2.77\%$ with $w = 1/(\Phi(F_{\text{obs}})^2$. Including correction for isotropic secondary extinction according to the formalism proposed by Becker [6] lowered the R-value to $R = 1.58\%$, $R_w = 1.90\%$ The thermal parameters were (in units × 10^4 Å^2) $u_{11} = 235(4)$, $u_{33} = 153(5)$ for Ti, $u_{11} = 369(16)$, $u_{33} = 332(26)$ for boron (e.s.d. in parenthesis). The anisotropy of the thermal vibration of titanium is noteworthy. The movement perpendicular to the hexagonal network along [001] is considerably less than the one in the hexagonal plane. Ti has more freedom of movement in the hexagonal plane between the boron atoms.

The calculations were then continued with multipole refinements using the "rigid pseudo-atom model" [7,8] to model the atomic deformations. The method has been described in detail by Kirfel et al. [9] for the case of $LiBO_2$ and by Kirfel [10] for $Ca(BO_2)_2$. In such an

Table 1
Crystal data and parameters

Formula	$TiB_{1.89}$	
Crystals	Black	
Crystal size (ellipsoidal, strong anisotropy)	100 m × 200 m	
Crystal system and space group	Hexagonal $P6/mmm$–D^1_{6h}	
Lattice constant (Å)	$a_0 = 3.026(1)$ $c_0 = 3.226(1)$	
C_0/a_0	1.066	
V (Å^3)	25.58	
Atomic positions		
Ti 1 (a)	0 0 0	Point symmetry $6/mmm$
B 2 (d)	$\frac{1}{3}\frac{1}{3}\frac{1}{2}$	Point symmetry $6m2$
Density (g/cm^3)	4.51	
Molecular weight (g/mol)	69.52	
Radiation	Mo-$K\alpha$	Ag-$K\alpha$
Absorption coefficient (cm^{-1})	76.6	38.6
Absorption correction was made by P-scan		
Scanning mode	1–2 1 step scan	
21_{max}	144°	144°
$(\sin\frac{1}{8})_{\text{max}}$	1.34 Å^{-1}	1.70 Å^{-1}
Number of reflections recorded	1730	3089
Independent (unique) reflections	111	182
Number of unobserved reflections	0	0
Internal match R	0.045	0.058
Refinement	IAM (conventional) and multipole	
Weighting scheme	$w = 1/(\Phi(F_{\text{obs}})^2$	
R values	R (IAM) = 1.58%; R_w (IAM) = 1.90% R (multipole) = 1.19%	
GOF (goodness of fit)	1.03	

analysis, the electron density at atom p is described by

$$\Delta_{\mathrm{p}} = \Delta_{\mathrm{p,core}} + d\Delta_{\mathrm{p}} \qquad (1)$$

with $\Delta_{\mathrm{p,core}}$ the spherical part of the charge identical with the charge of the free atom in conventional refinement calculations. A spherical deformation of the density is achieved by adding monopole functions to the titanium and boron atoms. Deformations into bonding to neighboring atoms are described by multipole functions of higher order. The point symmetry of the atoms Ti: $6/mmm$ and boron: $6m2$ allow only few multipoles of higher order [7,8], namely a quadrupole and a hexadecapole for Ti, and a quadrupole, an octapole and a hexadecapole for boron. The calculations showed, that only the quadrupoles contribute significantly to a charge accumulation between the Ti and boron atoms. The final R value was 1.21%. This is an improvement of 23% against the conventional model.

With the parameters from the multipole refinements, Fourier sections were calculated and are shown in Fig. 2. There are considerable charge deficiencies, i.e., negative areas on the boron sites indicating a strong delocalization of the sp^2 hybrid valence electrons. Within the boron layers we find broadbands of positive deformation electron densities, 0.2 el/Å^3 with maximum density of 0.3 el/Å^3. These bands are forming a hexagonal layer system (B bonding) between the boron atoms. As indicated in Fig. 2(b) there is excess charge accumulation between the boron atoms, running along $\frac{1}{2}\frac{1}{2}z$, thus providing connections along the c-axis as required for the hardness. The metal atoms reveal a quadrupole deformation with charge accumulation in the Ti layers. Each Ti atom is surrounded by a positive charge density. A similar bonding behavior in titanium layers was also found in Ti_2O_3 [11]. The vibrational parameters u_{11} and u_{33} are nearly isotropic for boron ($u_{11} = 369$, $u_{33} = 332$), (in units $\times 10^4$ Å^2) for titanium ($u_{11} = 235$, $u_{33} = 153$) they are weak in the plane and strong perpendicular to the planes.

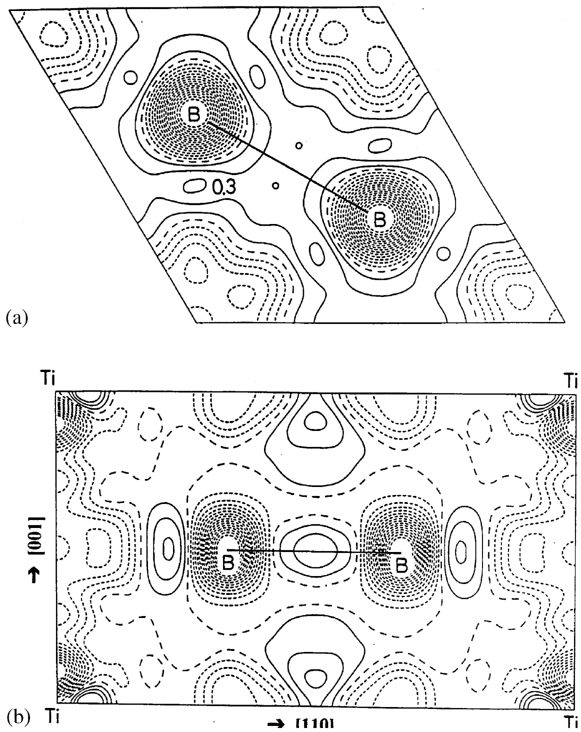

Fig. 2. Dynamic deformation density distribution $X - X_{\mathrm{mult}}$ for TiB_2 in the boron plane at $z = 0.5$ (b) in the (1–10) plane. Contours at 0.1 el/Å^3.

4. Charge integration

Using the method proposed by Sasaki et al. [12], we have calculated the charges of the atoms by spherical charge integration by direct Fourier summation with the structure factors $F(hkl)$. The maximum boron radius is 0.874 Å determined by half the B–B distance. The corresponding sphere contains only 3.6 electrons, a deficit of 1.4 electrons per boron atom. For titanium we find a minimum in the radial electron distribution at $R = 1.24$ Å and calculate 21 electrons in that sphere, indicating Ti^{1+}. With 2.8 electrons missing for the two boron atoms we are in all short of 3.8 electrons, which must be assumed outside the integration areas, i.e., in the conduction band. This finding leads to the following picture:

- A charge transfer from titanium to boron is improbable, i.e., we do not have negatively charged boron atoms.
- The missing electrons are delocalized into the conduction band, in agreement with themetallic behavior of TiB_2.

5. Discussion

The Fourier sections shown in Fig. 2 give detailed deformation electron densities between the atoms, i.e., they show the chemical bonding features. In the hexagonal boron network at $z = 0.5$, we find considerable charge deficiencies on the boron sites and simultaneously broadbands of charge accumulation, ca.0.25 el/Å^3, between the boron atoms. This finding indicates "graphitic" delocalization of the boron sp^2 hybrid orbitals, in agreement with quantum-chemical calculations [1]. The second Fourier section (110) includes again the hexagonal boron plane at $z = 0.5$, with considerable charge accumulation along the c-axis connecting the boron layers at $\frac{1}{2}, \frac{1}{2}, z$, i.e., half way between each pair of boron atoms and thus providing connections along the c-axis between the layers as required for the observed extreme hardness.

No covalent interactions are found either between Ti and boron or between the Ti atoms themselves. This picture is in full agreement with band and cluster calculations by Perkins et al. [1]. They calculated the following bond strengths: B–B in plane = 0.967 (strong), B–B along the z-axis = 0.030 (very weak), Ti–Ti in plane = 0.162, Ti–Ti along z-axis = 0.141, and Ti–B = 0.137 [13]. Qualitatively, we find good agreement between experiment and calculations and a picture of "graphitic" boron layers tied together in the c-direction, while the metal atoms occupy the voids.

Regarding the charge transfer into the conduction bands and the high electric conductivity, the band structure calculations by Perkins et al. [1] give a possible explanation. The most striking feature of these calculations is the close grouping of the metal ($3d$) states in the middle of the energy range. This band grouping is found also in the band structure of metallic titanium and is characteristic of transition metal compounds and metallic conduction [1]. Strong evidence of a "graphitic" like boron layer structure is present over the MK′эM circuit in the Brillouin zone (see Fig. 3 in Ref. [1]), and this is consistent with the AlB_2 band structure and also with the speculative theory by Lipscomb and Britton [14].

6. Conclusion

Following the discussion by Lipscomb and Britton [14] for AlB_2, we find a close similarity between the two compounds. In TiB_2 a charge transfer has to be assumed to the graphite-like two-dimensional network in the ab-plane with a stabilizing effect. The boron orbitals create considerable B-bonding contributions [15]. The extremely high melting point is in part due to the strongly localized Ti–Ti bonding. In general, the picture developed by this electron deformation density study gives a consistent picture for the behavior of the TiB_2 crystals: extreme and anisotropic hardness and high melting point.

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