

Valence electron distribution in zirconium dodecaboride

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First-principles calculations of the valence electron distribution in ZrB_{12} have been performed by the modified Thomas-Fermi statistical method. The charge density maps for some planes across Zr and B atoms are presented and discussed. Directional bonding introduced by boron atoms in the crystal lattice explains the superhardness of the material.

С помощью модифицированного статистического метода Томаса-Ферми выполнены расчеты из первых принципов распределения валентных электронов в ZrB_{12} . Приведены и обсуждаются карты зарядовой плотности некоторых плоскостей, в которых расположены атомы Zr и B. Сверхтвердость материала объясняется ориентированными связями, создаваемыми в кристаллической решетке атомами бора.

The search for new superhard materials is traditionally concentrated on compounds with short bond lengths, i.e., those consisting of light elements B, C, O, and N and having high cohesive energies [1]. An alternative approach is to look for compounds that include heavier elements but have a high coordination number as it was shown, for example, for transition metal nitrides [2]. Besides, recent experimental efforts are partly refocused on those materials that are not extremely hard but are thermally and chemically resistant. This is true, in particular, for intermetallic compounds with high boron content characterized by high abrasion and chemical resistance [3]. Among them, zirconium dodecaboride has recently received much attention since large high-quality single crystals of metallic ZrB_{12} were grown by Paderno *et al.* [4]. It was

found that bulk superconducting properties of the compound are similar to those of simple traditional materials but, in contrast to them, the energy gap is enhanced rather than degraded at the surface, as it would generally be in the case of conventional superconductors [5]. This first direct observation of an enhanced surface superconducting order parameter was explained by Tsindlekht *et al.* [5] as an effect of unique material characteristics of dodecaborides exceeding conventional superconductors due to their outstanding resistance to external mechanical and chemical factors. Direct mechanical experiments [6] on ZrB_{12} single crystals have shown that it is really a superhard (nearly 40 GPa) compound with various potential applications. The aim of this work is to give more insight into the nature of chemical bonding in zirconium do-

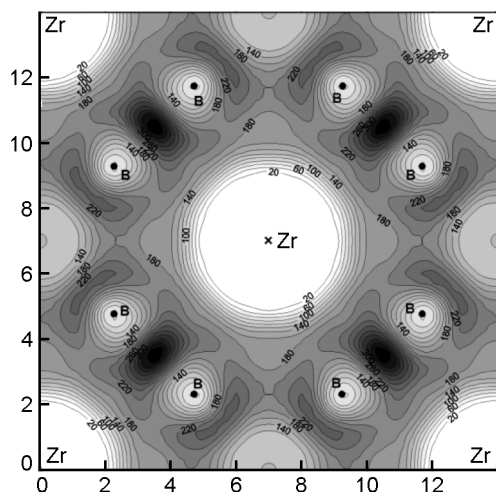


Fig. 1. Electron-density map of the (001) plane through five Zr and eight B atoms. Here and below, the distances are given in atomic units and the charge density values $\rho(r)$ are given in e/cell .

decaboride (and thus its hardness) by calculating the spatial valence electron density distribution using a modified Thomas-Fermi statistical method proposed by I.M.Reznik [7].

Zirconium dodecaboride belongs to the UB_{12} structure type that can be formally represented as a rock-salt structure with cubo-octahedral B_{12} clusters occupying chlorine sites and metal atoms positioned at sodium sites [8, 9]. Its electronic band spectra were calculated by Shein and Ivanovskii [10] within the framework of the self-consistent full-potential linearized muffin-tin orbital method. Those authors have shown that superconducting properties of the compound should be stable against changes in the chemical composition of the system that does correspond to our experience [5]. In what follows, we shall present first-principles self-consistent simulations of the valence electron density in ZrB_{12} that were carried out using a simple and effective theory [7]. The method [7] is based on the concepts of the local density approximation and generalizes the well-known Thomas-Fermi (TF) statistical approach by taking into account small arbitrary additions to a smoothly varying potential in a crystal. The electron density is represented as a series of corrections to the TF result that can be partially summarized. For some compounds investigated before by other authors, it was shown [7] that the data obtained by this method agree well with more refined theoretical calculations and thus it can be re-

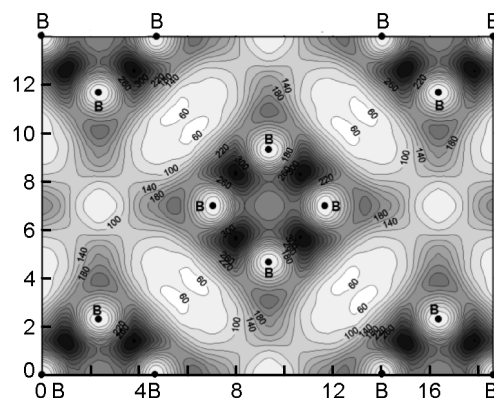


Fig. 2. Electron-density map of a parallel (001) plane through sixteen B atoms.

garded as an effective tool to study chemical bonding effects, especially in compounds with a large number of atoms in unit cell. The initial characteristics required to obtain the valence electron distribution are ionic pseudo-potentials well known in literature and a particular form of the exchange-correlation potential that was approximated according to [11]. The values of the crystal lattice parameters for zirconium dodecaboride with the unit cell containing 52 atoms were taken from the recent study of its crystal structure [12] at $T = 140$ K.

The charge density maps for two (001) planes in ZrB_{12} are presented in Figs. 1 and 2. The first one includes five zirconium and eight boron atoms whereas the second plane (parallel and shifted along the z-axis) incorporates only boron atoms. The profiles reveal that the B-B covalent bond between nearest intra- and intercluster boron atoms holds a considerable amount of charge, while at the center of the boron cluster and in the vicinity of zirconium atoms, the charge drops to quite a low value. The effective charges of Zr and B calculated within Wigner-Seitz cells around the ions the boron atoms. The different character of chemical bonding within boron and zirconium subsystems and between them supports the idea about two totally different contributions to the phonon spectrum: a quasi-Debye background from the boron one and an independent Einstein-like contribution associated with oscillations of Zr atoms [13]. At the same time, an assumption about the nature of a low-lying phonon mode forming a superconducting state in ZrB_{12} (attributed in [13] to vibrations of zirconium ions) should be viewed with caution as it disagrees with our data indicating that the main electron transport in the com-

pound studied should occur within the boron subsystem.

Resuming, using first-principles calculations based on a modified Thomas-Fermi statistical method [7], we have studied the valence electron density distribution in zirconium dodecaboride and shown that electrons are partly drawn away from Zr atoms and injected into the boron subsystem where the main part of the valence charge is confined to a great extent between nearest B atoms, making the bonding covalent. Such a covalent subsystem with short bond lengths, in contrast to ionic compounds with omnidirectional electrostatic interactions, is characterized by high bond-bending force constants. Our calculations show that, according to the classification [14], zirconium dodecaboride belongs to a third class of superhard materials, namely, to partially covalent compounds of transition metals with light elements where the presence of a three-dimensional directional covalent-bonding boron network is responsible for advanced material properties. We hope that our results will stimulate a search of harder conducting materials among other hexa- and dodecaborides.

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За допомогою модифікованого статистичного методу Томаса-Фермі виконано розрахунки з перших принципів розподілу валентних електронів у ZrB_{12} . Наведено та обговорено мапи зарядової густини деяких плоскостей, у яких розташовані атоми Zr та B. Надтвердість матеріалу пояснюється орієнтованими зв'язками, що їх створюють у кристалічній ґратці атоми бору.

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