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PHYSICS

A STUDY OF THERMODYNAMIC PROPERTIES OF TRANSITION METAL DIBORIDES

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Abstract

The diborides are members of a broad class of materials known as the boron-rich solids, which consist of extended networks of covalently bonded boron (B) atoms stabilized through donation of electrons from the metal atoms. Although the structures of the diborides are unique, their physical properties are somewhat similar to those of nitrides and carbides; they are extremely hard and have very high melting points. They are attractive for the same types of applications as super hard, refractory materials, such as in composites and in hard coatings. The proposal presents an overview of some of the important properties of transition metal diborides (TMB2), as these are of interest for fundamental reasons as well as for practical applications.

Keywords: TMB2; AlB2; Physical properties

Introduction

The quest for the nature of interatomic interactions in solids is of paramount importance as it leads to an understanding of their thermodynamical, elastic and numerous other physical properties. The thermodynamical properties either completely dictate the nature of the response of the materials or control the driving force for kinetic steps. Pressure is one of the fundamental thermodynamic variables, which can be varied over a range of more than sixty orders of magnitude, from the vacuum of outer space to pressures in the interior of neutron stars. The exploration of matter at extreme conditions is a central theme in a broad range of scientific disciplines (e.g. material science chemistry, physics, and Earth and planetary science). The application of pressure and temperature can induce both continuous and discontinuous changes in atomic and electronic structure. Learning how atomic and electronic arrangements change under extreme conditions provide insight into the nature of phase transformations, chemical reaction, and also evolution in micro- and nanostructural components, such as crystallite size, dislocations, voids, and grain boundaries. Once these processes are understood, it will be possible to predict responses of materials under thermomechanical extremes using advanced computational tools. Further, this fundamental knowledge will open new avenues for designing and synthesizing materials with unique properties. Using these thermomechanical extremes will allow tuning the atomic structure and the very nature of chemical bonds to produce revolutionary new materials.

The properties study of materials at high pressures and high temperature is always inevitable to extend our present understanding regarding the behaviour of the materials to these external influences as well as for the future technological developments. Research at elevated pressure and temperature provide a new insight into synthesis of materials with properties important for industrial, technical and scientific applications [1]. These include super hard materials, high-temperature superconductors, ferroelectrics, multiferroics, high energy density materials, hydrogen-storage materials, materials for computers and communications, and nano-materials. High-pressure studies provide otherwise unattainable information about the phase diagrams, thermodynamic properties, and electronic structure which can predict directions for search of materials with desirable properties.

Transition metal diborides are of interest for fundamental reasons as well as for practical applications. The diborides are members of a broad class of materials known as the boron-rich solids [2], which consist of extended networks of covalently bonded boron (B) atoms stabilized through donation of electrons from the metal atoms. Most of the metal diborides have the AlB_2 structure in which layers of close-packed metal atoms alternate with planes of B atoms with a graphite-like geometric structure. The B sheets in the diborides of the AlB_2 structure would be isoelectronic with graphite [3] if the bonding involved a full transfer of two electrons to give $M^{2+}B_2^{-2}$. However, the fact that the B–B bond length in the diborides ranges from 1.7 to 1.8A°, values typical of B–B single bonds, immediately suggests that there is an insignificant degree of p bonding between the B atoms. This conclusion is supported by recent electronic structure calculations and other data indicating that the metal–boron bonding is largely covalent in nature [4-6].

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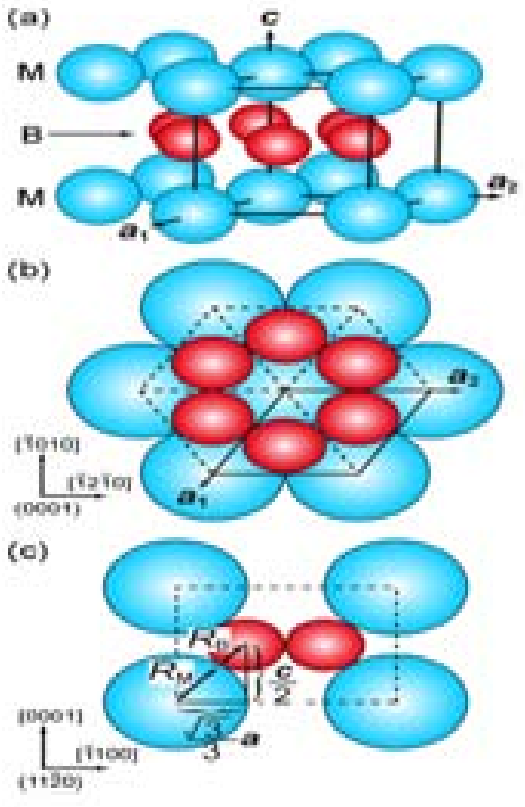
Although the structures of the diborides are unique, their physical properties are somewhat similar to those of nitrides and carbides; they are extremely hard and have very high melting points [7]. The diborides are good electrical conductors with resistivities that are often lower than those of the parent metal. They are attractive for the same types of applications as other hard, refractory materials, such as in composites and in hard coatings Traditional applications of such materials are based on their interesting combination of mechanical and transport properties.

Crystal Structure of Metal Diborides

The hexagonal AlB_2 structure, into which these transition-metal diborides crystallize, is build up of hexagonal nets of pure transition-metal atoms and triangle nets of pure boron atoms, which are alternately stacked along the c-axis, as shown in Fig. 1.

Figure.1. (a) Crystal structure of metal diborides with the hexagonal AlB_2 structure.
The frame indicates a unit cell. Projection of the crystal structure along the
(b) [0 0 0 1] and
(c) [1 1 2 0] directions.



The crystal structure can hence be regarded as a layered structure. If we describe the crystal structure as a packing of touching spheres with RM and RB (radii of M and B atoms), simple geometrical consideration gives the M–M distance (=2RM) as a, the B–B distance (=2RB) as a/3 1/2 and the M–B distance (=RM + RB) as (a2/3 + c2/4)1/2, where a and c denote the lattice constants along the a- and c-axes, respectively. Hence, the ideal c/a axial ratio of 1.0746 (= (4/3)1/4) is deduced together with the ideal atomic size ratio RM/RB = 31/2 = 1.732.

In fact, c/a axial ratios for many transition-metal diborides are close to the ideal value [8] while those for lanthanoid-metal diborides axial ratios indicates that the c/a axial ratios of some diborides formed with, for example, Cr, V, and Ta are a little smaller than the ideal value, while those of other diborides formed with, for example, Hf, Zr, and most of the lanthanoid metals are a little larger than the ideal one, and that diborides formed with Al, Ti, and Nb possess the c/a axial ratios very close to the ideal value. When considering the fact that the crystal structure can be regarded as a layered structure, physical properties are expected to be highly anisotropic and the extent of the anisotropy varies from diboride to diboride, depending on their c/a axial ratios. However, mainly because of the inherent difficulty in growing monocrystals of transition- metal diborides due to their high melting points [8-11], almost nothing is known about how their physical properties vary with crystallographic directions (anisotropy) and how the extent of anisotropy varies from diboride to diboride for most of these transition-metal diborides.

Transition metal diborides

The brief account of some of these diborides is given in the following sections.

TiB_2

TiB_2 is a generic representative of several titanium–boron compounds, because it is the most stable, due to its high hardness, extreme melting point and chemical inertness.TiB_2 is a candidate for a number of applications; it is used for wear parts and in composites with other materials and cutting tools [12,13]. In combination with other primarily oxide ceramics, TiB_2 is used to constitute composite materials in which the presence of the material serves to increase the strength and fracture toughness of the matrix. Both diborides of titanium and niobium, respectively, have excellent properties due essentially to the several unique properties which have the transition metal. The study by Matkovich et al. [14] refers to both of these aspects which are the latest: fundamental scientific and technological such as high melting point, hardness, chemical stability and metallic proper-ties: electric resistivity and thermal conductivity. Many experiments and theories have been extensively studied on these materials. The most frequency for intermetallic binary and ternary compounds, such as transition metal diborides that occur in the AlB_2-

structure type, have been studied in some detail because of their potential application in electronic devices to master different problems as current of electromigration, corrosion and diffusion into the semi-conductor substract.

AlB_2-type (spacegroup P6/mmm) have been studied where TM is a nearly transition metal, B is the Boron element (TM=Sc,Ti,V,Cr,Mn,Y,Zr,Nb,Mo,Hf,Ta) and the recent discovery of superconductivity in MgB_2 at 39K [15,16] has reinforced the scientific importance of AlB_2 type boride [17-19]. More precisely, TiB_2 is a target candidate for the development of light weight high temperature structural materials, since it has the highest melting point and the largest cohesive energy. According to Vajeeston [20] and Burdett et al. [21] who studied the transition metal borides with the AlB_2-structure found that the interaction of the orbitals of the transition metals with those of the planar graphite-like net of the Boron atoms and interaction with those of other metals are both important in influencing the properties of these species. We became interested in this work to study in detail the transition metal diboride which adopts the structure AlB_2. This is due to the great technological interest which they have now especially after the discovery of superconductivity in MgB_2. This discovery opened the door to many researchers of new science to reinforce the traditional and predict new materials with very specific properties.

HfB_2 and TaB_2

Ultra hard materials are used in many applications, from cutting and polishing tools to wear-resistant coatings [22]. Unfortunately, almost all ultra hard materials (diamond, cubic BN, etc.) are expensive because they either occur naturally in limited supplies or have to be made at high-pressure synthetically [23]. Therefore, intense research efforts have been carried out to design ultra hard materials [22,23]. The transition metal-diborides exhibit unique properties such as high-melting points, high-hardness values, and excellent oxidation resistance [22-28]. Therefore, they are promising materials for new heat-resistant, corrosion-resistant, and wear-resistant alloys and coatings [29]. HfB_2 and TaB_2 are member of the large family of transition metal-diborides compounds and they belongs to the hexagonal AlB_2 structure with the space group P6/mmm (space number 191). There are three atoms in the unit cell, all of them on the special positions: X: (0, 0, 0), B: (1/3, 2/3, ½) and B: (2/3, 1/3, ½). A number of theoretical [30-39] and experimental [19–22] studies exists in the literature dealing with structural, elastic, and electronic properties of HfB_2 and TaB_2. Specifically, Shein and Ivanovskii [30] have reported the structural and elastic properties using the full-potential linearized augmented plane-wave (FPLAPW) method with the generalized gradient approximation (GGA) for HfB_2 and TaB_2. Deligoz et al. [31(a)] investigated the structural parameters (the lattice constants and bond length) and phonon dispersion relations in XB2 (X = Hf, Ta) compounds using the first-principles total energy calculations. Systematic trend in lattice constants and heats of formation have been studied for these compounds by Oguchi [31(b)]. Vajeeston et al. [32] have calculated the electronic structure and ground state properties using the self-consistent tight-binding linear muffin-tin orbital (TB-LMTO) method for same compounds. Kaur et al. [33] have studied the cohesive and thermal properties of these compounds using a rigid ion model (RIM). The simulation results of the electronic structures of HfB_2 and TaB_2 have been reported by Ivanovskii et al. [34]. The bonding nature, elastic property and hardness have been investigated by Zhang et al. [35] for HfB_2 using the first-principles total energy plane wave pseudopotential (PW-PP) method and reported that, HfB_2 shows a metallic behavior in P6/mmm structure. The band structure and Fermi surface parameters have been studied by Shein and Ivanovskii [36] using the self-consistent full-potential linearized muffin-tin orbital (FLMTO) method for TaB_2. Rosner and Pickett [37] have performed electronic structure calculations together with resistivity, susceptibility, and specific heat measurements on the TaB2. Their results show that TaB_2 exhibits a metallic character in this structure. Hao et al. [38] have investigated the cohesive energy, heat of formation, elastic constant and electronic band structure of HfB_2 and TaB_2 in the Pmmn space group using the ab initio pseudopotential method. Singh [39] has studied electron–phonon interaction in TaB_2 using full-potential density-functional-based methods. The phonon density of states of TaB_2 have been measured by Heid et al. [40] using the technique of inelastic neutron scattering. Mechanical properties have been measured by Zhang et al. [41] for TaB_2 at 2100^o C. However, the other physical properties of these compounds have received less or none attention. To our knowledge, lattice dynamical and thermodynamical properties, which are the important bulk properties for solids, have not been considered theoretically for these compounds so far.

ZrB_2

The crystal structure of ZrB_2 is designated as AlB_2-type transition metal diborides with the space group symmetry P6/mmm. It is simply a hexagonal lattice in which close packed TM (transition metal) layers are present alternative with graphite- like B layers. Choosing appropriate primitive lattice vectors, the atoms are positioned at TM (0,0,0), B (13, 16, 12), in the unit cell. Traditional applications of such materials are based on their interesting combination of mechanical and transport properties: high melting temperature, high stiffness and hardness, high thermal and electrical conductivities [42]. The knowledge of such basic characteristics as stiffness and thermal

expansion coefficient is obviously important for applications of ZrB_2 as a refractory material, either on its own or as a matrix of a reinforced composite [43].

Naidyuk et al. [44] investigated electron–phonon interaction (EPI) in ZrB_2 by point-contact spectroscopy. Fermi surfaces presented by Shein and Ivanovskii [45] and Rosner et al. [46]. Vajeeston et al. [47] explained the bonding nature with DOS (density of state) and charge density plots. Singh [48] made a theoretical study of EPI in ZrB_2 and TaB_2. Recent advances in GaN optoelectronics have seen ZrB_2 as a promising substrate for epitaxial growth of high quality GaN films [49]. There is very little lattice mismatch between the two materials (0.63%), and their thermal expansion coefficients are also quite similar [42]. The knowledge of elastic and thermal properties of single crystals of ZrB_2 is important for this application. Mahmud et al. [50] and Milman et al. [51(a)] studied the structural, mechanical and elastic behavior, stiffness and thermal expansion coefficient of ZrB_2 by the ab initio density functional method with the gradient- corrected approximation. The structural parameters, elastic constants and thermodynamic properties of ZrB2 under pressure were investigated by using first-principles plane-wave pseudopotential density functional theory within the generalized gradient approximation (GGA) by Hongzhi Fu et al. [51(b)]. It was found that the elastic constants and the Debye temperature of ZrB_2 increase monotonically and the anisotropies weaken with pressure. The compressibility of a single crystal of ZrB_2 was investigated by Pereira et al. [18].

NbB_2

Since the discovery of superconductivity at Tc = 39 K in MgB_2 [15], the physical properties of the group V transition metal diborides with simple hexagonal AlB_2-type structure have attracted significant interest. In particular, the diborides of transition metals observed by Buzea et al [52] are not superconducting except for NbB_2. Hexagonal NbB_2 (space group P6/mmm, a = 3.116 A°, c = 3.264 A° [53]) has been reported to show superconductivity, T_c = 3.87 K [54]. The transition temperature T_c in $Nb_{1-x}B_2$ ($0 < x < 1$) increases to around 9 K, especially in Nb-deficient samples, though NbB_2 did not show superconductivity at T < 1.8 K [55]. A series of studies [56-60] confirmed these results; in particular, the highest Tc ~ 9.8 K was observed in $Nb_{1-x}B_2$ (B/Nb = 2.34) [57]. Due to a great deal of attention on NbB_2, several research groups have investigated the physical properties of NbB_2. Islam et al [61,62] studied the zero-pressure elastic constants and electronic structure of NbB_2 using ab initio density functional theory and found that the superconducting transition temperature decreases under pressure. Using the full-potential linearized augmented plane-wave (FP-LAPW) method, the influence of lattice vacancies on the structural, cohesive, and electronic properties of Nb and Mo diborides were obtained by Shein et al [29]. With the full-potential density-functional based methods, Singh [63(a)] investigated the significant differences in electron–phonon interaction of MgB_2 and NbB_2, which lead to the distinction of their superconducting transition temperatures. The structural parameters, elastic constants and electronic structure of NbB2 under pressure were investigated by using first-principles plane-wave pseudopotential density functional theory within the generalized gradient approximation (GGA) by Xiao-Feng Li et al. [63(b)]. It was found that the elastic constants and the Debye temperature of NbB_2 increases monotonically and the anisotropies weaken with pressure. The band structure and density of states (DOS) of NbB_2 under pressure were also presented. It was concluded that it is the σ hole that determines the superconductivity in NbB_2, and the features of the σ bands are unchanged after applying pressure except for a shift of position. The density of states (DOS) at the Fermi level decreases with increasing pressure, in conjunction with Bardeen–Cooper–Schrieffer (BCS) theory, which can predict T_c decreasing with pressure, in agreement with the trend of the theoretical T_c versus pressure. The electronic structure and structure equilibrium parameters of some AlB_2 type transition metal diborides were calculated by Vajeeston et al [47] using the self-consistent tight-binding linear muffin-tin orbital method. The phonon density of states of transition metal diborides TMB_2 (TM =Ti, V, Ta, Nb, and Y) has been measured using the technique of inelastic neutron scattering [64].

OsB_2

Since the discovery of the superconductivity in MgB_2 with remarkably high temperature T_c = 39 K [15], many structurally related metal diborides TB_2 (T=Ti, Zr, Hf, V, Cr, Nb, Ta, Mo, Os) have been investigated in the quest for superconductivity behavior [36,56,65-68]. As a member of metal diborides, OsB_2 has been reported to be superconductors with T_c = 2.1K early in 1975 [69]. Recently, Chen et al. [70] carried out density functional calculations on structural and electronic properties of OsB_2 using the full potential linearized augmented plane wave plus local orbital method (FPLAPW+lo). Chiodo et al. [71] obtained the electronic structure using the projector augmented-wave (PAW) method. Moreover, Hao et al. [72] investigated the elastic anisotropy of OsB_2 at zero temperature and zero pressure. Hebbache et al. [73] theoretically showed that OsB_2 is a new superhard material and has a metallic character. However, Gou et al. [74] indicated that OsB_2 is an incompressible material, but not a superhard material. Simunek [75] also did not think OsB_2 be a super hard material. The comprehensive analysis of elastic constants can

provide a deeper insight into mechanical behavior and hardness of materials.

VB_2

Vanadium diboride (VB_2) is one of the transition metal diborides with the hexagonal AlB_2 structure, and it has attracted significant attention for a long time. This is mainly due to this compound's special mechanical, chemical and transport properties, such as high melting temperature, high elastic modulus, high chemical stability, good wear resistance, good electrical conductivity and low specific-weight [76-78]. The discovery of superconductivity in MgB_2 at 39K [15] has reinforced the importance of AlB_2-type borides. These characteristics make it a potential candidate for several promising applications. For instance, it has used as cutting tools, high-temperature materials, surface protection materials and wear-resistant components [79]. It is known that vanadium diboride crystallizes in the hexagonal structure with the space group P6/mmm. It is simply a hexagonal lattice in which close packed V-layers are present alternately with graphite-like B-layers. Choosing appropriate primitive lattice vectors, all of atoms on the special position in the unit cell: the vanadium atom at (000) and boron atom at (1/3 2/31/2). The structure is simply defined by two lattice parameters: a and c (a=2.997, c=3.056 [36]). A hexagonal VB_2 crystal has six different elastic coefficients (C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}), but only five of them are independent since $C_{66}= (C_{11}-C_{12})/2$.

Due to a great deal of interest on this compound, several researchers have investigated some of the properties of VB_2. Shein and Ivanovskii [30] studied band structure and the Fermi surface parameters of this compound. Phonon density of states of VB_2 was measured by Heid et al. [40]. Deligoz et al. [80] studied lattice dynamical properties of this compound. And magneto transport properties and the Fermi surface of VB_2 are investigated by Karki et al. [81]. Pereira et al. [18] studied compressibility of AlB_2-type transition metal diborides experimentally. Properties under pressure are important for such a super-hard material and it closely related to the high-technology applications in many fields.

RuB_2

Superhard materials have attracted considerable attention during the recent years due to the importance in fundamental science and technological applications, such as cutting tools, high temperature environments, and hard coating applications. A great effort is currently focused on the synthesis and characterization of superhard materials exhibiting simultaneously very low compressibilities, wide thermodynamic ranges of chemical stability, and high scratch resistance as well as surface durability.

RuB_2 was synthesized and was reported to be an ultra-incompressible material [82]. Recently, Chiodo et al. [83] investigated its mechanical properties and electronic properties. Wang et al. [84] studied the lattice dynamics and superconductivity. Suh et al. [85] investigated the electronic structure by nuclear magnetic resonance (NMR). Hao et al. [86] explored the elastic anisotropy of RuB_2 from first- principles. Ren et al. [87] predicted RuB_2 undergoes a phase transition from the orthorhombic phase to the hexagonal phase from first-principles calculations.

Conclusion

The recent discovery of superconductivity in MgB_2 at 39K has reinforced the scientific importance of AlB_2 type (spacegroupP6/mmm) boride, where TM is an early transition metal and B is the Boron element (TM=Sc,Ti,V,Cr,Mn,Y,Zr,Nb,Mo,Hf,Ta). The above study refers to the fundamental, scientific and technological interest such as high melting point, hardness, chemical stability and metallic properties: electric resistivity and thermal conductivity. Many experiments and theories have been extensively studied on these materials. The most frequency for intermetallic binary and ternary compounds, such as transition metal diborides that occur in the AlB_2-structure type, have been studied in some detail because of their potential application in electronic devices to master different problems as current of electro migration, corrosion and diffusion into the semi-conductor substract.

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