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Magnetic moment collapse induced by high-pressure in semi-borides TM_2B (TM = Fe, Co). A first-principles study

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ABSTRACT

The high-pressure effects are investigated on the structure, magnetic phase transition, and anisotropic elastic properties of the 3d transition-metal semi-borides TM_2B (TM = Fe, Co) by using the generalized gradient approximation (GGA) within the framework of density functional theory (DFT). At equilibrium spin polarization, calculations show that the Fe_2B and Co_2B compounds are ferromagnetic (FM). In the applied pressure range from 0 to 90 GPa, the magnetic moment of Fe_2B and Co_2B slowly decreases and then abruptly drops to zero at 85 GPa, indicating a state transition from the ferromagnetic to the nonmagnetic (NM) state (a first-order quantum phase transition). The collapse of the magnetic moment is accompanied by an abrupt change in the lattice parameters and elastic constants. In addition to this phenomenon, the density of states (DOS), and anisotropic elastic properties are presented at 0 GPa and at the critical transition pressure. Furthermore, I have plotted the three-dimensional (3D) surfaces and planar contours for the Young and bulk moduli of the compounds at several crystallographic planes, ((100) and (001)) to reveal their elastic anisotropy. On the basis of anisotropic elastic properties, I have predicted the easy and hard axes of magnetization for the TM_2B compounds.

1. Introduction

The coating is produced via the process of boriding (or boronizing), which includes the deposition of boron and an additional heat treatment, e.g. in the form of a thermochemical process to form the boride layers [1]. The boriding process offer excellent surface properties such as high hardness, increased wear and corrosion resistance and the stability of mechanical properties at high temperature [2–4]. The transition metal borides stand out due to their considered practical importance and fundamental interest for science, technology and industrial applications. Iron borides(FeB/Fe_2B) in particular, are widely used as hard and protective coatings on steel surfaces for improved wear and corrosion resistance of the material [1,5].

Cobalt boride (CoB /Co_2B) coatings were developed on the surface of a CoCrMo alloy using the powder-pack boriding process at temperatures between 1223 and 1273 K using different exposure times for each temperature [6].

Furthermore, the magneto-structural interaction is an important phenomenon in magnetic practical materials, hence, the magnetism of some borides plays a crucial role for the development of memories for mass storage. An example of this can be found in spintronics which are an integration of magnetic materials, in order to realize nanosized devices with better features.

The presence and nature of unconventional magnetic phases of semi-borides may be clarified by tuning them systematically with the help of an external parameter such as pressure. One can obtain much information on structures from the behavior under pressure. For example, magnetic collapse is a widely observed phenomenon, as a transition from a ferromagnetic state to the nonmagnetic state

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under pressure. This character of magnetic collapse is probably the earliest prediction of what may be named a 'novel' phase of magnetic metals near a quantum phase transition (QPT), which, might a sign of superconducting.

The emergence of superconductivity in the ferromagnetic state with the presence of a strong first-order QPT may be reconciled in a model proposed by Sandeman et al. [7].

The electronic and elastic properties of the semi borides X_2B(X = Cr, Mn, Fe, Co, Ni, Mo, W) compounds have been investigated in detail [8,9]. The interesting phenomenon mentioned in semi-borides motivated Wang et al. [10] to further resolve the complex structures and the corresponding mechanism for the soft phonons of these borides, which would help in the further clarification of the intrinsic strength and hardness, which may predict new crystal phases for superhard materials. However, the anisotropic elastic properties and pressure effect for these compounds have not been presented. Modern experiments can extend the hydrostatic pressure outside 200 GPa [11]. The pressure changes directly the inter-atomic interaction. The itinerancy of the electrons will be changed accordingly.

The improving experimental facilities, encourage the extension of our theoretical work to high pressure, in order to understand, and predict new phenomena.

The motivation behind the study of these systems, is that they are ferromagnetic. My aim was to explore those materials by applying pressure, and when I observed that those materials lose their magnetic moment suddenly at 85 Gpa, I extended the applied pressure to 90 Gpa, to see if the components maintain this loss or not. However, it is obvious that this character is an intrinsic property for those compounds, an abrupt magnetic collapse, that could be a phenomenon of what we call a 'novel' phase of magnetic metals near a quantum phase transition (QPT).

The main phenomena I am going to address is the quantum magnetic phase transition at high pressure and the related effect on the structure, magnetic moment, and anisotropic elastic properties of the semi-boride coating.

They are able to provide much information on the structures concerning the behavior under pressure.

The understanding of transition metal borides as protective coatings on steel surfaces, especially mechanical properties requires a knowledge about their elastic constants and polycrystalline elastic moduli.

Owing to their industrial application, the present work aims to investigate the pressure effects on the structure, magnetic phase transition, and anisotropic elastic properties of the Fe_2B and Co_2B compounds, and the main motivation which encouraged us most is the abrupt collapse magnetically induced by high pressure in the semi borides TM_2B.

Mechanical anisotropies in both cases (FM and NM) are discussed by calculating different anisotropic indexes and factors. I have plotted the three dimensional (3D) surfaces and planar contours of bulk and Young moduli of TM_2B (TM = Fe, Co) compounds at several crystallographic planes, ((100) and (001)) to reveal their elastic anisotropy.

I demonstrate that all previous properties change strongly with increasing pressure.

My hope is that this study will kindle further dialogues, provide useful guidance and motivate other researchers to undertake this huge project in order to give a thorough understanding of the semi borides TM2B compounds.

2. Structural aspects and calculation methods

The crystal structure of the 3d transition-metal semi-borides TM_2B described throughout this paper is isomorphic to the $A1_2Cu$ structure: space group 14/mcm. The tetragonal unit cell contains four molecular units. Fig. 1, shows a projected view of the $A1_2Cu$ structure along (by the left) b, a, and c axes. The boron atoms (small green balls) form a quadratic lattice (view along the c axis), which is repeated with a periodicity at 0, 0, 1/2. The metal transition atoms (large orange balls) form two layers: one at 0, 0, 1/4 (dashed line) and one at 0, 0, 3/4. Each boron atom is therefore surrounded by eight metal transition atoms and two boron atoms. Each transition-metal atom has 11 transition-metal neighbors: three at short and eight at a long range.

Total energy calculations were performed within density functional theory (DFT) [12]. The CASTEP code was used for the whole study, which uses the plane wave expansion method in reciprocal space [13]. The ultra-soft Vanderbilt pseudo-potentials (USPP) were employed to represent the electrostatic interactions between the valence electrons and ionic cores [14], which were used with the following valence electronic configuration's: Fe: $3d^6 4s^2$, Co: $3d^7 4s^2$, and B: $2s^2 2p^1$. The exchange-correlation energy was evaluated with the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerh (PBE) scheme [15]. The kinetic energy cut-off value was selected as 500 eV, which was sufficient to obtain reliable results.

Total energies were evaluated in the first irreducible Brillouin zone (BZ) with the following Monk-horst–Pack grids [16]: (10 × 10 × 10) for all compounds.

The convergence criteria for the total energy and structure optimization were set with fine quality with the energy tolerance of 10^{-6} eV/atom. The Broydene-Fletchere-Goldarbe-Shanno (BFGS) optimization method was performed to obtain the equilibrium crystal structures of TM_2B with the maximum atomic displacement and force set to 0.002 Å and 10^{-4} eV/Å.

The cohesive energy (E_{coh}) of a material, (a useful fundamental property), is a measure of the relative binding forces. The stability of our compounds can be evaluated by calculating two energy parameters, the cohesive energy E_{coh} and the formation energy E_f, defined as follows:

$$E_{coh}(TM_2B) = \frac{E_{total}(TM_2B,\ Cell) - 2nE_{iso}(TM) - nE_{iso}(B)}{n}, \tag{1}$$

$$E_f(TM_2B) = E_{coh}(TM_2B) - 2E_{coh}(TM) - E_{coh}(B). \tag{2}$$

E_{coh} (TM_2B) is the cohesive energy of TM_2B per unit formula; E_f (TM_2B) is its formation energy; E_{coh} *(TM)* is the cohesive energy of