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Electronic structure and elastic properties of $Y_{n+1}Co_{3n+5}B_{2n}$ ($n = 1, 2, 3, \infty$)

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Abstract

We have studied the electronic structure and elastic properties of $Y_{n+1}Co_{3n+5}B_{2n}$ (space group $P6/mmm$), where $n = 1, 2, 3$ and ∞ , using *ab initio* calculations. These ternary borides exhibit a bulk-modulus-to- C_{44} ratio from 1.6 to 1.9, which is rather unusual for ceramics. This may be understood on the basis of the electronic structure: predominantly covalent–ionic YCo_3B_2 layers are interleaved with predominantly metallic YCo_5 layers. Covalent–ionic bonding between B and Co may give rise to a large bulk modulus, while weak coupling between the YCo_3B_2 and YCo_5 layers may be responsible for the low C_{44} value. On the basis of the similarity in electronic structure and elasticity data, it is reasonable to assume that the $Y_{n+1}Co_{3n+5}B_{2n}$ compounds investigated here may exhibit similar properties to the so-called MAX phases (Barsoum 2000 *Prog. Solid State Chem.* **28** 201).

1. Introduction

$Y_{n+1}Co_{3n+5}B_{2n}$ ($n = 1, 2, 3, \infty$) compounds (space group $P6/mmm$) can be synthesized by melting in a high-frequency furnace [1]. These compounds possess interesting ferromagnetic properties due to their high magnetocrystalline anisotropy [1]. For instance, YCo_4B ($n = 1$) exhibits a saturation magnetization of $3.36 \mu_B \text{ fu}^{-1}$ and the Curie temperature of 375 K, based on SQUID and susceptibility measurements [2]. As n increases from 1 to ∞ , the Curie temperature decreases from 375 to 2 K [1]. While the magnetic properties are comparatively well explored, theoretical or experimental investigations of the elastic properties are not discussed in the literature.

Y in $Y_{n+1}Co_{3n+5}B_{2n}$ compounds can be replaced with rare-earth elements (R), for instance Ce [2, 3], Gd [2] and Tb [4]. These phases crystallize with a distinctive structural regularity as a function of n and are derived from RCo_5 by replacing Co with B. Layers of RCo_5 are interleaved with n layers of RCo_3B_2 [1, 4]. For instance, in YCo_4B ($n = 1$) Y occupies 1a

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and 1b Wyckoff positions, Co fills 2c and 6i sites, whereas B occupies 2d positions (see [1] for a more detailed structural description). These compounds are structurally similar to the so-called hexagonal MAX phases, where layers of MX (M = a transition metal from groups IIIB, IVB, VB and VIB, X = C or N) are interleaved with A layers (A = mostly IIIA and IVA elements) [5, 6]. Due to this layered nature, MAX phases exhibit a combination of metallic and ceramic properties [5, 6]. In general, MAX phases can be characterized as good thermal and electrical conductors [7, 8], they are machinable [7], they exhibit high stiffness, high strength at elevated temperatures [7, 9], good thermal shock and oxidation resistance [7, 10–12]. Therefore, it is of fundamental interest to establish whether this property combination is limited to MAX phases or whether it is also applicable to $Y_{n+1}Co_{3n+5}B_{2n}$ compounds.

In this work, we study electronic structure and elastic properties of $Y_{n+1}Co_{3n+5}B_{2n}$ ($n = 1, 2, 3, \infty$) phases using *ab initio* calculations. It is our ambition to establish a correlation between the chemical bonding, bulk modulus and shearing of these ternary borides. These compounds possess a bulk-modulus-to- C_{44} ratio from 1.6 to 1.9, a rather unusual ratio for borides. This may be understood on the basis of the electronic structure analysis: predominantly covalent–ionic YCo_3B_2 layers are interleaved with predominantly metallic YCo_5 layers. On the basis of the similarity in electronic structure and elasticity data, it is reasonable to assume that the $Y_{n+1}Co_{3n+5}B_{2n}$ compounds investigated here may exhibit similar properties to MAX phases.

2. Theoretical methods

Calculations were carried out using density functional theory [13], as implemented in the Vienna *ab initio* simulation program (VASP), wherein projector augmented wave potentials are employed [14]. The generalized-gradient approximation was applied in all calculations with the so-called Blöchl corrections for the total energy [15]. The integration in the Brillouin zone is done on special k -points, which are determined following the Monkhorst–Pack approach [16]. Unit cells containing 6–24 atoms [1] were studied on a mesh of $7 \times 7 \times 7$ irreducible k -points. The convergence criterion for the total energy was 0.01 meV within a 400 eV cut-off. Spin polarization was considered for YCo_4B since it possesses the largest Curie temperature [2]. The initial magnetization was $12 \mu_B$ /atom and the magnetic moments were relaxed without any constraints. All $Y_{n+1}Co_{3n+5}B_{2n}$ phases were relaxed with respect to atomic positions (internal free parameters), the lattice parameter a and the c/a ratio. After relaxation, the equilibrium values for a and c/a were obtained by fitting the total energy versus a or c/a with third-order polynomials. Bulk moduli were obtained by fitting the energy–volume curves to the Birch–Murnaghan equation of states [17]. Shearing was studied in terms of the elastic constant C_{44} , as obtained according to the method developed by Fast and co-workers, where the C_{44} deformation results in triclinic symmetry [18]. Furthermore, the density of states (DOS) as well as the electron density distributions were calculated.

3. Results and discussion

$Y_{n+1}Co_{3n+5}B_{2n}$ phases were reported to be ferromagnetic below 2–375 K, depending on n [1]. Therefore, it is important to estimate the influence of spin polarization on the elastic properties. Since YCo_4B possesses the largest Curie temperature [2], we studied the spin polarization for this phase. In table 1, the calculated lattice parameter, c/a ratio, equilibrium volume, bulk modulus and local magnetic moment for paramagnetic and ferromagnetic configurations of YCo_4B are given. The calculated ferromagnetic state of YCo_4B is consistent with the literature [2, 19]. As spin polarization is included in the calculations, the deviation

Table 1. Calculated lattice parameter (a), c/a ratio, volume (V), bulk modulus (B) and local magnetic moment (m) for paramagnetic (PM) and ferromagnetic (FM) configurations of YCo_4B .

	a (Å)	c/a	V (Å ³ /atom)	B (GPa)	m (μ_B /atom)	
					Co (2c)	Co (6i)
PM	4.999	1.349	12.165	187	—	—
FM	5.003	1.367	12.354	174	1.607	0.758

Table 2. Calculated lattice parameter (a), c/a ratio, volume (V), bulk modulus (B) and elastic constant (C_{44}) for $Y_{n+1}Co_{3n+5}B_{2n}$ ($n = 1, 2, 3, \infty$) phases, as obtained by the VASP code. Also, a comparison is made between the calculated and experimental equilibrium volumes.

	a (Å)	c/a	V (Å ³ /atom)	V (Å ³ /atom) exp	B (GPa)	C_{44} (GPa)
YCo_4B	4.999	1.349	12.165	12.578 ^a	187	98
$Y_3Co_{11}B_4$	5.026	1.926	11.763	12.048 ^a	192	106
$Y_2Co_7B_3$	5.021	2.531	11.560	11.806 ^a	195	113
YCo_3B_2	5.014	0.600	10.923	11.085 ^a	206	126

^a See [1].**Table 3.** Calculated internal free parameters for $Y_{n+1}Co_{3n+5}B_{2n}$ ($n = 1, 2, 3, \infty$) compounds.

	Y (2e)	Co (6i ₁)	Co (6i ₂)	B (4h)
YCo_4B	—	0.2850	—	—
$Y_3Co_{11}B_4$	0.3402	0.1995	—	0.3486
$Y_2Co_7B_3$	0.2596	0.1524	0.3837	0.2672
YCo_3B_2	—	—	—	—

of the equilibrium volume from the experimental value [1] decreases from 3.4% to 1.8%. The difference in bulk modulus for YCo_4B between the paramagnetic and ferromagnetic configurations of 7.0% is small compared to the common deviation between experimentally and theoretically determined values for the elastic properties, which is of the order of 20% [18]. Hence, we have neglected spin polarization for all further discussions of the elastic properties of $Y_{n+1}Co_{3n+5}B_{2n}$.

In table 2, the calculated lattice parameter, c/a ratio, equilibrium volume, bulk modulus and C_{44} elastic constant for $Y_{n+1}Co_{3n+5}B_{2n}$ are given. The calculated equilibrium volumes deviate by 1.5%–3.4% from the experimental values [1] and are hence in very good agreement. Furthermore, the internal parameters obtained (see table 3) are consistent with the measured values [1]. As n increases from 1 to ∞ (see table 2), the bulk modulus and the C_{44} elastic constant increase from 187 and 98 GPa to 206 and 126 GPa, respectively. This accounts for the bulk-modulus-to- C_{44} ratio of 1.6–1.9. Diamond and Al possess bulk-modulus-to- C_{44} ratios of 0.8 and 2.6, respectively [20], while van der Waals bonded hexagonal BN [21] and MAX phases [22, 23] exhibit bulk-modulus-to- C_{44} ratios of 2.6 and 1.2–1.7, respectively. On the basis of the similarity in bulk-modulus-to- C_{44} ratio, it may be speculated that the borides studied here are also prone to shearing and that plastic and elastic properties comparable to those of MAX phases may be observed. In order to determine the origin of this unusual behaviour, we study their electronic structure.

In figure 1, electron density distributions in the $(11\bar{2}0)$ plane for YCo_4B ($n = 1$) and YCo_3B_2 ($n = \infty$) are shown. $Y_{n+1}Co_{3n+5}B_{2n}$ phases are built of YCo_5 layers, which are interleaved with n layers of YCo_3B_2 . From these electron density distributions it can be seen

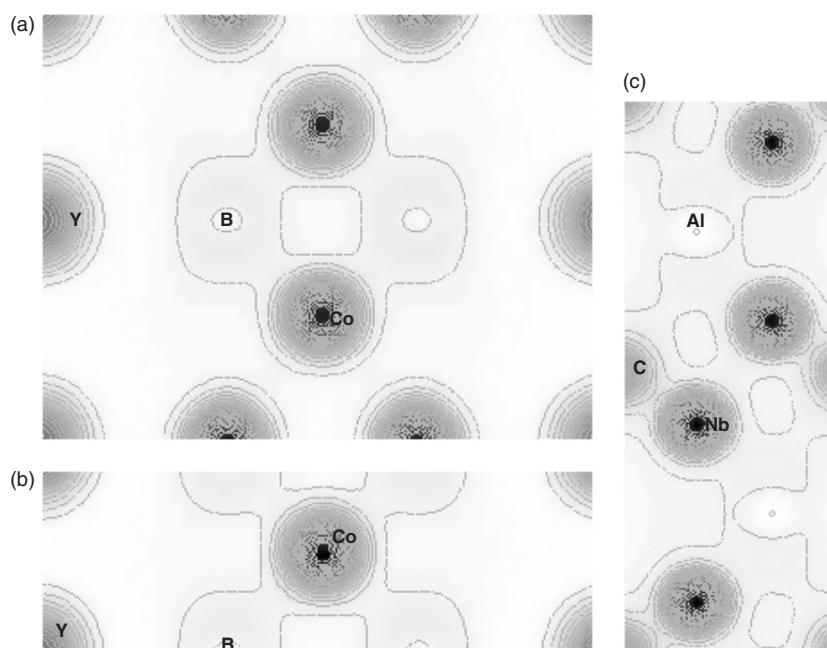


Figure 1. Electron density distribution in the $(11\bar{2}0)$ plane for (a) YCo_4B , (b) YCo_3B_2 and (c) Nb_2AlC . The electron density increases from 0.08 (white) to 9.25 (grey) electrons \AA^{-3} for $\text{Y}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ compounds and from 0.01 (white) to 4.70 (grey) electrons \AA^{-3} for Nb_2AlC .

that YCo_4B (figure 1(a)) contains an YCo_3B_2 unit (figure 1(b)). Hence, all bonding types encountered in $\text{Y}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ are found in YCo_4B , making it a suitable demonstrator. At least three distinctive features can be identified in these electron density distributions. Firstly, B and Co share electrons, which is consistent with covalent bonding and may be responsible for the large bulk modulus values (see table 2). Secondly, the electron density of 0 electrons \AA^{-3} , occurring within covalent crystals in nonbonding directions, is not present in these phases, signifying a pronounced electron delocalization. This may give rise to a metallic bonding character and may in turn be responsible for the low C_{44} values (see table 2). Thirdly, layers of high and low electron density are interleaved (see figure 1(a)). This resembles the electron density distribution in the $(11\bar{2}0)$ plane for Nb_2AlC [24], a typical MAX phase, which is given here for comparison (figure 1(c)). The alternating stacks of boride and metallic layers in these ternary borides correspond to the alternating stacks of A elements and carbides (or nitrides) in the MAX phases [25, 26]. Barsoum and co-workers have described the MAX phases as a new class of solids, exhibiting a combination of metallic and ceramic properties [5, 6]. On the basis of the chemical bonding resemblance and elastic properties presented here and discussed above, it is reasonable to assume that $\text{Y}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ compounds may exhibit similar properties.

In order to further explore the bonding nature of these ternary borides, we study the total DOS thereof, as given in figure 2. There are several general remarks that can be made about the DOS data. First of all, for all compounds the Fermi level is occupied, which implies that $\text{Y}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ phases conduct electricity and heat. This is rather unusual for ceramics, but is consistent with the MAX phase case [5, 25, 27] and can be understood on the basis of the previously discussed electron density distributions (see figure 1). Furthermore, the DOS data are continuous, signifying that the chemical bonding is dominated by covalent and metallic

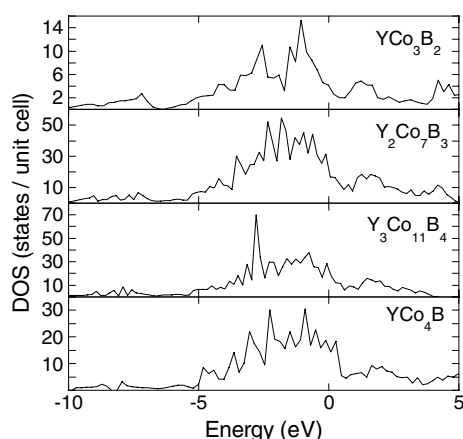


Figure 2. Total density of states (DOS) for $Y_{n+1}Co_{3n+5}B_{2n}$ ($n = 1, 2, 3, \infty$) compounds, as obtained by the VASP code. The Fermi level is set to 0 eV.

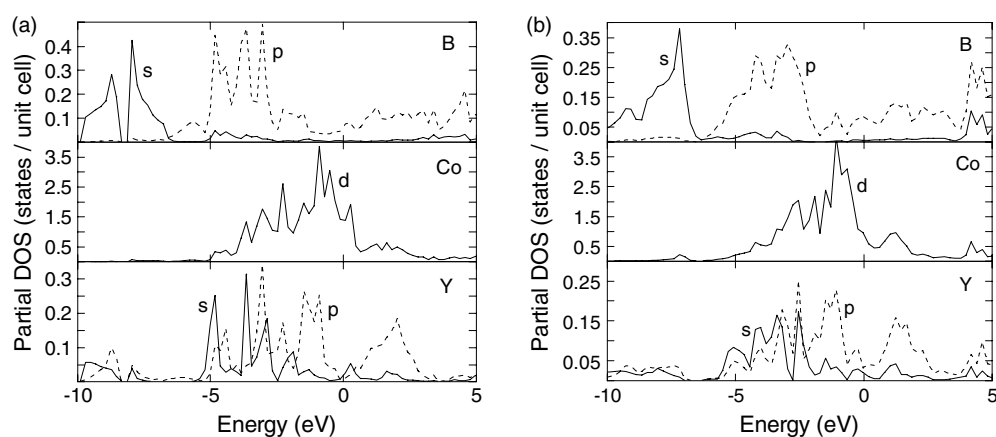


Figure 3. Partial density of states (DOS) for (a) YCo_4B and (b) YCo_3B_2 . The Fermi level is set to 0 eV.

contributions, while the ionic contributions are weak. These results are consistent with previous work [28]. In order to provide information on chemical bonding with respect to both the lattice site and the orbital angular momentum quantum number, we study the partial DOS of the two demonstrator phases: YCo_4B ($n = 1$) and YCo_3B_2 ($n = \infty$), as given in figure 3. In both YCo_4B (figure 3(a)) and YCo_3B_2 (figure 3(b)), deep valence states in the region from -10 to -6 eV originate from B 2s orbitals and partly from Y 4s and 4p states. Extensive overlapping between B 2p, Co 5d, Y 4s and 4p states in the region from -6 eV to the Fermi level can be observed. This is consistent with hybridization of atomic orbitals and covalent bonding. However, B 2p and Co 5d states are more strongly hybridized than any other orbital combination, giving rise to covalent bonding between these two constituents. The Fermi level is occupied mostly by the Co 5d states, which in turn signifies that these ternary borides possess metallic character. These findings are consistent with the total DOS and electron density distribution analysis, as presented above.

4. Conclusions

We have studied the correlation of the electronic structure with the elastic properties for $Y_{n+1}Co_{3n+5}B_{2n}$ using *ab initio* calculations. These ternary phases exhibit a bulk-modulus-to- C_{44} ratio from 1.6 to 1.9, a rather unusual ratio for borides. This may be understood on the basis of the electronic structure: predominantly covalent–ionic YCo_3B_2 layers are interleaved with predominantly metallic YCo_5 layers. Furthermore, covalent–ionic bonding between B and Co may give rise to a large bulk modulus, while the weak coupling between the YCo_3B_2 and YCo_5 layers probably accounts for the low C_{44} value. On the basis of the resemblance in electronic structure and elastic properties, it is reasonable to assume that the $Y_{n+1}Co_{3n+5}B_{2n}$ compounds may possess similar properties to the so-called MAX phases.

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