

Alternating covalent-ionic and metallic bonding in perovskite borides studied using *ab initio* methods

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Using *ab initio* calculations, we have studied 20 boron-based perovskites (RM_3B , where R and M are rare earth and $4d$ metals, respectively). We show that the coupling between M - R and M - B layers in RM_3B can be switched from predominantly covalent-ionic to metallic in character by varying the population of the Md shells. Based on the electron density distribution resemblance to the so-called MAX phases [Sun *et al.*, Phys. Rev. B **70**, 092102 (2004)], it is reasonable to assume that alternating covalent-ionic and metallic bonding in these compounds may give rise to similar properties as observed for MAX phases.

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We study rare earth transition metal boride perovskites (space group $Pm\bar{3}m$, prototype $CaTiO_3$) with the formula RM_3B , where R and M designate rare earth and $4d$ metals, respectively. In this structure, R atoms occupy primitive cubic sites, M atoms fill fcc positions, and B is located at bcc Bravais nodes.¹ B is thus characterized by a sixfold coordination, which is common for icosahedra (B_{12} units) based compounds,^{2,3} but not for all borides. Several of RM_3B compounds are known,^{1,4,5} but very limited information is available with respect to the electronic structure thereof. Based on *ab initio* calculations, the existence of covalent Rh- B bonds in $ScRh_3B$ and YRh_3B was suggested,^{1,6} but there is no correlation between electronic structure and mechanical properties made in the literature.

In this work, we present theoretical results on 20 RM_3B phases, out of which 17 are unknown. It is our ambition to contribute towards understanding the correlation between electronic structure and mechanical properties. Based on comparing the electron density distribution of RM_3B phases with the so-called MAX phases,⁷ it is reasonable to assume that alternating covalent-ionic and metallic bonding in these compounds may give rise to similar properties as observed for MAX phases.

The computational investigation had the typical density functional theory approach. We used the Vienna *ab initio* simulation package (VASP), wherein ultrasoft pseudopotentials and a plane-wave basis set are employed.⁸⁻¹⁰ The generalized-gradient approximation was applied in all calculations.¹¹ The integration in the Brillouin zone is done on special k points determined after Monkhorst-Pack.⁹ Reduced unit cells with five atoms (one formula unit of RM_3B type) were studied on a mesh of 220 irreducible k points. The convergence criterion for the total energy (E) was 0.01 meV. Spin polarization was also considered, but due to only minute differences in E (order of 0.01–1 meV), magnetic contributions were neglected. All structures were relaxed with respect to lattice parameter, i.e., Wigner-Seitz primitive cell volume (V), and their electron density distributions (EDD) were evaluated so as to understand the bonding comprised. The E - V curves obtained were used to calculate bulk moduli by fitting them to third-order polynomials. Furthermore, elastic constants (C_{11} - C_{12} and C_{44} as tetragonal and

monoclinic deformations of the cubic symmetry, respectively) were computed after Liu and Singh¹² and then employed to obtain shear and elastic moduli as well as Poisson's ratios within the Voigt approximation.¹³

Figure 1 outlines EDD in (110) planes for RhY alloy [space group $Pm\bar{3}m$, prototype CsCl (Ref. 14)] as well as three RM_3B configurations: Y_4B , YCd_3B , and YRh_3B . The mutual feature of the four demonstrator crystals is that they all appear layered in the (110) plane or any plane from the

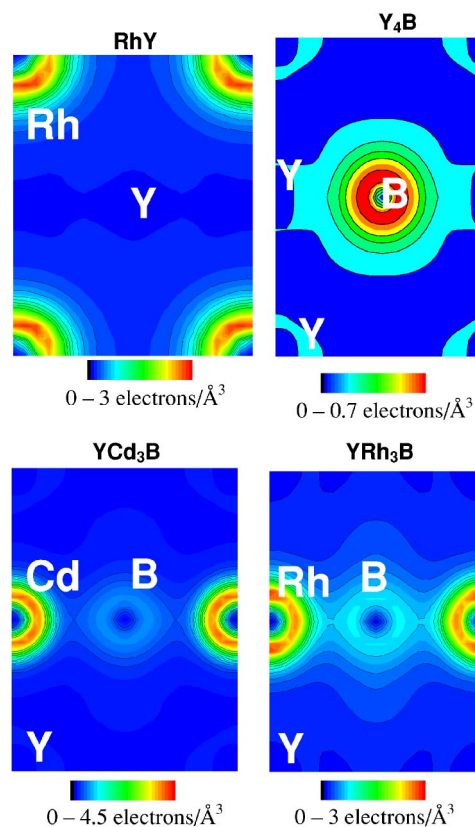


FIG. 1. (Color online) EDDs in (110) planes for RhY, Y_4B , YCd_3B , and YRh_3B . Clearly, the bonding between Rh and B exhibits the highest degree of directionality (covalent-ionic in character) inherited throughout the plane.

TABLE I. Structure and properties of boron based perovskites as obtained by the VASP code. R , a , B , G , E , ν , and M - B designate rare earth metal, lattice parameter, bulk modulus, shear modulus, elastic modulus, Poisson's ratio, and transition metal-boron bond length, respectively.

		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$R=Y$	a (Å)	5.152	4.780	4.523	4.357	4.267	4.206	4.207	4.322	4.500	4.701
	B (GPa)	58	97	145	180	191	200	208	150	102	64
	G (GPa)	21	22	26	28	55	76	96	44	35	16
	E (GPa)	56	61	74	80	151	202	250	120	94	44
	ν	0.34	0.39	0.42	0.43	0.37	0.33	0.30	0.37	0.35	0.38
	M - B (Å)	2.58	2.39	2.26	2.18	2.13	2.10	2.10	2.16	2.25	2.35
$R=Sc$	a (Å)	4.762	4.710	4.450	4.280	4.189	4.131	4.132	4.243	4.421	4.652
	B (GPa)	70	103	150	192	209	216	210	159	107	69
	M - B (Å)	2.38	2.36	2.23	2.14	2.09	2.07	2.07	2.12	2.21	2.33

same family. In the case of the RhY alloy, a metallic superlattice, layers of pure Rh are interleaved with Y layers. Similarly, the RM_3B compounds are characterized by M - R layers interleaved with M - B layers. This electronic structure is typical for perovskites (e.g., KNiF_3).¹⁵ We have investigated the electronic structure of RM_3B configurations, bonding thereof, and the coupling between M - R and M - B layers, as a function of the atomic number Z of M . Generally, we find two groups of RM_3B compounds: weakly and strongly coupled layers in the (110) plane. For $39 \leq Z \leq 41$ and $46 \leq Z \leq 48$ metallic behavior prevails. Y_4B and YCd_3B exemplify this group (see Fig. 1). This can be understood by a presence of homogeneous EDD, with screened Coulomb interactions, resulting in weakly coupled layers. The similarity in EDD with the RhY alloy is striking. For the $42 \leq Z \leq 45$ group, YRh_3B serves to demonstrate the general characteristics (see Fig. 1). A discernible redistribution of EDD with pronounced directionality occurs in these compounds, which is consistent with the notion of mixed covalent-ionic bonding. This is also in accordance with previous work on ScRh_3B (Ref. 1) and YRh_3B .⁶ Thus, strongly coupled layers in the (110) plane characterize this group of RM_3B compounds.

Our finding of strong coupling within the $42 \leq Z \leq 45$ group is consistent with the behavior of transition metals. It is well known that the strongest bonding is observed when their d shells are half-filled.¹⁶ This can be explained by overlapping of spin wave functions.¹⁷ Symmetric overlapping accounts for strong bonding between nearest neighbors and the total spin is maximized (half-filled shells). On the other hand, asymmetric overlapping results in weaker bonding between nearest neighbors. This is consistent with the magnitude of our lattice parameters (see Table I). The strongest coupling and directional EDD are found for the smallest lattice parameter (average 4.3 Å), which can be understood considering Coulomb force screening between electron-depleted R atoms and negatively charged M - B units (see Fig. 1). Smaller lattice parameters and less charge smeared between ions increases the magnitude of the Coulomb force screening. Hence, the strongest coupling is expected for the smallest lattice parameter, which is consistent with the argu-

ments above. The calculated lattice parameters for YRh_3B and ScRh_3B are in good agreement with the experimental values reported in the literature,^{1,4,18} differing only by 0.9% and 1.3%, respectively. For the weakly coupled layers ($39 \leq Z \leq 41$ and $46 \leq Z \leq 48$), the calculated lattice parameters are larger (average 4.7 Å). This is consistent with the concept of weak coupling.

The fact that RM_3B structures appear layered in the (110) plane and can be classified according to weak and strong coupling is expected to affect their properties. Figure 2 outlines the behavior of calculated bulk and shear moduli. For the weakly coupled layers in the (110) planes ($39 \leq Z \leq 41$ and $46 \leq Z \leq 48$), both bulk and shear moduli exhibit small average values of 103 and 27 GPa, respectively. This is a typical behavior for metallic compounds and is in agreement with our EDD (see Fig. 1). These Y-containing RM_3B compounds behave similarly to $R=Sc$, with the maximum of 216 GPa found for ScRu_3B (see Table I). For the strongly coupled layers ($42 \leq Z \leq 45$), both the bulk and shear moduli are larger on average: 195 and 64 GPa, respectively. However, our values are lower than the bulk moduli of the underlying transition metals. For instance, the bulk modulus of

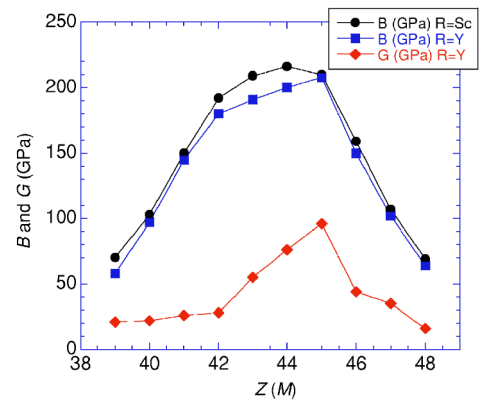


FIG. 2. (Color online) Bulk (B) and shear (G) moduli for boron-based perovskites as a function of atomic number (Z) for M ($4d$ metals). A high B -to- G ratio is an indicative of the unusual properties for these compounds.

YMo₃B is 180 GPa, while for Mo this value¹⁹ is 273 GPa. This is typical for many borides: the bulk modulus of MoB₂ (space group *P6/mmm*, prototype AlB₂) is only 160 GPa.²⁰ Another example is the bulk modulus of Nb and NbB₂, with values of 170 and 101 GPa, respectively.^{19,20} Furthermore, the ratio of bulk and shear modulus for the strongly coupled *RM*₃B compounds is between 6.4 and 2.2, while Poisson's ratio varies from 0.43 to 0.30. Evidently, the metallic character is not totally constrained by the strong coupling, which is consistent with previously reported hardness values⁴ for YRh₃B in the range of 8 GPa. Hence, this group of *RM*₃B compounds clearly behaves plastically (or metallically), as indicated by our predicted low shear modulus and high Poisson's ratio. However, our calculated bulk moduli are comparable (within 10%) to the values for these ceramics: α-Al₂O₃, SiC, and GaN,²¹ rather attractive combination of metallic and ceramic properties. Recently, this combination of properties has been demonstrated^{22–27} for the so-called MAX phases (space group *P6₃/mmc*), where an early transition metal carbide or nitride (MX) is interleaved with either a IIIA or a IVA group element. Moreover, the (110) planes in the borides presented here are equivalent to the (11 $\bar{2}$) planes in the MAX phases.⁷ The alternating stacks of metals and borides in these perovskites (see Fig. 1) correspond to the alternating stacks of A elements and carbides (or nitrides) in the MAX phases. Barsoum and coworkers have categorized the MAX phases as a new class of solids,²² exhibiting rather unusual and fascinating properties: high stiffness, plastic deformability, good electrical and thermal conduction as well as resistance to oxidation. For example, the bulk-to-

shear modulus ratios²² for Ti₃SiC₂ and Ti₃AlC₂ were reported to be 1.3, while the hardness values²² stated are comparable to the ones claimed for YRh₃B.⁴ The similarity in mechanical properties to the here-investigated *RM*₃B compounds is rather obvious. Therefore, based on the resemblance between the (110) plane of *RM*₃B compounds and the corresponding plane of the MAX phases,⁷ as well as the discussed bulk and shear modulus ratio together with the experimentally observed low hardness values, it is sound to assume that *RM*₃B compounds may exhibit a similar combination of metallic and ceramic properties.

In conclusion, we have carried out *ab initio* calculations for 20 B-based perovskites of the *RM*₃B type. These phases are characterized by interleaving of *M-R* and *M-B* layers. We show that the coupling of these layers can be controlled by the *M d*-shell population; i.e., the atomic number *Z*. Predominantly covalent-ionic coupling occurs for the half-filled *M d* shells ($42 \leq Z \leq 45$). Here, the bulk and shear moduli reach up to 208 and 96 GPa, respectively. Based on the similarity in EDD between *RM*₃B and MAX phases, it is reasonable to assume that alternating covalent-ionic and metallic bonding in these compounds may give rise to similar properties as observed for MAX phases. We hope our calculations will stimulate experimental research on these compounds.

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