PHYSICAL REVIEW B **71**, 092102 (2005)

Structure and bonding of M_2SbP (M=Ti,Zr,Hf)

Denis Music,* Zhimei Sun, and Jochen M. Schneider
Materials Chemistry, RWTH-Aachen, Kopernikusstrasse 16, D-52074 Aachen, Germany

(Received 8 October 2004; published 15 March 2005)

Using *ab initio* calculations, we have studied the chemical bonding and elastic properties of M_2SbP (space group $P6_3/mmc$, prototype Cr_2AlC), where M=Ti, Zr, and Hf. The bonding is of covalent-ionic nature with the presence of metallic character. These compounds exhibit nanolaminated structure where MP layers are interleaved with Sb. While the structure is identical, both the bonding and the elastic properties of these phosphides are similar to the so-called MAX phases [M. W. Barsoum, Prog. Solid State Chem. **28**, 201 (2000)].

DOI: 10.1103/PhysRevB.71.092102 PACS number(s): 61.66.Fn, 62.20.Dc, 71.20.Ps

$M_{n+1}AX_n$ phases, where M is an early transition metal, A is a group IIIA or IVA element, X is either C and/or N, and $n=1-3$, have recently drawn a lot of attention due to the combination of properties usually associated with metals and ceramics (for details see Ref. 1, and references cited therein). Most of the MAX phases are of M_2AX stoichiometry (space group $P6_3/mmc$, prototype Cr_2AlC). In general, MAX phases are good thermal and electrical conductors,[2] they exhibit high moduli, but are relatively soft and easily machinable.[1–3] In our previous work,[4] coupling between MC and A nanolaminates has been identified as a classification criterion. One group comprises strongly coupled M_2AC phases, where the bulk modulus of the binary MC is conserved, and the other where this is not the case. This was understood in terms of the valence electron population.

In this report, we study the chemical bonding and elastic properties of to the above discussed MAX phases isostructural compounds based on phosphides. *Ab initio* calculations are employed to explore the effect of M on bonding and elasticity for M_2SbP, where M=Ti, Zr, and Hf, which were synthesized by powder sintering at 800 °C.[5] Based on the here-presented comparison of M_2SbP to the MAX phases with respect to structure and bonding, we suggest a rather close resemblance.

Our calculations are based on the density functional theory,[6] using the VASP code, in conjunction with the generalized-gradient approximation and projector augmented wave potentials.[7–12] The following parameters were applied in the calculations: 0.1 meV relaxation convergence for ions, 0.01 meV electronic relaxation convergence, Davidson optimization of the wave functions, reciprocal-space integration with a Monkhorst-Pack scheme,[11] energy cutoff of 340 meV, k-points grid of $7\times7\times7$, and the tetrahedron method with Blöchl corrections[12] for the total energy. We have performed the relaxations for both the lattice parameter a, the c/a hexagonal ratio, the internal free parameters z, but without spin polarization since it gave only minute corrections for other M_2AX phases studied previously.[13] The relaxations performed have optimized the internal free parameters as well. The equilibrium volume (V_0), the bulk modulus (B), and its pressure derivative (B') were obtained by a least-square fit of the calculated E-V curves using the Birch-Murnaghan equation of state.[14] We have also calculated the c_{44} elastic constant via the method after Fast *et al.*[15] The total density of states (DOS) and the partial density of states (PDOS) are obtained using the relaxed structures at V_0.

The calculated DOS data are presented in Fig. 1 for M_2SbP, where M=Ti, Zr, and Hf. It is apparent that these phases are alike, signifying similarity in chemical bonding. An important feature is the existence of a pseudogap in the DOS in the vicinity of the Fermi level, which is an indication for stability.[16] In order to understand the origin of this behavior and explain the nature of chemical bonding in these phases, we study the PDOS of Ti_2SbP, a representative, given in Fig. 2. It is evident that a covalent interaction occurs between the constituting elements due to the fact that states are degenerate with respect to both angular momentum and lattice site. P 3p and Ti 3d as well as Sb 4p and Ti 3d states are hybridized. Also, due to the difference in electronegativity between the comprising elements, some ionic character can be expected. The bonding character may be described as a mixture of covalent-ionic and, due to the d resonance in the vicinity of the Fermi level, metallic. The pseudogap, common to all M_2SbP phases studied (see Fig. 1), is likely to split the bonding and antibonding orbitals. This behavior is consistent with previous reports on MAX phases.[4,17,18] Furthermore, it has been found for Nb_3SiC_2[19] that the balanced crystal orbital overlap population analysis[20] is consistent with the PDOS analysis suggesting splitting in PDOS. How-

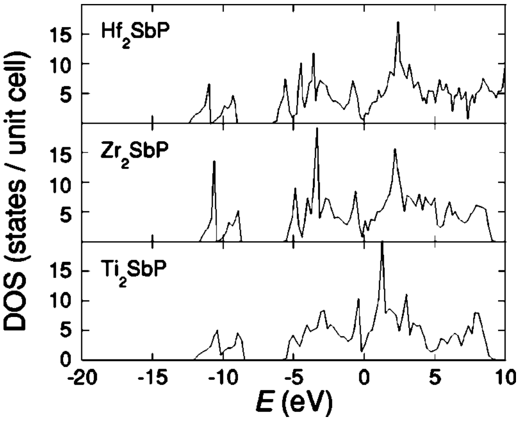

FIG. 1. Total DOS for M_2SbP, where M=Ti, Zr, and Hf, as a function of energy (E). Fermi level is set to 0 eV.

TABLE I. Calculated and experimental equilibrium volume (V_0), lattice constants ($a, c, c/a$), and internal parameters (z) for M=Ti, Zr, Hf in M_2SbP, as well as calculated bulk modulus (B), its pressure derivative (B'), and c_{44} elastic constant.

	Ti_2SbP		Zr_2SbP		Hf_2SbP	
	Calc.	Expt.[a]	Calc.	Expt.[a]	Calc.	Expt.[a]
V_0 (Å^3/atom)	18.22	18.00	21.47	20.87	20.73	20.22
a (Å)	3.651	3.640	3.841	3.816	3.808	3.785
c (Å)	12.63	12.55	13.44	13.24	13.21	13.04
c/a	3.46	3.45	3.50	3.47	3.47	3.45
z (M)	0.100	0.100	0.103	0.103	0.102	
B (GPa)	115		116		125	
B' (GPa)	4.25		4.30		4.19	
c_{44} (GPa)	111		110		116	

[a] See Ref. 5.

ever, there is also a difference with respect to the role of the A element. In the MAX phases,[4,17] the A-M hybridization is weaker than the Sb-M hybridization in the M_2SbP phases. At the same time, the chemical bonding between M and X elements in the MAX phases and between M and P in the here-studied phosphides is rather similar.

Since M_2SbP, with M=Ti, Zr, Hf, and M_2AX phases are isostructural and of similar chemical bonding, it can be expected that the properties may also be comparable. Table I summarizes the structural data and the elastic properties. It is worth noting that our V_0 are within 2.8% deviated from the experimental data[5] and that the internal free parameter of M is reproduced. The bulk moduli of M_2SbP phases are in the range of 115–125 GPa, comparable to the M_2AC phases[4,17,18] containing Ti and other elements of the same column in the periodic table. To the best of our knowledge, the elastic properties of these M_2SbP phases have never been calculated or measured. Because of the previously discussed Sb-M hybridization (see Fig. 2), we expect strong coupling in the c direction. Indeed, we find c_{44} in the range of 110–116 GPa, rather close to the bulk moduli (see Table I). This accounts for the c_{44}/B ratio of 0.93–0.97, which is larger than in the so-far-investigated M_2AX phases[21,22] where the ratio ranges from 0.75 to 0.87. For comparison, the c_{44}/B ratios of Al and diamond are 0.39 and 1.30, respectively.[23] Hence, based on the comparison of chemical bonding, elasticity, and structure, we suggest that M_2SbP phases resemble MAX phases. Experimental work is undoubtedly required to explore this resemblance and we hope that our calculations may inspire future research on the M_2SbP phases.

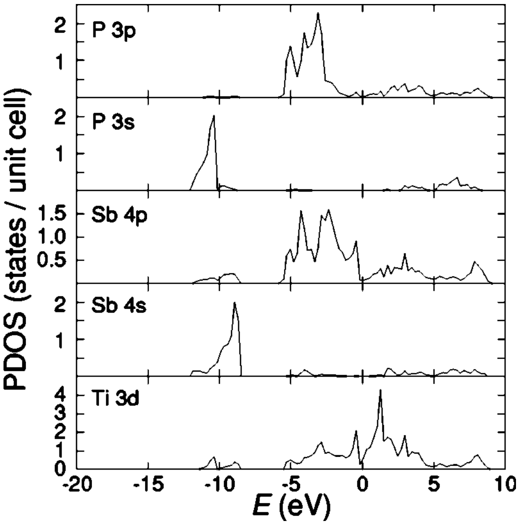

FIG. 2. PDOS for Ti_2SbP as a function of energy (E). Fermi level is aligned with 0 eV.

In summary, we have studied the chemical bonding and elastic properties of M_2SbP, where M=Ti, Zr, and Hf, by means of *ab initio* calculations. The bonds are of covalent-ionic nature with some metallic character. The here-studied phosphides possess nanolaminated structure where MP layers are interleaved with Sb. Based on the comparison with respect to the structure and bonding in MAX phases, we suggest that M_2SbP compounds resemble MAX phases.

We acknowledge sponsorship of the Swedish Research Council (VR) and the Alexander von Humboldt Foundation, the Federal Ministry of Education and Research, and the Program for Investment in the Future. All calculations were carried out at NSC, Linköping, Sweden, and made possible through Swedish National Allocations Committee.

---

*Electronic address: music@mch.rwth-aachen.de

[1] M. W. Barsoum, Prog. Solid State Chem. **28**, 201 (2000).
[2] M. W. Barsoum and T. El-Raghy, J. Am. Ceram. Soc. **79**, 1953 (1996).
[3] B. Manoun, S. K. Saxena, H. P. Liermann, R. P. Gulve, E. Hoffman, M. W. Barsoum, G. Hug, and C. S. Zha, Appl. Phys. Lett. **85**, 1514 (2004).
[4] Z. Sun, D. Music, R. Ahuja, S. Li, and J. M. Schneider, Phys. Rev. B **70**, 092102 (2004).
[5] H. Bolle, Monatsch. Chem. **104**, 166 (1973).
[6] W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).
[7] G. Kresse and J. Hafner, Phys. Rev. B **48**, 13 115 (1993).
[8] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14 251 (1994).
[9] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[10] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[11] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[12] P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994).
[13] J. M. Schneider, Z. Sun, R. Mertens, F. Uestel, and R. Ahuja, Solid State Commun. **130**, 445 (2004).
[14] F. Birch, J. Geophys. Res. **83**, 1257 (1978).
[15] L. Fast, J. M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. B **51**, 17 431 (1995).
[16] C. D. Gelatt Jr., A. R. Williams, and V. L. Moruzzi, Phys. Rev. B **27**, 2005 (1983).

[17] J. Wang and Y. Zhou, Phys. Rev. B **69**, 214111 (2004).
[18] Z. Sun, R. Ahuja, S. Li, and J. M. Schneider, Appl. Phys. Lett. **83**, 899 (2003).
[19] A. Grechnev, S. Li, R. Ahuja, O. Eriksson, U. Jansson, and O. Wilhelmsson, Appl. Phys. Lett. **85**, 3071 (2004).
[20] A. Grechnev, R. Ahuja, and O. Eriksson, J. Phys.: Condens. Matter **15**, 7751 (2003).
[21] B. Holm, R. Ahuja, S. Li, and B. Johansson, J. Appl. Phys. **91**, 9874 (2002).
[22] Z. Sun, S. Li, R. Ahuja, and J. M. Schneider, Solid State Commun. **129**, 589 (2004).
[23] C. Kitell, *Introduction to Solid State Physics* (Wiley, New York, 1996), pp. 59, 91, 92.