

Ground state structures in the polonium based II–VI compounds

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Abstract

We have performed ab-initio self-consistent calculations using the full-potential linear augmented plane-wave method to investigate the structural and the electronic properties of the less known II–VI compounds: ZnPo, CdPo, and HgPo. Total energy calculations of the cubic zinc-blende, wurtzite, rocksalt, cesium chloride, orthorhombic Cmcm, and tetragonal PbO phases are investigated. Ground state parameters are computed, and compared with available theoretical and experimental works. The zinc-blende structure is found to be the ground state phase of ZnPo and CdPo, while HgPo prefers the tetragonal PbO structure. The calculated band structure of II-Po shows features that differ considerably from those of typical II–VI semiconductors. In particular we found an inverted band gap, reflecting a semi-metallic character for these compounds. © 2006 Elsevier Ltd. All rights reserved.

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1. Introduction

Semiconductors compounds of the II–VI group have been extensively studied theoretically and experimentally during the last half century. This is mainly due to their applications in optoelectronic devices, which reached a high experimental level. Most theoretical works [1–8] have been devoted to materials from the groups II and VI of the periodic table, such as Zn, Cd, Hg, and O, S, Se, Te. However, less attention was paid to the remaining heavier II-Po elements: ZnPo, CdPo, and HgPo. It is expected that most II-Po compounds should have a small or even negative gap [9].

Recently, Chen et al. [9] have calculated the band structure of the II-Po group assuming a zinc-blende phase. However less is known about the ground state structure of the II-polonium group. A detailed knowledge of the stability of these compounds in conjunction with their electronic properties is important from a fundamental point of view.

In this paper we present a systematic predictive study of the structural and electronic properties of the II-Po compounds by

using the state-of-the-art of ab-initio self consistent full potential linearized augmented plane wave method (FPLAPW). The rest of the paper is presented as follow. The computational method is described in Section 2. Results for the structural and electronic properties are presented in Section 3. A summary of the work will be given in Section 4.

2. Method

The calculations are performed in the framework of the density functional theory DFT. We have employed the full potential linearized augmented plane wave (FPLAPW) method as implemented in the WIEN2k code [10]. The exchange and correlation effects are treated using the generalized gradient approximation (GGA) [11], and the local density approximation (LDA) [12]. We expand the basis function up to $R_{MT}K_{MAX} = 7$ (R_{MT} is the plane wave radii, K_{MAX} is the maximum modulus for the reciprocal lattice vectors). The maximum value for partial waves inside the atomic sphere is $l = 10$. A fully relativistic approximation is used for core electrons, and scalar relativistic approximations are used for valence electrons. Spin orbit coupling is included using the second-variation method. Muffin-tin radii (R_{MT}) of

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Table 1
Present results for structural parameters of the ground state phase of II-Po compounds

	Gss*		a (Å)	c (Å)	z	B (GPa)
ZnPo	(ZB)	This work (GGA)	6.401			39.06
		This work (LDA)	6.232			50.72
		LDA ^a (pseudopotential)	6.201			51.0
		Exp. ^b	6.309			
CdPo	(ZB)	This work (GGA)	6.819			31.41
		This work (LDA)	6.595			40.55
		LDA ^a (pseudopotential)	6.624			37.2
		Exp. ^b	6.665			
HgPo	(PbO)	This work (GGA)	4.994	4.882	0.40	44.90
	ZB	This work (GGA)	6.881			31.63

a and c are the lattice constants, z is the cell-internal structural parameter, and B is the bulk modulus. Gss: Ground state structure.

^a Ref. [9].

^b Ref. [16].

2.1(2.7) bohr are chosen for Zn(Po) atoms, 2.3(2.7) bohr for Cd(Po) atoms, and 2.7(3.0) bohr for Hg(Po) atoms. Accurate Brillouin zone integrations are performed using the standard special k points technique of Monkhorst and Pack (MP) [13]. The corresponding integrating points over the irreducible Brillouin zone are 20 k points for CsCl and NaCl phases, 30 k points for the zinc-blende (ZB) and the tetragonal PbO (structure tP4-type(B10), space group P4/nmm [14]) phases, 48 k points for the Wurtzite (W) phase and 64 k points for the orthorhombic Cmcm phase.

3. Results and discussion

Total energy versus volume data for the zinc-blende, wurtzite, rocksalt, CsCl, Cmcm and PbO phases are shown in Fig. 1, 2 and 3 for ZnPo, CdPo and HgPo respectively. The calculated total energies are fitted with Murnaghan's equation [15] of states to obtain structural parameters. The calculated structural parameters for the ground state phase are given in Table 1. We found that the zinc-blende phase is clearly the most stable structure of ZnPo and CdPo. Our calculated LDA lattice parameter for ZnPo and CdPo agrees with recent LDA first-principles pseudopotential calculations [9]. Our results show the usual trends of LDA and GGA; with respect to LDA, the GGA increases the lattice constant. The arithmetic average of the LDA and GGA calculated lattice constant of ZnPo(CdPo) is equal to 6.31 Å(6.61 Å), which agrees well with the measured value of 6.309 Å(6.66 Å) [16].

For HgPo, we are not aware of any theoretical or experimental work about its structural properties. Among the five phases considered, we found that the PbO tetragonal phase is the most stable. While all III–V or II–VI semiconductors crystallize in either the zinc-blende or the hexagonal wurtzite phases. Similar results, were found recently for heavier III–V compounds (TlSb, TlBi, InBi) which have the PbO ground state structure [17,18].

The calculated relativistic band structures, including spin–orbit (SO) coupling, for ZnPo, CdPo, and HgPo are shown in Fig. 4, 5 and 6 respectively. The relativistic effects are important for II–Po compounds. We found that the SO splittings

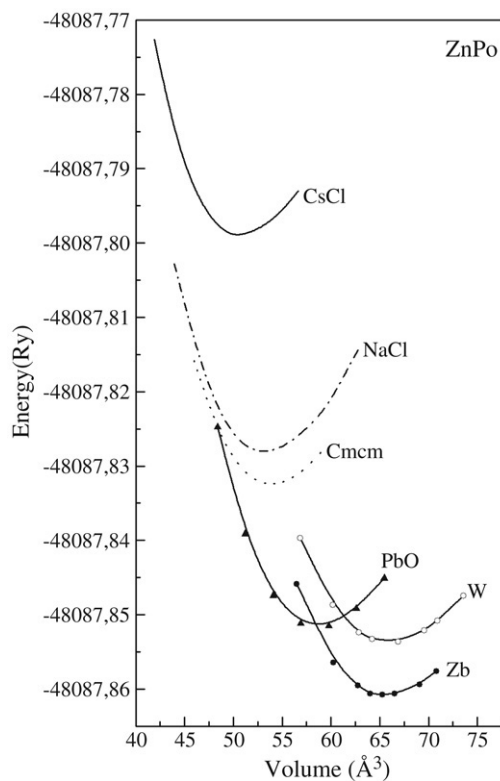


Fig. 1. Total energy versus volume for the zinc-blende (ZB), wurtzite (W), rocksalt (NaCl), CsCl, Cmcm, and tetragonal (PbO) phases of ZnPo.

correspond to 2.27 eV, 2.19 eV and 2.7 eV for ZnPo, CdPo, and HgPo, respectively.

We notice that all the studied compounds exhibit a negative band gap as found for the mercury chalcogenide II–VI compounds [9,19]. The energy of the s -like Γ_{6c} state, which is the conduction band minimum (CBM) at the Γ point, is below the p -like valence-band maximum (VBM) with the Γ_{8v} symmetry, since the conduction state Γ_{6c} is below the valence state Γ_{8v} (Fig. 7). These materials are called ‘negative-band gap’ materials, which means that they have semi-metallic character. In the other situations, the band gap could be either positive, which is always the sign of semiconductor character

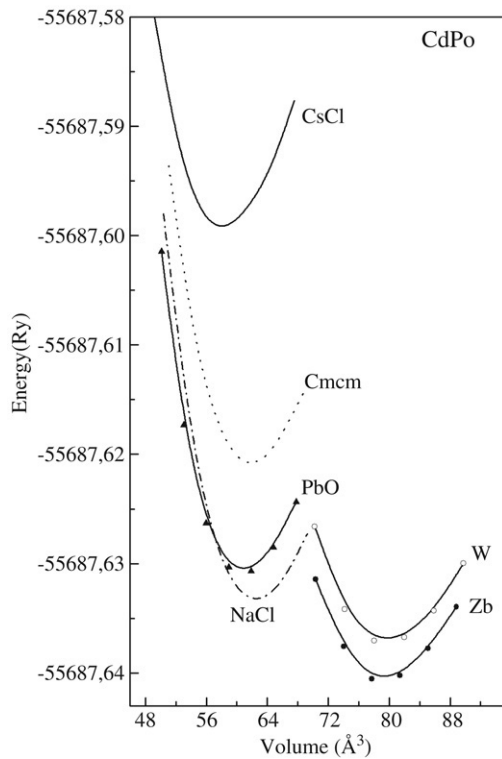


Fig. 2. Total energy versus volume for the zinc-blende (ZB), wurtzite (W), rocksalt (NaCl), CsCl, Cmc, and tetragonal (PbO) phases of CdPo.

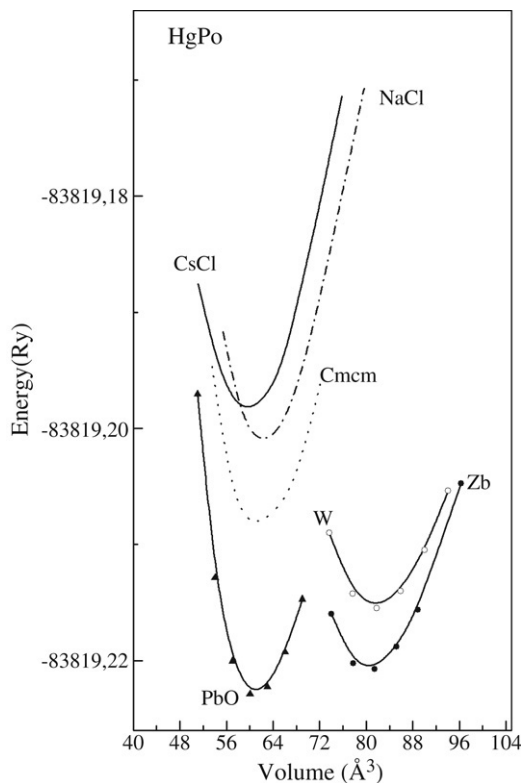


Fig. 3. Total energy versus volume for the zinc-blende (ZB), wurtzite (W), rocksalt (NaCl), CsCl, Cmc, and tetragonal (PbO) phases of HgPo.

or even insulator character if the band gap is important, or completely absent with only crossings of bands in all energetic

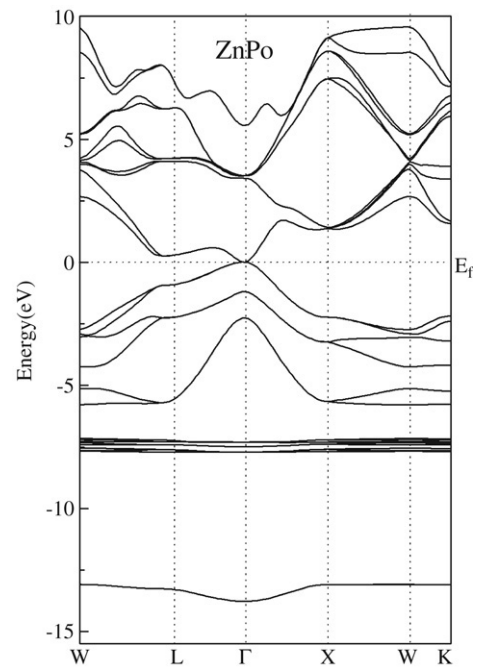


Fig. 4. Calculated relativistic band structure of ZnPo.

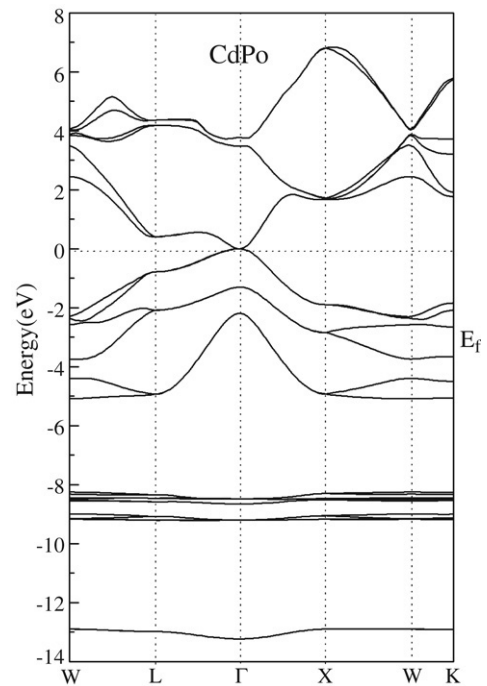


Fig. 5. Calculated relativistic band structure of CdPo.

levels which reflects a metallic character. The inversion of band gap is caused by the fact that the concave upwards conduction band has dropped in energy and becomes concave downwards, and it is now occupied.

However, it is well known that the energy band gaps are not given accurately by the GGA because it doesn't truly represent quasi-particle excitation energies. Consequently the inverted gaps are overestimated for the II-polonium materials. The inverted band structure is a consequence of the very large

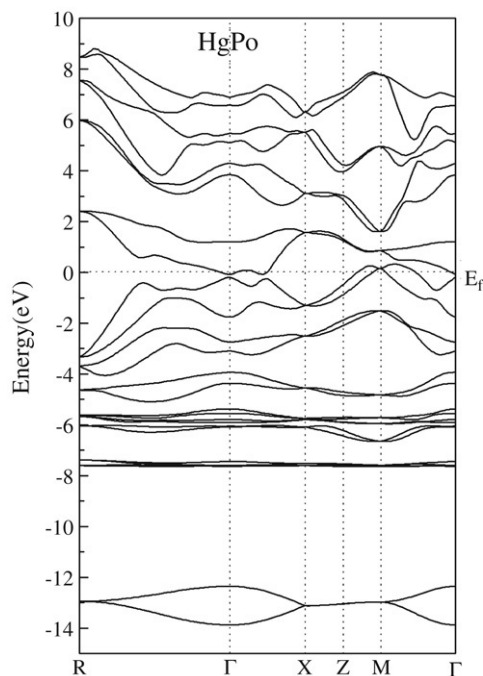


Fig. 6. Calculated relativistic band structure of HgPo in the PbO phase.

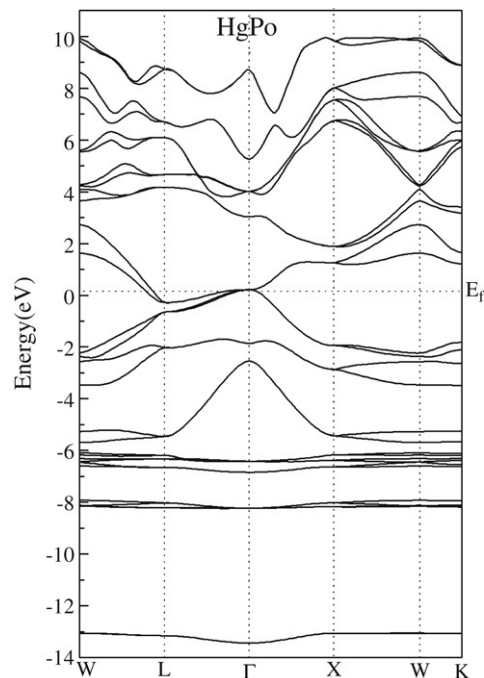


Fig. 8. Calculated band structure of HgPo in the zinc-blende phase.

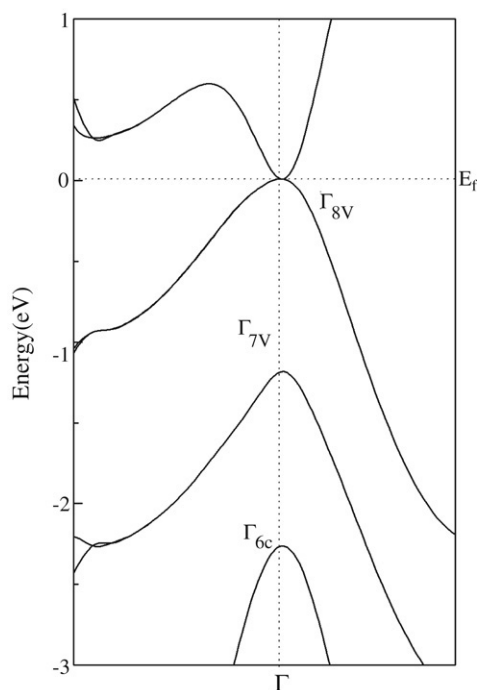


Fig. 7. Calculated relativistic band structure of ZnPo between -1 and 1 eV.

relativistic effects in the II-Po compounds which push up the Po p bands.

Since the DFT calculations do not predict the structures with total accuracy, and the total energy difference of 0.01 eV/cell between the ZB and PbO phases of HgPo, it is conceivable that HgPo may have the zinc-blende structure. The calculated structural parameters and the band structure for the ZB phase of HgPo are given respectively in Table 1 and Fig. 8.

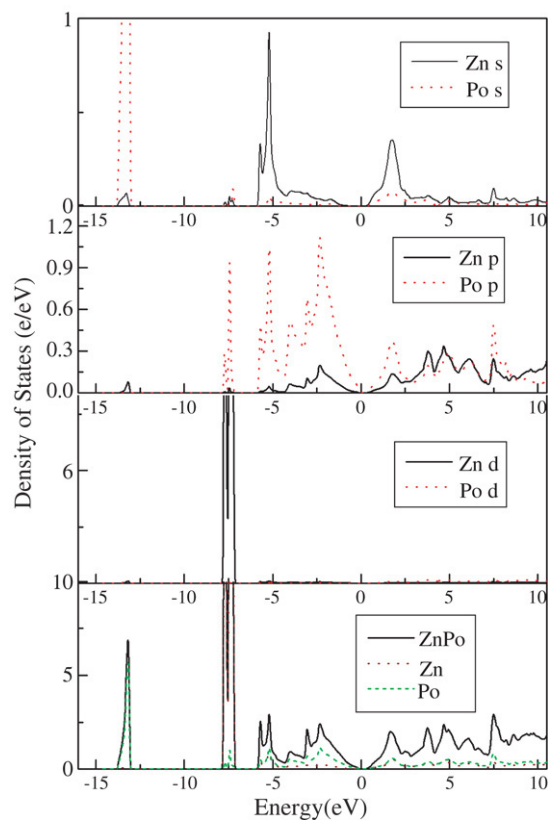


Fig. 9. Calculated total and partial density of states of ZnPo.

Figs. 9–12 show the calculated total and partial density of states for ZnPo, CdPo and HgPo, respectively. The lowest valence bands at around -13 eV is derived essentially from the s electrons of Po. The lowest valence bands between -8 eV and -6 eV are entirely derived from the d electrons of Zn,

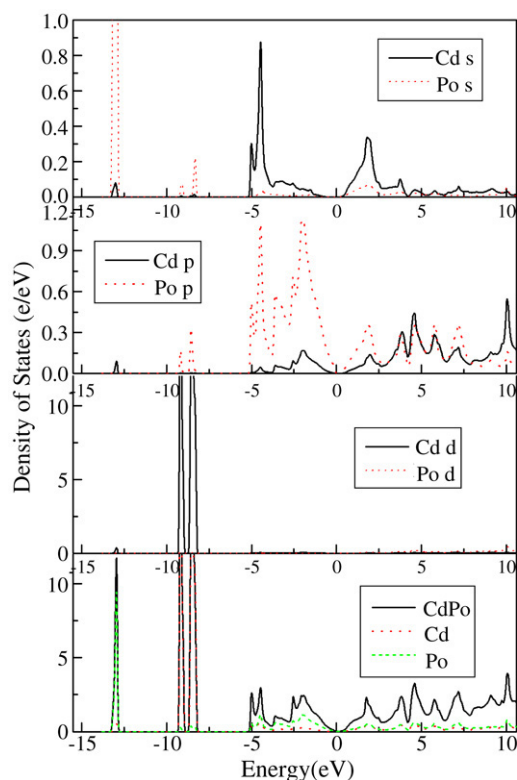


Fig. 10. Calculated total and partial density of states of CdPo.

Cd and Hg. These outer filled d electrons of the cations play an important role in II–VI compounds, as pointed by Wei and Zunger [1]. The highest valence bands are characterized by the contributions of the Zn, Cd and Hg s electrons and the Po p electrons, with a relatively small admixture of Zn, Cd and Hg d electrons.

To complete the entire basic background for the II–Po compounds, let us investigate their bonding properties. We show in Fig. 13, the valence charge density distribution without d electrons in the (110) plane of ZnPo as prototype. We notice a strong charge transfer from the Zn to the Po atom, reflecting an important ionic character of the bonds in this compound. The situation is expected to be similar, i.e. strongly ionic, for the remaining II–Po compounds.

4. Summary

This study reports a detailed investigation on the ground state and electronic properties of the II–Po compounds using the FPLAPW method. The most relevant conclusions are the following:

- (i) The zinc blende structure is found to be the most stable for ZnPo and CdPo, while HgPo prefers the tetragonal PbO structure. The calculated structural parameters are found to be in good agreement with available theoretical and experimental work.
- (ii) Relativistic effects play a key role in the electronic structure of II–Po compounds.
- (iii) The calculated band structure shows features that differ considerably from those of typical II–VI semiconductors.

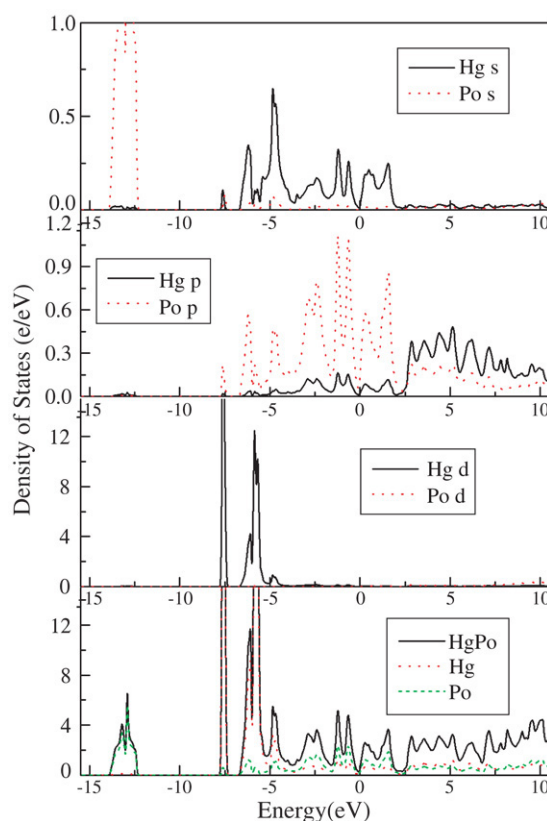


Fig. 11. Calculated total and partial density of states of HgPo in the PbO phase.

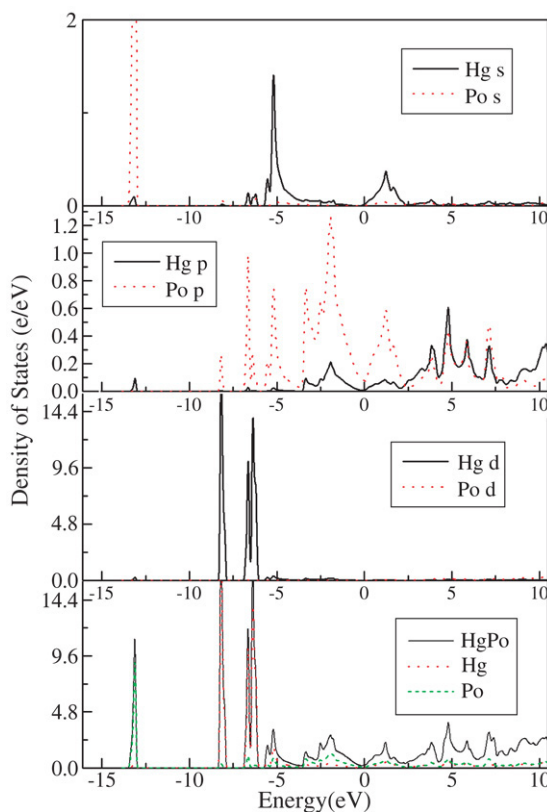


Fig. 12. Calculated total and partial density of states of HgPo in the zinc-blende phase.

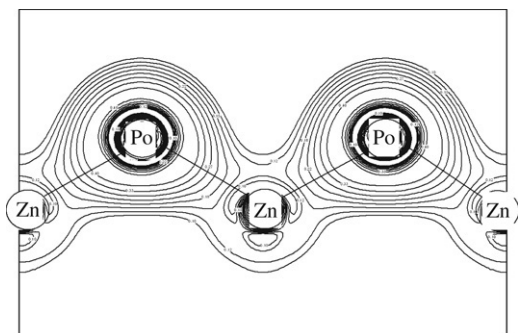


Fig. 13. Total valence charge density for ZnPo in the (110) plane.

In particular an inverted band gap was found, which reflects a semi-metallic character for II-Po compounds.

- (iv) The II-Po compounds are characterized by a strongly ionic character of the bond.

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