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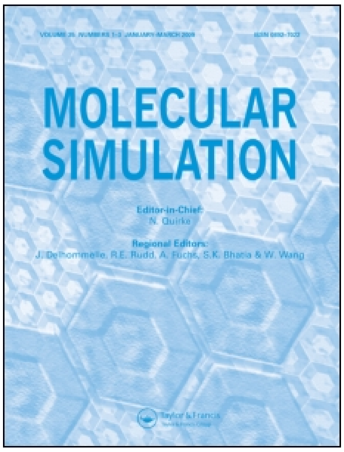

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Electronic Structure of Platinum-Group Minerals: Prediction of Semiconductor Band Gaps

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ELECTRONIC STRUCTURE OF PLATINUM-GROUP MINERALS: PREDICTION OF SEMICONDUCTOR BAND GAPS

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We report first-principle electronic structure calculations of the three representative minerals of the platinum group: cooperite (PtS), braggite ($PdPt_3S_4$) and sperrylite ($PtAs_2$) using the Tight-Binding Linear Muffin Tin Orbital (TB-LMTO) technique. We predict non-metallic behaviour for all three minerals with semiconductor band gaps of 1.31, 0.89 and 0.34 eV, respectively. In particular, our calculation is in excellent agreement with the experimental value of 1.4 eV deduced from diffuse-reflectance measurement for cooperite. We argue that the strong bonding between the Pt 5*d* and S(As) 3*p*(4*p*) states plays a crucial role in the formation of the semiconductor band gap.

Keywords: Platinum group minerals; electronic structure; band gaps

I. INTRODUCTION

Precious materials like cooperite (PtS), braggite (Pt, Pd, Ni)S and sperrylite ($PtAs_2$) are the most important source of platinum in the world's largest deposits of platinum-group minerals (PGM) [1] which also contain the sulfides of other transition metals such as Os, Ir, Ru, Pd, Fe, Ni and Cu [2].

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[*] Corresponding author.

The mining industry is interested in their electronic, magnetic, optical, structural and thermodynamic properties since these affect ore formation, mineral processing and environmental mineralogy. However, as far as we know, little experimental work has so far been carried out on the it non-metallic behaviour of PGM. Recently, the plane-wave pseudopotential method has been used to study cohesion and electronic properties of a wide range of transition metal sulphides including the (Pt, Pd, Ni) sulfides [3]. In particular, the formation of a deep pseudogap at the Fermi level is argued to be the driving electronic mechanism for the stabilization of the Pt and Pd monosulfides. In addition, we have recently studied the equation of state (EOS), electronic structure, optical and bonding properties of pyrite and marcasite by using an improved TB-LMTO technique [4, 5]. We have found [4, 5] a larger band gap on marcasite compared with pyrite and related it to the crucial role of the hybridization between Fe 3*d* and S 3*p* states. The purpose of this paper is to perform self-consistent electronic structure calculations of cooperite (PtS), braggite ($PdPt_3S_4$) and sperrylite ($PtAs_2$) using the TB-LMTO method. Our calculations predict the formation of a semiconductor band gap for all three platinum-group minerals. For PtS a relatively big indirect gap of 1.31 eV has been found in contradiction to the previous calculation [3] but it in good agreement with the experimental measurement of 1.4 eV [6].

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II. COMPUTATIONAL DETAILS

In the present study the electronic structure was calculated self-consistently using the TB-LMTO technique, the details of which have been described in [7]. We use the scalar-relativistic version in the atomic-sphere-approximation including the combined correction (ASA + CC). Exchange and correlation contributions to both atomic and crystal potentials were included through the local-density-functional description using the von Barth-Hedin formula [8]. In the ASA + CC, the one electron potential entering the Schrödinger equation is a superposition of overlapping spherical potential wells with position **R** and radii $s_{\mathbf{R}}$ which leads to a kinetic-energy error that is proportional to the 4th power of the relative sphere overlap [9].

$$\omega_{\mathbf{RR}}' \equiv \frac{s_{\mathbf{R}} + s_{\mathbf{R}}'}{|\mathbf{R} - \mathbf{R}'|} - 1 \tag{1}$$

In many mineral structure-types such as the cooperite, braggite and sperrylite, the use of only atom-centred spheres within ASA would cause substantial errors, either due to large overlap and misrepresentation of the potential, or due to neglect of charge in the van der Waals gap. Therefore, it is necessary to pack the van der Waals gap with interstitial spheres. In general, the requirements for choosing sphere positions and radii are that the superposition of the spherical potentials approximate the full three-dimensional potential as accurately as possible, so that the overlap error for the kinetic energy remains acceptable. Here, following the reference [9], the full potential is modelled by the superposition of neutral-atom Hartree potentials. The atomic-centred spheres are then determined by tracing the potential along the lines connecting nearest-neighbour atoms and finding the saddle-points. For a given atom with position **R**, the distance to the closest saddle-point is taken as the radius of its sphere and usually touches the sphere constructed in the same way for other atoms. The ASA radii are then obtained by inflating these atom-centred non-overlapping spheres until they either fill space or until their overlap $\omega_{\mathbf{RR}'}$ reaches a maximum of 16%. In the latter case, the potential between the atomic potentials must be represented by additional interstitial spheres, which are usually repulsive. The positions of these interstitial spheres are first chosen among the non-occupied symmetry positions of the space group. Then their radii are chosen in such way that the maximum overlap between an atomic and an interstitial sphere is 18% and maximum overlap between two interstitial spheres is 20%. This procedure is automated in the computer program of [7].

The above procedure leads to 2 and 5 new empty sphere symmetry positions per unit cell in order to fill space between the atomic positions within the cooperite and braggite structure types, respectively. Their positions together with the experimental atomic parameters for cooperite [10] and braggite [11] are given in Table I. Regarding sperrylite $PtAs_2$, its structure type is identical to pyrite with cubic space group symmetry $Pa\bar{3}$ (cP12). The experimental values of the lattice and internal parameters are: $a = 5.97$ Å, $u = 0.383$ [10] with an additional empty sphere symmetry position E (24*d*) as has been discussed in [4]. The basis set for our calculations consisted of Pt 6*s*, 6*p*, 5*d*; Pd 5*s*, 5*p*, 4*d*; S 3*s*, 3*p*, 3*d*; As 4*s*, 4*p*, 4*d* with 1*s*, 2*p* states for the interstitial empty sphere. All **k**-space integrations were performed by the tetrahedron method [12]. Convergence to self-consistency was achieved with a grid of 60, 18 and 11 irreducible **k** points, subsequently 315, 90 and 119 **k** points were used to calculate the total energy and the densities of states (DOS) for the cooperite, braggite and sperrylite structures, respectively. In all calculations, the tolerance in the total energy before self-consistency was deemed to have been achieved was 10^{-2} mRy per unit cell.

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III. RESULTS

A. Electronics Structure of Cooperite PtS

Our total energy minimization with respect to the lattice parameters for PtS gives $a = 3.522$ Å and $c = 6.095$ Å compared to the experimental values of 3.47 Å and 6.11 Å, respectively [10]. The corresponding band structure and DOS are presented in Figure 1. Our calculations indicate that PtS is a semiconductor with an indirect band gap of 1.31 eV. This large value of the band gap contradict a recent plane-wave basis calculation using the Vienna *ab initio* simulation program (VASP) [3] where essentially zero band gap was predicted at the Fermi energy. The non-metallic behaviour of PtS can be

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TABLE I Experimental lattice constants and internal parameters for cooperite and braggite. Pearson notations of space group symmetry are given in parenthesis

	PtS[a] *P*4$_2$/*mmc* (*tP*4)				*Pd$_2$Pt$_5$NiS$_8$*[b] *P*4$_2$/*m* (*tP*16)		
–	$a = 3.47$ Å	$b = a$	$c = 6.11$ Å	–	$a = 6.38$ Å	$b = a$	$c = 6.57$ Å
Pt(2*c*)	0.0	0.5	0.0	Pd(2*d*)	0.0	0.5	0.5
S(2*e*)	0.0	0.0	0.25	(Pt, Ni)$_1$(2*e*)	0.0	0.0	0.25
E1(2*a*)	0.5	0.0	0.0	(Pt, Ni)$_2$(4*j*)	.2572	.4667	0.0
E2(2*f*)	0.5	0.5	0.25	S(8*k*)	.3121	.1903	.2267
–	–	–	–	E1(2*f*)	0.5	0.5	0.25
–	–	–	–	E2(4*j*)	–.0149	.2430	0.0
–	–	–	–	E3(4*j*)	.1909	.0324	0.0
–	–	–	–	E4(4*j*)	.4731	–.3043	0.0
–	–	–	–	E5(8*k*)	.0939	.3897	.2516

[a] Ref. [10].
[b] Ref. [11].

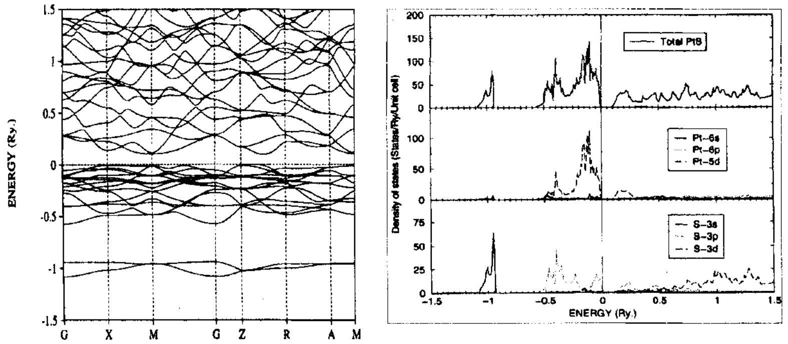

FIGURE 1 Self-consistent band structure, total and partial densities of states for cooperite (PtS). The energy zero is set at the top of the valence band.

inferred from experiment where diffuse-reflectance measurements and absorption curves indicate a possible energy gap of 1.4 eV [6]. Although our calculated band gap agrees very well with the latter value, more experimental evidence is needed to verify our theoretical value.

The partial DOS calculations shown in Figure 1 indicate that apart from the low-lying S(3*s*) band, a very strong bonding-antibonding splitting in the Pt(5*d*)−S(3*p*) band complex is the main origin of the formation of the semiconductor band gap as has already been well documented for the case of $RuAl_2$ and $RuGa_2$ [13]. Hence, we emphasize again here that just as in iron pyrite and marcasite [4, 5] that the energy gap in platinum sulfide depends critically on the covalent bonding properties rather than the conventional picture of the importance of ionic bonding within transition metal sulfides.

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B. Electronic Structure of Braggite $PdPt_3S_4$

In order to study qualitatively the electronic structure of braggite, we have replaced all (Pt, Ni) mixed experimental positions presented in Table I by platinum atoms. By keeping all the internal parameters unrelaxed, we have minimized the total energy with respect to the lattice constants for $PdPt_3S_4$ and found that $a = 6.393$ Å and $c = 6.654$ Å. The theoretical values are slightly larger than the experimental values due probably to the different atomic sizes between platinum and nickel. The calculated band structure and the DOS of $PdPt_3S_4$ are shown in Figure 2. We have predicted a direct semiconductor band gap of 0.89 eV at the Γ point. The shape of total DOS of braggite is not too far from that of cooperite discussed above in Figure 1. A closer inspection of the partial DOS, however, shows that the main contribution to the valence band comes essentially from the Pt(5*d*) states whereas the Pd(4*d*) contribution here is relatively small. We note that the electronic structure of PdS has also been calculated in the braggite structure-type in [3] where only a deep pseudogap at the Fermi energy has been found. It would be highly desirable for future work to analyse the influence of nickel substitution on the electronic structure and stability of braggite.

C. Electronic Structure of Sperrylite $PtAs_2$

As we have mentioned above, the crystal structure of sperrylite ($PtAs_2$) is identical to iron pyrite (FeS_2). Moreover, since the total number of valence electrons per formula unit is the same for both compounds, we can expect

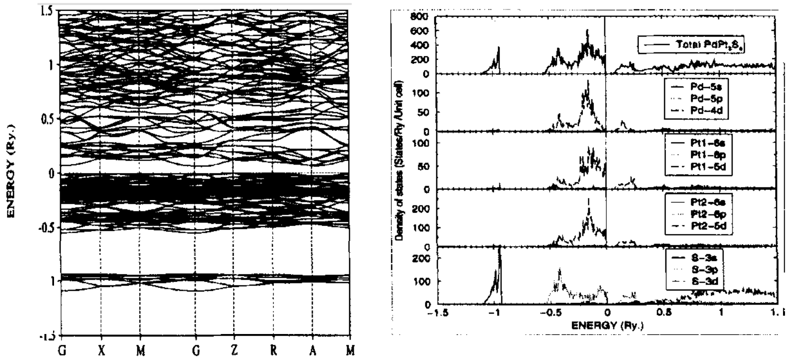

FIGURE 2 The same as Figure 1 for braggite $PdPt_3S_4$.

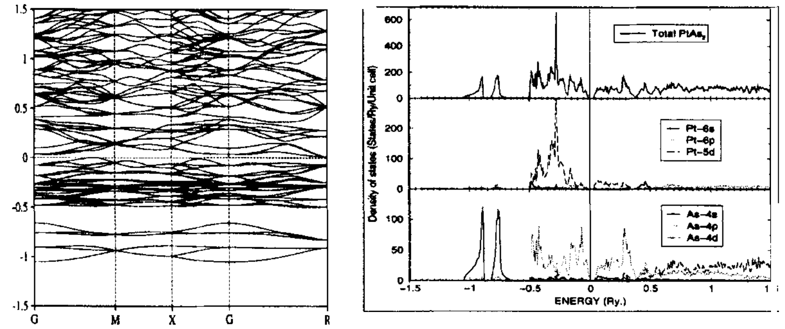

FIGURE 3 The same as Figure 1 for sperrylite $PtAs_2$.

the formation of a semiconductor gap in $PtAs_2$ as is observed in FeS_2. Without relaxing the internal parameter u, we have found from our calculations the total energy minimum at $a = 5.98$ Å in good agreement with experimental value of 5.97 Å. The corresponding band structure and the DOS are shown in Figure 3, indicating an indirect semiconductor gap of 0.34 eV compared to the predicted value of 0.71 eV for FeS_2 [4, 5]. We see that the As(4*s*) states form a separate bonding-antibonding gap at high binding energy similar to the those of S(3*s*) states in pyrite FeS_2. The semiconductor gap again originates from the Pt(5*d*) and As(4*p*) hybridization effect. As far as we know, experimental evidence for a semiconductor behaviour in sperrylite has been mentioned only in [1] and our calculations are the first theoretical predictions in the literature.

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IV. CONCLUSIONS

We conclude that by using an improved and relible TB-LMTO technique we are able to predict non-metallic behaviour of the three platinum-group minerals: cooperite (PtS), braggite ($PdPt_3S$) and sperrylite ($PtAs_2$). A consistent account of the semiconductor band gaps and bonding properties for these materials is related to the crucial role of the hybridization between the Pt(5*d*) and S(3*s*) or As(4*p*) states. Our predicted value of the band gap for cooperite in a very good agreement with experiment. We very much hope that our theoretical calculations will stimulate further experimental work on determining the band gaps in PGM. It also remains for future research to carry out full total energy relaxations in order to clarify the equation of states, relative structural stability, optical and bonding properties of these interesting minerals.

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