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**Structural and electronic properties of a new material — SrOs<sub>2</sub>O<sub>6</sub>\***© P.A. Agzamova<sup>1,2</sup>, S.V. Streltsov<sup>1,2</sup><sup>1</sup> M.N. Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia<sup>2</sup> Ural Federal University after the first President of Russia B.N. Yeltsin, Yekaterinburg, Russia

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It was shown theoretically that a new material SrOs<sub>2</sub>O<sub>6</sub> can exist; the crystal structure of SrOs<sub>2</sub>O<sub>6</sub> is formed by the layers of OsO<sub>6</sub> octahedra having common edges and forming a honeycomb type lattice. The structural and electronic properties of SrOs<sub>2</sub>O<sub>6</sub> were investigated by the first-principal calculations. An antiferromagnetic structure was found to be energetically favorable for the studied compound.

**Keywords:** ab initio calculations, low dimensional magnetism, band structure.

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**1. Introduction**

Layered systems based on transition metals, which have a honeycomb lattice, are under intense study nowadays. Some of them, e.g.,  $\alpha$ -RuCl<sub>3</sub>, Na<sub>2</sub>IrO<sub>3</sub> or Li<sub>2</sub>IrO<sub>3</sub> are of interest due to possible realization of the spin-liquid state and are examples of systems whose magnetic properties are described by the Kitayev–Heisenberg model [1–3]. Other compounds have a state of the valence bond liquid [4–6].

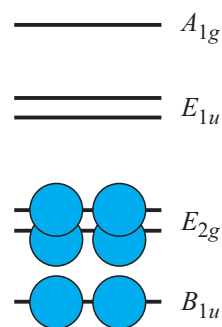
An important feature of such systems in cases when the transition metal has a partially filled  $t_{2g}$ -shell is the existence of quasi-molecular hexagon-centered orbitals. Quasi-molecular orbitals yield a particular electronic spectrum, while band states can be classified by means of irreducible representations of group  $D_{6h}$  (in the same way as with the benzene molecule) [7,8]. However, such factors as spin-orbital interaction, number of valence electrons, dimerization trend, various crystal lattice distortions determine whether the state with quasi-molecular orbitals can be realized or not [9]. The materials where the formation of quasi-molecular orbitals may significantly affect the system's physical properties include such oxides of Ru as SrRu<sub>2</sub>O<sub>6</sub> [10–14] and AgRuO<sub>3</sub> [15,16]. It should be noted that the Ru ion in such compounds has the valency 5+, which corresponds to three electrons on the  $t_{2g}$ -shell of the given ion or six  $d$ -electrons on an elementary cell. In this case, quasi-molecular orbitals of  $B_{1u}$  and  $E_{2g}$  symmetry are completely filled and a gap opens in the band spectrum, see Fig. 1 and [9]. It is important that splittings in this spectrum are determined by values of integrals of transition  $t_{pd}$  from site to site via  $p$ -orbitals of the ligand [7]. In this respect, it is interesting to find out how the pattern

of quasi-molecular orbitals, the electronic structure on the whole and the system's physical properties will change when the  $4d$ -ion of the transition metal is substituted by  $5d$ . In this case an increase of the principle quantum number will result in a larger extension of  $d$ -orbitals, and, consequently, an increase of  $t_{pd}$  [17,18].

This paper deals with modelling of structural and electronic properties of the SrOs<sub>2</sub>O<sub>6</sub> compound based on  $5d$ -metal Os. A calculation of the enthalpy of formation has shown this material to be stable. The crystalline structure and the band spectrum of this system have been studied.

**2. Calculation details**

In this paper, structural and electronic properties of the SrOs<sub>2</sub>O<sub>6</sub> compound have been calculated within the framework of the density functional theory (DFT) methods using VASP (Vienna Ab-initio Simulation Package) [19]. The calculations were performed within the framework of general gradient approximation (GGA), in the PBE



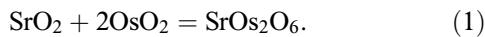
**Figure 1.** Electron distribution over quasi-molecular orbitals in case of electron configuration  $d^3$ .

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(Perdew–Burke–Ernzerhof) formulation [20]. Energy of plane wave cutoff  $E_{cutoff}$  in the calculations was taken equal to 520 eV. Number of  $k$ -points in the first Brillouin zone was chosen to correspond to its  $5 \times 5 \times 5$  mesh (the Monkhorst–Pack scheme) [21] for all the structures under study. The calculations were performed using the approximation of projected augmented waves — PAW-potentials [22] Sr ( $4s4p5s$ ), Os ( $5p6s5d$ ) and O ( $s^2p^4$ ). The initial parameters of the crystalline structure were taken for SrO<sub>2</sub> from [23] and for OsO<sub>2</sub> from [24].

### 3. Results and discussion

Enthalpy of formation of the SrOs<sub>2</sub>O<sub>6</sub> compound was calculated by considering the chemical reaction



At the first stage, the dependencies of total energy on volume for SrOs<sub>2</sub>O<sub>6</sub>, SrO<sub>2</sub> and OsO<sub>2</sub> have been obtained by a series of calculations where the elementary cell volume varied within  $\pm 10\%$  from the average value (Fig. 2).

In order to assess the values of equilibrium volume and energy, the dependencies  $E(V)$  were approximated by the Birch–Murnaghan equation of state of the 3-rd order

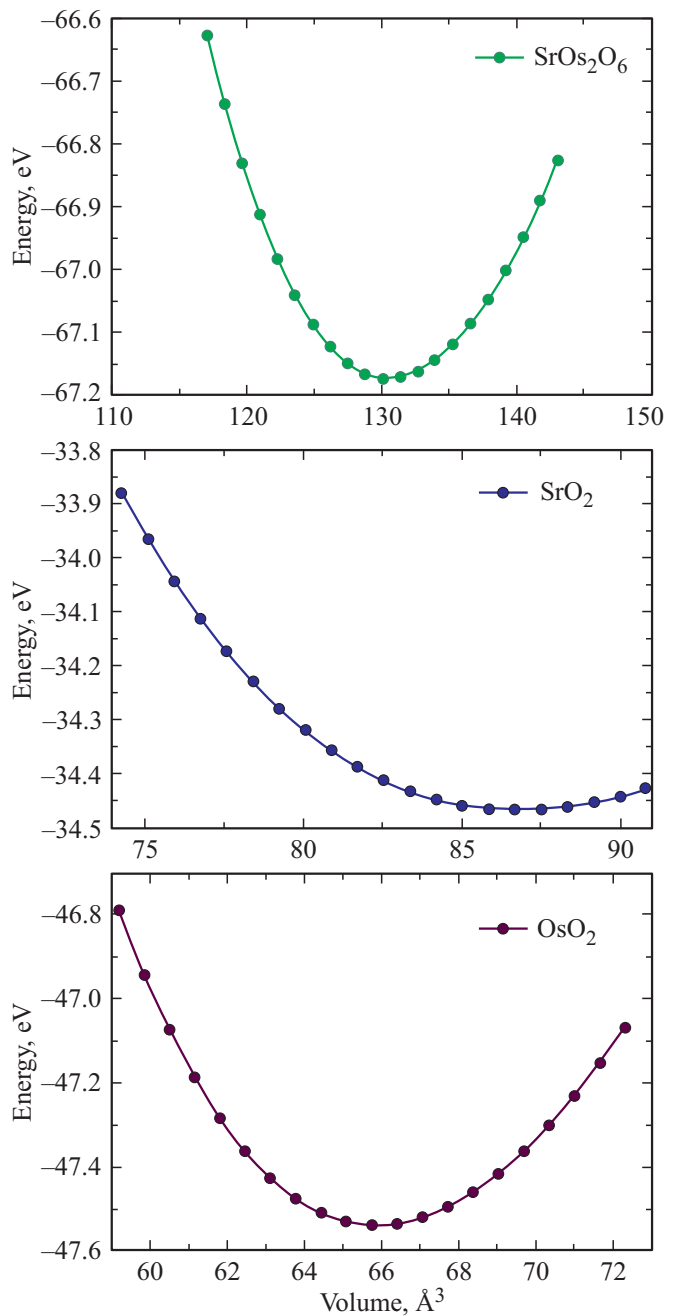
$$E(V) = E_0 + \frac{9V_0B_0}{16} \left( \left( \left( \frac{V_0}{V} \right)^{2/3} - 1 \right)^3 B'_0 + \left( \left( \frac{V_0}{V} \right)^{2/3} - 1 \right)^2 \left( 6 - 4 \left( \frac{V_0}{V} \right)^{2/3} \right) \right), \quad (2)$$

where  $V_0$  is the elementary cell volume at the normal pressure,  $E_0$  is the energy corresponding to the equilibrium volume,  $B_0$  is the modulus (coefficient) of all-round compression and  $B'_0$  is the derivative of modulus  $B_0$  by pressure. The values of quantities  $E_0$ ,  $V_0$ ,  $B_0$ ,  $B'_0$ , obtained by approximation, are given in Table 1.

The analysis of Table 1 shows that the calculated values of equilibrium volumes  $V_0$  are close to the experimental ones, so that quantity  $(V_0 - V_0^{\text{exp}})/V_0^{\text{exp}}$  is 5.2% for SrO<sub>2</sub> [23] and 0.022 for OsO<sub>2</sub> [24]. The obtained values are within a mean-square error of DFT-calculations [25].

**Table 1.** Parameters of the equation of state for the SrOs<sub>2</sub>O<sub>6</sub>, SrO<sub>2</sub>, OsO<sub>2</sub> compounds, obtained by approximation of dependencies  $E(V)$  by the Birch–Murnaghan equation of state of the 3-rd order

Parameter	SrOs <sub>2</sub> O <sub>6</sub>	SrO <sub>2</sub>	OsO <sub>2</sub>
$E_0$ , eV	−67.2	−34.5	−47.5
$V_0$ , Å <sup>3</sup>	130.5	86.8	65.9
$B_0$ , GPa	106.4	77.3	286.3
$B'_0$	3.8	4.7	4.7

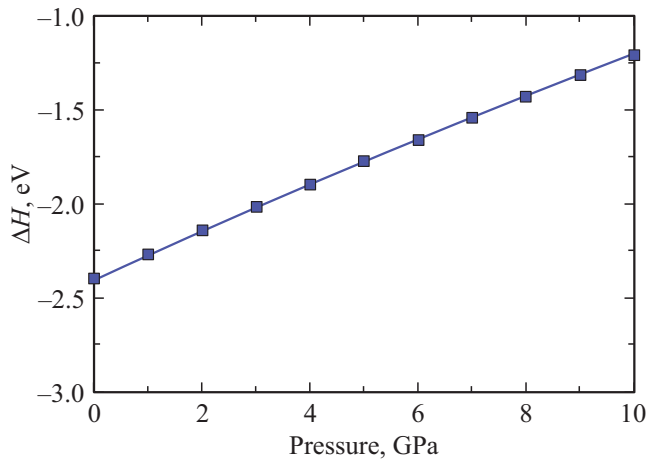


**Figure 2.** Dependencies of total energy on elementary cell volume for SrOs<sub>2</sub>O<sub>6</sub>, SrO<sub>2</sub> and OsO<sub>2</sub>.

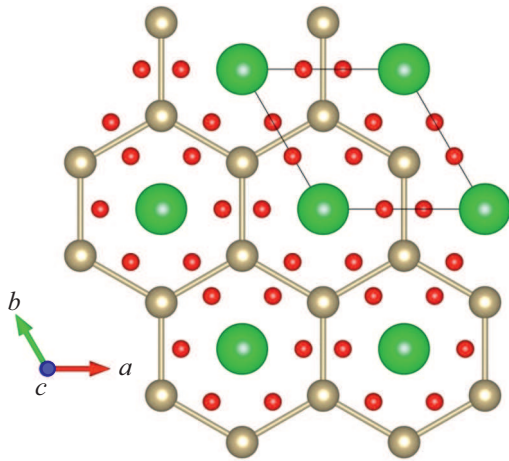
Thermodynamic stability of SrOs<sub>2</sub>O<sub>6</sub> was studied by comparing the enthalpies for SrOs<sub>2</sub>O<sub>6</sub> and SrO<sub>2</sub> + 2OsO<sub>2</sub> involved in reaction (1), which is shown in Fig. 3.

Figure 3 shows that the SrOs<sub>2</sub>O<sub>6</sub> compound remains stable under the normal conditions, which makes it possible to further study its crystalline and electronic structures, as well as the band spectrum.

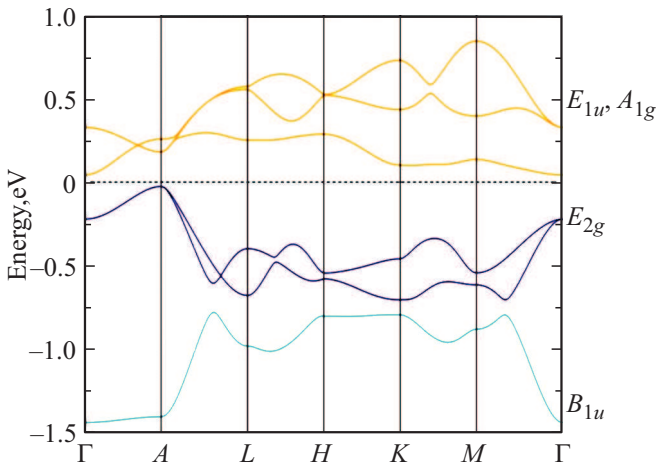
The crystalline structure of SrOs<sub>2</sub>O<sub>6</sub> is described by a symmetry group  $P-31m$ ; the lattice parameters and atom positions optimized in DFT are given in Table 2. The Os atoms are at the tops of the hexagons that form a honey-



**Figure 3.** Dependency of calculated relative enthalpy  $\Delta H$  of  $\text{SrOs}_2\text{O}_6$  as related to  $(\text{SrO}_2 + 2\text{OsO}_2)$  on pressure.



**Figure 4.** Projection of the crystalline structure of  $\text{SrOs}_2\text{O}_6$  on  $ab$  plane. The Os atoms are represented by medium-sized (brown) balls connected by lines that show formation of hexagons. Oxygen atoms — small (red) balls, and Sr — the largest (green) balls in the centers of hexagons.



**Figure 5.** Band structure of  $\text{SrOs}_2\text{O}_6$  obtained for the non-magnetic state.

**Table 2.** Lattice parameters and atom coordinates for the  $\text{SrOs}_2\text{O}_6$  compound

Symmetry	Lattice parameters	Atom positions
$P-31m$	$a = 5.37152 \text{ \AA}$ $c = 5.25716 \text{ \AA}$	Sr: $a$ (0.000, 0.000, 0.000) Os: $d$ (0.333 0.667 0.500) O: $k$ (0.378 0.000 0.301)

comb lattice, see Fig. 4. The Sr and O atoms are between the planes formed by Os atoms. Thus, the  $\text{SrOs}_2\text{O}_6$  compound is isostructural to the  $\text{SrRu}_2\text{O}_6$  compound, and it can be expected that its electronic spectrum can be described by the concept of quasi-molecular orbitals, centered on  $\text{Os}^{5+}$  hexagons, suggested in [5], while band states can be classified by means of irreducible representations of  $D_{6h}$  group.

Figure 5 shows the band structure obtained by a DFT calculation without account of magnetic interaction for the  $\text{SrOs}_2\text{O}_6$  compound. There are six bands near the Fermi level; they can be described using quasi-molecular orbitals with symmetry  $A_{1g}$ ,  $E_{1u}$ ,  $E_{2g}$ ,  $B_{1u}$  ( $E_{1u}$  and  $E_{2g}$  are doubly degenerate) [10]. These bands mainly have the Os  $t_{2g}$  character the Os  $t_{2g}$  pattern (two Os atoms in an elementary cell). Three of them are empty ( $A_{1g}$  and doubly degenerated  $E_{1u}$ ) and are separated by a gap from  $E_{2g}$  and  $B_{1u}$ , in the same way as in  $\text{SrRu}_2\text{O}_6$ .

In addition to the nonmagnetic DFT-calculations, simulations were done for the ferromagnetic and antiferromagnetic (the nearest neighbors are antiferromagnetic) configurations of spins of  $\text{Os}^{5+}$  ions. The calculations have showed that the energy, corresponding to the antiferromagnetic state, is lower the energy, corresponding to the ferromagnetic state. The energy difference is  $\delta E = 0.145 \text{ eV/f.u.}$  (f.u. — formula unit). This result means that the antiferromagnetic state is more favorable and can be expected to appear in the low-temperature region of  $\text{SrOs}_2\text{O}_6$ . The magnetic moment, calculated from the first principles, for the antiferromagnetic configuration of spins of  $\text{Os}^{5+}$  ions is heavily suppressed and equals to  $1.34 \mu_B$ , where  $\mu_B$  is the Bohr magneton, which is due to both to the significant hybridization with oxygen and because of formation of quasi-molecular orbitals.

## 4. Conclusion

This paper outlines the modelling of structural and electronic properties of a new material — osmium oxide (V)  $\text{SrOs}_2\text{O}_6$  from the first principles. This compound has been shown to be thermodynamically stable under the normal conditions. The crystalline structure of  $\text{SrOs}_2\text{O}_6$  and the band spectrum have been obtained for the non-magnetic state, which is described by the concept of quasi-molecular orbitals centered on  $\text{Os}^{5+}$  hexagons, thereat, the band states can be classified using the irreducible representations

of  $D_{6h}$  group. The antiferromagnetic state has been shown to be energetically favorable for  $\text{SrOs}_2\text{O}_6$ .

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### Conflict of interest

The authors declare that they have no conflict of interest.

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