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Structural and electronic properties of a new material — $SrOs_2O_6$*

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It was shown theoretically that a new material $SrOs_2O_6$ can exist; the crystal structure of $SrOs_2O_6$ is formed by the layers of OsO_6 octahedra having common edges and forming a honeycomb type lattice. The structural and electronic properties of $SrOs_2O_6$ 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., α-$RuCl_3$, Na_2IrO_3 or Li_2IrO_3 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 $SrRu_2O_6$ [10–14] and $AgRuO_3$ [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 $SrOs_2O_6$ 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 $SrOs_2O_6$ 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

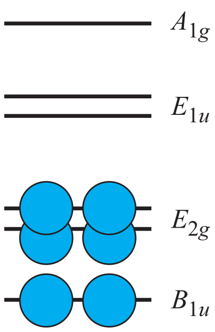

Figure 1. Electron distribution over quasi-molecular orbitals in case of electron configuration d^3.

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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 $5\times5\times5$ 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_2 from [23] and for OsO_2 from [24].

3. Results and discussion

Enthalpy of formation of the $SrOs_2O_6$ compound was calculated by considering the chemical reaction

$$SrO_2 + 2OsO_2 = SrOs_2O_6. \qquad (1)$$

At the first stage, the dependencies of total energy on volume for $SrOs_2O_6$, SrO_2 and OsO_2 have been obtained by a series of calculations where the elementary cell volume varied within ±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

$$E(V)=E_0+\frac{9V_0B_0}{16}\left(\left(\left(\frac{V_0}{V}\right)^{2/3}-1\right)^3 B_0' + \left(\left(\frac{V_0}{V}\right)^{2/3}-1\right)^2\left(6-4\left(\frac{V_0}{V}\right)^{2/3}\right)\right), \qquad (2)$$

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 $(V_0-V_0^{\mathrm{exp}})/V_0^{\mathrm{exp}}$ is 5.2% for SrO_2 [23] and 0.022 for OsO_2 [24]. The obtained values are within a mean-square error of DFT-calculations [25].

Table 1. Parameters of the equation of state for the $SrOs_2O_6$, SrO_2, OsO_2 compounds, obtained by approximation of dependencies $E(V)$ by the Birch–Murnaghan equation of state of the 3-rd order

Parameter	$SrOs_2O_6$	SrO_2	OsO_2
E_0, eV	−67.2	−34.5	−47.5
V_0, Å	130.5	86.8	65.9
B_0, GPa	106.4	77.3	286.3
B_0'	3.8	4.7	4.7

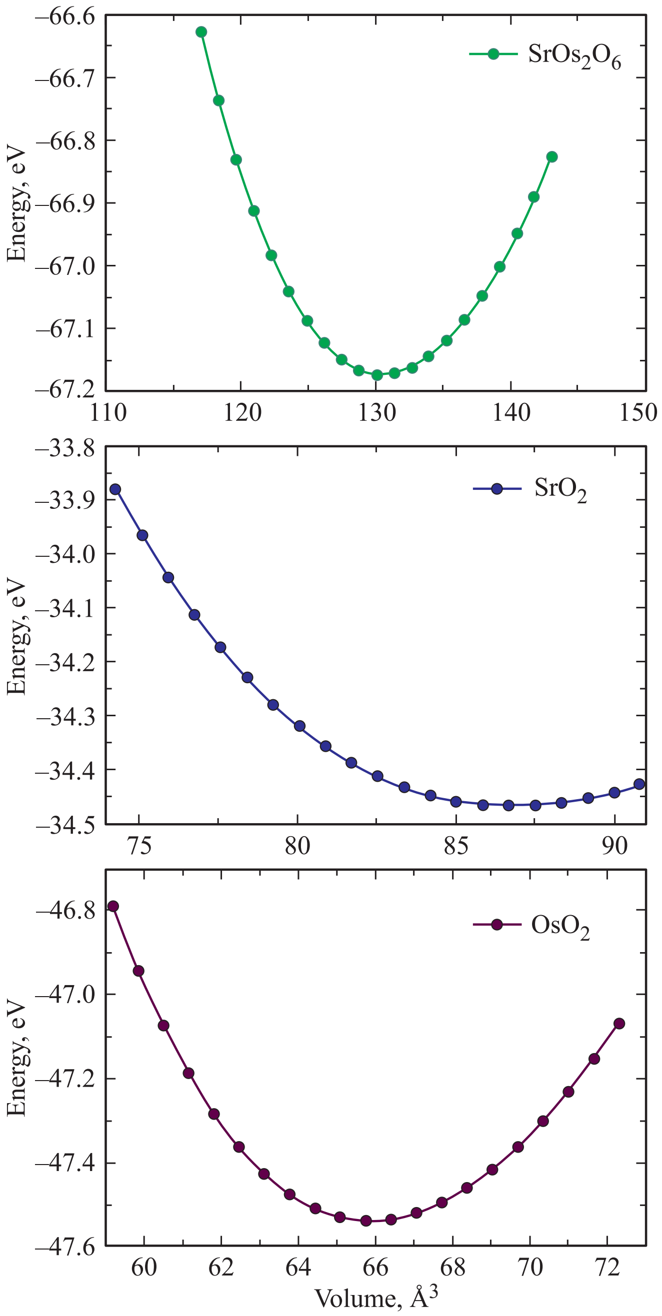

Figure 2. Dependencies of total energy on elementary cell volume for $SrOs_2O_6$, SrO_2 and OsO_2.

Thermodynamic stability of $SrOs_2O_6$ was studied by comparing the enthalpies for $SrOs_2O_6$ and $SrO_2 + 2OsO_2$ involved in reaction (1), which is shown in Fig. 3.

Figure 3 shows that the $SrOs_2O_6$ 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 $SrOs_2O_6$ 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-

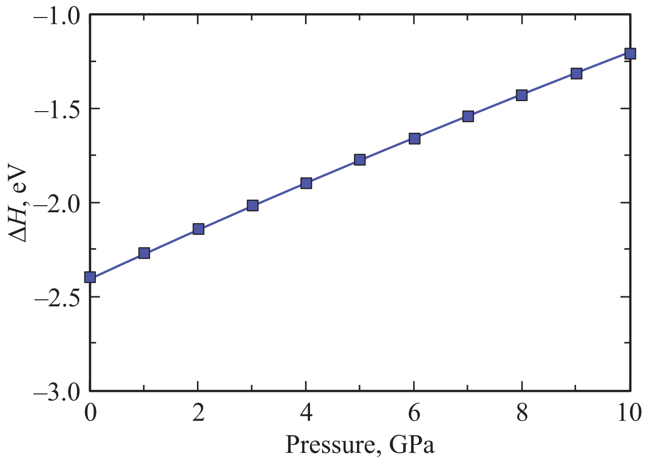

Figure 3. Dependency of calculated relative enthalpy ΔH of $SrOs_2O_6$ as related to $(SrO_2 + 2OsO_2)$ on pressure.

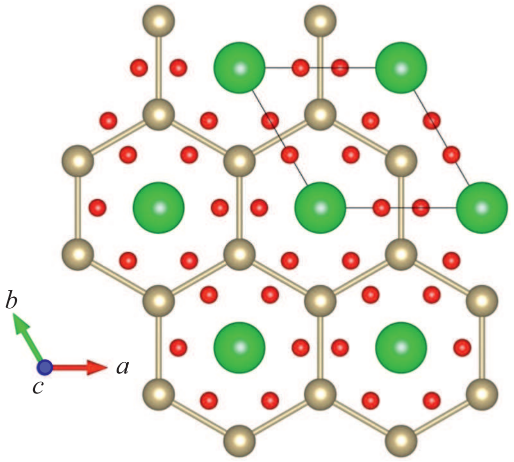

Figure 4. Projection of the crystalline structure of $SrOs_2O_6$ on *ab* plane. The Os atoms are represented by medium-sized (brown) balls connected by lines that show formation of hexagons. Oxygen atoms — small (red) balls, and Sr — the largest (green) balls in the centers of hexagons..

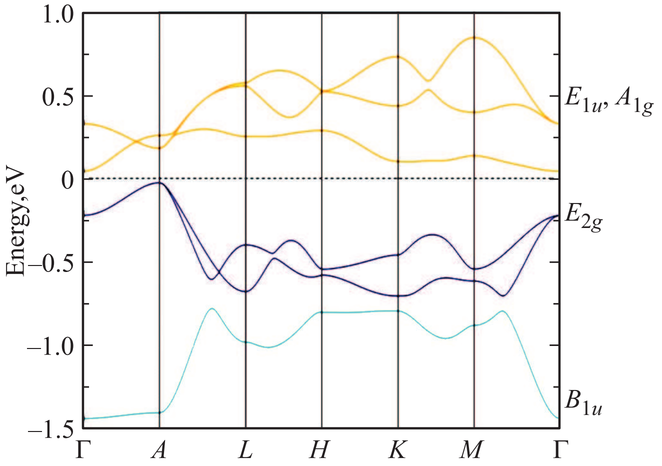

Figure 5. Band structure of $SrOs_2O_6$ obtained for the non-magnetic state.

Table 2. Lattice parameters and atom coordinates for the $SrOs_2O_6$ compound

Symmetry	Lattice parameters	Atom positions
$P{-}31m$	$a = 5.37152\,\text{Å}$ $c = 5.25716\,\text{Å}$	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 $SrOs_2O_6$ compound is isostructural to the $SrRu_2O_6$ compound, and it can be expected that its electronic spectrum can be described by the concept of quasi-molecular orbitals, centered on 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 $SrOs_2O_6$ 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 $SrRu_2O_6$.

In addition to the nonmagnetic DFT-calculations, simulations were done for the ferromagnetic and antiferromagnetic (the nearest neighbors are antiferromagnetic) configurations of spins of 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 $\delta E = 0.145$ 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 $SrOs_2O_6$. The magnetic moment, calculated from the first principles, for the antiferromagnetic configuration of spins of Os^{5+} ions is heavily suppressed and equals to $1.34\mu_B$, where μ_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) $SrOs_2O_6$ from the first principles. This compound has been shown to be thermodynamically stable under the normal conditions. The crystalline structure of $SrOs_2O_6$ and the band spectrum have been obtained for the non-magnetic state, which is described by the concept of quasi-molecular orbitals centered on 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 $SrOs_2O_6$.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S.M. Winter, A.A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, R. Valenti. J. Phys. Condens. Matter **29**, 493002 (2017).

[2] H. Takagi, T. Takayama, G. Jackeli, G. Khaliullin, S.E. Nagler. Nature Rev. Phys. **1**, 264 (2019).

[3] D.I. Khomskii, S.V. Streltsov. Chem. Rev. **121**, 2992 (2021).

[4] S.A.J. Kimber, I.I. Mazin, J. Shen, H.O. Jeschke, S.V. Streltsov, D.N. Argyriou, R. Valenti, D.I. Khomskii. Phys. Rev. B **89**, 081408 (2014).

[5] Z.V. Pchelkina, A.L. Pitman, A. Moewes, E.Z. Kurmaev, T.-Y. Tan, D.C. Peets, J.-G. Park, S.V. Streltsov. Phys. Rev. B **91**, 115138 (2015).

[6] J. Park, T. Tan, D.T. Adroja, A. Daoud-Aladine, S. Choi, D. Cho, S. Lee, J. Kim, H. Sim, T. Morioka, H. Nojiri, V.V Krishnamurthy, P. Manuel, M.R. Lees, S.V. Streltsov, D.I. Khomskii, J.-G. Park. Sci. Rep. **6**, 25238 (2016).

[7] I.I. Mazin, H.O. Jeschke, K. Foyevtsova, R. Valentí, D.I. Khomskii. Phys. Rev. Lett. **109**, 197201 (2012).

[8] Z.V. Pchelkina, S.V. Streltsov, I.I. Mazin. Phys. Rev. B **94**, 205148 (2016).

[9] S.V. Streltsov. Phys. Met. Metallogr. **119**, 1276 (2018).

[10] S. Streltsov, I.I. Mazin, K. Foyevtsova. Phys. Rev. B **92**, 134408 (2015).

[11] C.I. Hiley, M.R. Lees, J.M. Fisher, D. Thompsett, S. Agrestini, R.I. Smith, R.I. Walton. Angew. Chem. Int. Ed. **53**, 4423 (2014).

[12] W. Tian, C. Svoboda, M. Ochi, M. Matsuda, H.B. Cao, J. Cheng, B.C. Sales, D.G. Mandrus, R. Arita, N. Trivedi, J. Yan. Phys. Rev. B **92**, 100404 (2015).

[13] H. Suzuki, H. Gretarsson, H. Ishikawa, K. Ueda, Z. Yang, H. Liu, H. Kim, D. Kukusta, A. Yaresko, M. Minola, J.A. Sears, S. Francoual, H. Wille, J. Nuss, H. Takagi, B.J. Kim, G. Khaliullin, H. Yavaş, B. Keimer. Nature Mater. **18**, 563 (2019).

[14] Y.S. Ponosov, E.V Komleva, D.A. Zamyatin, R.I. Walton, S.V Streltsov. Phys. Rev. B **99**, 85103 (2019).

[15] B.E. Prasad, S. Kanungo, M. Jansen, A.C. Komarek, B. Yan, P. Manuel, C. Felser. Chem. Eur. J. **23**, 1521 (2017).

[16] W. Schnelle, B.E. Prasad, C. Felser, M. Jansen, E.V. Komleva, S.V. Streltsov, I.I. Mazin, D. Khalyavin, P. Manuel, S. Pal, D.V.S. Muthu, A.K. Sood, E.S. Klyushina, B. Lake, J.-C. Orain, H. Luetkens. Phys. Rev. B **103**, 214413 (2021).

[17] W.A. Harrison. Elementary Electronic Structure. World Scientific, Singapore (1999).

[18] S.V. Streltsov, D.I. Khomskii. Phys.-Usp. **60**, 1121 (2017).

[19] G. Kresse, J. Hafner. Phys. Rev. B **47** 558 (1993).

[20] J.P. Perdew, K. Burke, M. Ernzerhof. Phys. Rev. Lett. **77**, 3865 (1996).

[21] H. Monkhorst, J. Pack. Phys.Rev. B **13**, 5188 (1976).

[22] G. Kresse, D. Joubert. Phys. Rev. B **59**, 1758 (1999).

[23] J.D. Bernal, E. Djatlowa, I. Kasarnowsky, S. Reichstein, A.G. Ward. Z. Kristallogr. Cryst. Mater. **92**, 344–354 (1935).

[24] Y.C. Venudhar, L. Iyengar, K.V. Krishna Rao. Cryst. Res. Technol. **20**, 1393 (1985).

[25] R.M. Martin. Electronic Structure: Basic Theory and Practical Methods. Cambridge University Press, Cambridge (2004).