Research Letter

Electronic Properties of $\text{NdOs}_4\text{Sb}_{12}$

Donald H. Galvan

Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, 22800 Ensenada, Baja California, Mexico

Correspondence should be addressed to Donald H. Galvan, dgalvan@che.utexas.edu

Received 11 July 2007; Accepted 9 November 2007

Recommended by Tsutomu Ohzuku

Theoretical calculations on $\text{NdOs}_4\text{Sb}_{12}$ -filled skutterudite are reported. The calculated energy bands yield indication of a semimetallic behavior, while the projected density of states provides support for the existence of hybridization formed by Nd f-, Os d-, and Sb p-states.

Copyright © 2007 Donald H. Galvan. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. INTRODUCTION

The filled skutterudite compounds general structural formula RT_4X_{12} (where R = alkaline (Na, K), alkaline earth (Ca, Sr, Ba), lanthanide or actinide atoms; T = transition metal atoms (Fe, Ru or Os); X = pnictogen atoms (P, As, Sb)). These compounds crystallize [1] in the cubic $\text{LaFe}_4\text{P}_{12}$ -filled skutterudite with space group Im-3-T_h^5 , No. 204, which displays interesting physical properties, due to the various degree of hybridization of the 4 f of the R ion with the ligand states (T_4X_{12}) sublattice. The phenomena displayed by the filled skutterudite include small hybridization gap semiconductivity (known as “Kondo insulator” behavior) [2], valence fluctuation and heavy Fermion behavior [3–6], non-Fermi liquid behavior [7], metal-to-insulator transition [8], magnetic order [9, 10], superconductivity [11, 12], ferromagnetism [13], and recently, certain filled skutterudites [14, 15] have shown high values of the thermoelectric figure of merit Z . Therefore, these materials have elucidated interest as candidates for thermoelectric applications.

2. COMPUTATIONAL DETAILS

The calculations reported in this work were carried out by means of the tight-binding method [16] within the extended Huckel [17] framework using YAEHMOP [18] computer package with f orbitals. More details about the mathematical formulation of this method are given elsewhere [19] and are omitted here for brevity.

The structure of $\text{NdOs}_4\text{Sb}_{12}$ is illustrated in Figure 1 from Ho et al. [20]. Large spheres represent Nd, medium-size

spheres depict Os, and smaller spheres represent Sb atoms, respectively. It is characterized by the space group: Im-3-T_h^5 No. 204, $Z = 2$, with primitive vector $a = 0.93075(2)$ nm, with the Nd atom located in the position $(2a)$, the Os atoms located at $(8c)$, and the Sb atoms located at $(24g)$ with $y = 0.15597(3)$ and $z = 0.34017$ of π/a .

3. RESULTS AND DISCUSSION

The band structure for $\text{NdOs}_4\text{Sb}_{12}$ was calculated using 51 k points, sampling the first Brillouin zone (FBZ) as shown in Figure 2. The Fermi level (E_f) is indicated in the figure by a horizontal dotted line. The inset in Figure 2 depicts the Wigner-Seitz cell for a base center cubic (BCC) configuration spanning from Γ (0 0 0) to H (0 $\pi/2a$ 0) to N ($\pi/4a$ $\pi/4a$ 0) to Γ (0 0 0) to P ($\pi/4a$ $\pi/4a$ $\pi/4a$) which generates the three-dimensional cell. From the band structure calculations on this compound, and shown in Figure 2, one immediately see that E_f is located in a highly localized band indicating that $\text{NdOs}_4\text{Sb}_{12}$ shows metallic behavior. One of the important characteristics displayed for skutterudites is a tendency to form a pseudogap, especially when a single antimonide p-band crosses the Fermi level. This band is pushed down by the repulsion with Nd f-states.

Ho et al. [20] reported an investigation on $\text{NdOs}_4\text{Sb}_{12}$ single crystal by transport properties and specific heat measurements and obtained results leading to the possibility for heavy Fermion behavior with a large electronic specific heat $\gamma \cong 421$ mJ/mol-K² and with an effective mass $m^* \cong 80 m_e$ (m_e : electron mass). Moreover, magnetization

FIGURE 1

FIGURE 2

FIGURE 3

measurements on the sample indicated a ferromagnetic transition of the order of 0.9 K with a mean-field ferromagnetic behavior.

A general belief in heavy Fermion compounds is the prediction that due to the existence of hybridization between localized f-electrons and conduction electrons, a gap must be open/close to the Fermi level [21, 22]. However, the universality of this asseveration is still an open debate.

Total and projected density of states (PDOS) for $\text{NdOs}_4\text{Sb}_{12}$ was calculated separately for each atom in question in order to obtain the appropriate contribution to the total DOS. For Nd (f, d, p, and s); Os (d, p, and s) and Sb (p and s) contributions were calculated separately. The information is provided in Figure 3, where the vertical axis is energy $E(\text{eV})$ versus % contribution in the horizontal axis. Considering the highest peak as 100%, and the other contributions are scaled according to these peak. Also, the hatched lines are the selected projected DOS from each orbital.

Another objective searched in this investigation is to provide evidence for the existence (or absence) of a hybridization between orbitals from the atoms that form the unit cell in $\text{NdOs}_4\text{Sb}_{12}$. This information is provided in Figure 3, where only Nd f-, Os d-, and Sb p-orbitals contribute to form the hybridization. Notice that Nd f-orbitals are located at the middle of the E_f and contribute with $\cong 60\%$, Os d-orbitals contribute with $\cong 22\%$ and Sb p-orbitals contribute with $\cong 5\%$ to the total DOS. Also, notice that there is a large value of the DOS at the E_f , a strong support to the heavy Fermion behavior as has been reported experimentally [20].

4. CONCLUDING REMARKS

The following conclusions could be drawn from the calculations described herein for $\text{NdOs}_4\text{Sb}_{12}$. Our band structure calculations yielded indication of the absence of a detected minigap, henceforth, our band structure calculations yielded

indication of the absence of a detected minigap as shown in Figure 2. Moreover, notice that a single band crosses the Fermi level yielding indication of the semimetallic behavior for this compound. Afterwards, a strong hybridization exists in $\text{NdOs}_4\text{Sb}_{12}$ formed by contributions from Nd f- with Os d- and Sb p-states, which make us suspect that the large contribution from the DOS at the Fermi level could be an indication of the heavy Fermion behavior.

REFERENCES

- [1] W. Jeitschko and D. J. Braun, "LaFe₄P₁₂ with filled CoAs₃-type structure and isotypic lanthanoid-transition metal polyphosphides," *Acta Crystallographica B*, vol. 33, pp. 3401–3406, 1977.
- [2] G. P. Meisner, M. S. Torikachvili, K. N. Yang, M. B. Maple, and R. P. Guertin, "UFe₄P₁₂ and CeFe₄P₁₂: nonmetallic isotypes of superconducting LaFe₄P₁₂," *Journal of Applied Physics*, vol. 57, no. 8, pp. 3073–3075, 1985.
- [3] D. T. Morelli and G. P. Meisner, "Low temperature properties of the filled skutterudite CeFe₄Sb₁₂," *Journal of Applied Physics*, vol. 77, pp. 3777–3781, 1995.
- [4] D. A. Gajewski, N. R. Dilley, E. D. Bauer, et al., "Heavy fermion behaviour of the cerium-filled skutterudites CeFe₄Sb₁₂ and Ce_{0.9}Fe₃CoSb₁₂," *Journal of Physics: Condensed Matter*, vol. 10, no. 31, pp. 6973–6985, 1998.
- [5] M. B. Maple, N. R. Dilley, D. A. Gajewski, et al., "Strongly correlated electron phenomena in filled skutterudite compounds," *Physica B*, vol. 259–261, pp. 8–9, 1999.
- [6] D. H. Galvan and C. Samaniego, "Electronic structure calculations for PrOs₄Sb₁₂ filled skutterudite. A theoretical approach using extended Huckel tight-binding method," *Physical Review B*, vol. 70, no. 4, Article ID 045108, 5 pages, 2004.
- [7] N. Takeda and M. Ishikawa, "Anomalous magnetic properties of CeRu₄Sb₁₂," *Physica B*, vol. 259–261, pp. 92–93, 1999.
- [8] C. Sekine, T. Uchiumi, I. Shirotni, and T. Yagi, "Metal-insulator transition in PrRu₄P₁₂ with skutterudite structure," *Physical Review Letters*, vol. 79, no. 17, pp. 3218–3221, 1997.
- [9] M. S. Torikachvili, C. Rossel, M. W. McElfresh, M. B. Maple, R. P. Guertin, and G. P. Meisner, "Low temperature specific heat and magnetoresistance of the ferromagnetic semiconductor UFe₄P₁₂," *Journal of Magnetism and Magnetic Materials*, vol. 54–57, pp. 365–366, 1986.
- [10] M. E. Danebrock, C. B. H. Evers, and W. Jeitschko, "Magnetic properties of alkaline earth and lanthanoid iron antimonides AFe₄Sb₁₂ (A = Ca, Sr, Ba, La-Nd, Sm, Eu) with the LaFe₄P₁₂ structure," *Journal of Physics and Chemistry of Solids*, vol. 57, no. 4, pp. 381–387, 1996.
- [11] G. P. Meisner, G. R. Stewart, M. S. Torikachvili, and M. B. Maple, in *Proceedings of the 17th International Conference on Low Temperature Physics*, U. Eckern, A. Schmid, W. Weber, and H. Wuhl, Eds., p. 711, Elsevier, Amsterdam, The Netherlands, August 1984.
- [12] I. Shirotni, T. Uchiumi, and K. Ohno, "Superconductivity of filled skutterudites LaRu₄As₁₂ and PrRu₄As₁₂," *Physical Review B*, vol. 56, no. 13, pp. 7866–7869, 1997.
- [13] E. Bauer, S. Berger, Ch. Paul, et al., "Crystal field effects and thermoelectric properties of PrFe₄Sb₁₂ skutterudite," *Physical Review B*, vol. 66, no. 21, Article ID 214421, 9 pages, 2002.
- [14] B. C. Sales, D. Mandrus, and R. K. Williams, "Filled skutterudite antimonides: a new class of thermoelectric materials," *Science*, vol. 272, no. 5266, pp. 1325–1328, 1996.
- [15] J.-P. Fleurial, A. Borshchevsky, T. Caillat, D. T. Morelli, and G. P. Meisner, in *Proceedings of the 15th International Conference on Thermoelectrics*, p. 186, IEEE Piscataway, Pasadena, Calif, USA, March 1996.
- [16] M.-H. Whangbo and R. Hoffmann, "The band structure of the tetracyanoplatinate chain," *Journal of the American Chemical Society*, vol. 100, no. 19, pp. 6093–6098, 1978.
- [17] R. Hoffmann, "An extended Hückel theory. I. Hydrocarbons," *Journal of Chemical Physics*, vol. 39, no. 6, pp. 1397–1412, 1963.
- [18] G. A. Landrum, "The YAEHMOP package," <http://overlap.chem.Cornell.edu:8080/yaehmop.html>. F orbitals are included in the calculation as a version 3.x, using W. V. Glassey's routine.
- [19] D. H. Galván, "Extended Hückel calculations on cubic boron nitride and diamond," *Journal of Materials Science Letters*, vol. 17, no. 10, pp. 805–810, 1998.
- [20] P.-C. Ho, W. M. Yuhasz, N. P. Butch, et al., "Ferromagnetism and possible heavy-fermion behavior in single crystals of NdOs₄Sb₁₂," *Physical Review B*, vol. 72, Article ID 094410, 9 pages, 2005.
- [21] A. J. Mills, M. Lavagna, and P. A. Lee, "Plasma oscillations in heavy-fermion materials," *Physical Review B*, vol. 36, no. 1, pp. 864–867, 1987.
- [22] P. Fulde, *Electron Correlations in Molecules & Solids*, Springer, Berlin, Germany, 2nd edition, 1993.