Physica B 405 (2010) 3213–3216

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Electronic band structure of new "122" pnictogen-free superconductor $SrPd_2Ge_2$ as compared with $SrNi_2Ge_2$ and $SrNi_2As_2$ from first principles calculations

I.R. Shein, A.L. Ivanovskii *

Institute of Solid State Chemistry, Ural Division, Russian Academy of Sciences, Pervomaiskaya St. 91, Ekaterinburg 620990, Russia

A R T I C L E   I N F O

Article history:
Received 31 August 2009
Accepted 21 April 2010

Keywords:
Tetragonal $SrPd_2Ge_2$
$SrNi_2Ge_2$
$SrNi_2As_2$
Structural
Electronic properties
ab initio calculations

A B S T R A C T

Very recently the new low-temperature (T_C~3 K) superconductor (SC) $SrPd_2Ge_2$ has been reported. This compound is isostructural with curently intensively studied group of so-called "122" SCs (based on tetragonal AM_2Pn_2 phases, where A are Sr, Ba; M are d metals and Pn are pnictogens: As or P), but it is pnictogen-free. Here, by means of first-principle FLAPW-GGA calculations, we have studied the electronic structure of new SC $SrPd_2Ge_2$. The band structure, total and partial densities of states and Fermi surface topology for $SrPd_2Ge_2$ are evaluated and discussed in comparison with those of isostructural $SrNi_2Ge_2$ and $SrNi_2As_2$ phases.

1. Introduction

Since Hosono et al. have found superconductivity with T_C~27 K in iron pnictides [1], so far, six related groups of novel superconducting materials have been uncovered in this class: ROMPn (so-called "1111" phases), AM_2Pn_2 (so-called "122" phases), AFeAs (so-called "111" phases), $FeSe_{1-x}$ and more complex $A_3M_2M'_2Pn_2O_5$ and $A_4M_2M'_2Pn_2O_6$ (so-called "32225" and "42226" (denoted sometimes also as 21113) phases, respectively). Here A are alkaline metals or alkaline earth metals, R are rare earth metals, M, M′ are transition metals and Pn are pnictogens.

All the mentioned materials are anisotropic (quasi-two-dimensional, 2D) systems with a crystal structure formed by negatively charged blocks $[M_2Pn_2]^{\delta-}$ alternating with positively charged blocks or atomic sheets. The superconductivity in all these systems is attributed to the $[M_2Pn_2]$ blocks, which make a decisive contribution to the near-Fermi region of these materials, while the positively charged blocks (for example, $[RO]^{\delta+}$ or $A^{\delta+}$) serve as the so-called charge reservoirs, see Refs. [2–9].

In particular, a broad family of the mentioned "122" superconductors (SC's) with transition temperatures up to T_C~38 K (see Refs. [2–5,10–16]) based on AFe_2As_2 phases (A=Ca, Sr or Ba) was prepared by hole doping, i.e. by partial substitution of alkaline metals for alkaline earth metals or by partial replacement of Fe (in $[Fe_2As_2]$ blocks) by other 3d transition metals as Mn, Co or Ni. Note that all these materials have a high content of *magnetic metals* (Fe, Mn, Co and Ni). Interestingly, the same result may be achieved by *partial substitution* of some *non-magnetic 4d, 5d metals* (Ru, Ir etc.) by *magnetic 3d metal* (Fe), see Refs. [17–20].

Moreover, very recently new "122" iron-free pnictides, namely, $SrNi_2As_2$, $^{18}BaNi_2As_2$, $BaNi_2P_2$, $^{20}SrRu_2As_2$, $BaRu_2As_2$ [20] $SrRh_2As_2$ [21], $BaRh_2P_2$ (T_C~1 K), $BaIr_2P_2$ and $BaRh_2As_2$ [22] were synthesized. These materials, where *magnetic metal* (Fe) *is completely replaced by the other 3d magnetic metal* (Ni) *or non-magnetic metals* (Ru, Rh) *arsenic is completely replaced by other pnictogen—phosphorus*, belong to the above mentioned "122" family and are low-temperature SCs (T_C~0.3–3.0 K), see Refs. [21–24].

Thus, the recent report [25] on the synthesis of a new low-temperature (T_C~3 K) SC $SrPd_2Ge_2$ isostructural with the group of "122" SCs, *but in contrast to these systems, is pnictogen-free*, seems very interesting.

In this paper by means of first-principle FLAPW-GGA calculations, we have investigated the structure and electronic properties of newly discovered SC $SrPd_2Ge_2$ in comparison with $SrNi_2Ge_2$ [26,27] and $SrNi_2As_2$ it allows us to compare the above properties of these isostructural phases as a function of the p-element type (Ge *versus* As, i.e. $SrPd_2Ge_2$, $SrNi_2Ge_2 \leftrightarrow SrNi_2As_2$) and the d-metal type (Pd *versus* Ni, i.e. $SrPd_2Ge_2 \leftrightarrow SrNi_2Ge_2$, $SrNi_2As_2$). As a result, the optimized lattice parameters, band structures, densities of states (DOSs), Fermi surfaces are presented and analyzed. The Sommerfeld constants (γ) and the Pauli paramagnetic susceptibility (χ) are estimated.

* Corresponding author.
E-mail address: ivanovskii@ihim.uran.ru (A.L. Ivanovskii).

0921-4526/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2010.04.039

2. Models and method

All the considered ternary "122" phases $SrPd_2Ge_2$, $SrNi_2Ge_2$ and $SrNi_2As_2$ crystallize in the quasi-two-dimensional $ThCr_2Si_2$-type tetragonal structure, space group I4/mmm; $Z=2$. The structure is built up of $[M_2X_2]$ blocks (where M=Pd, Ni; X=Ge or As) alternating with Sr atomic sheets stacked along the *z*-axis, as shown in Fig. 1. The atomic positions are Sr: 2*a* (0, 0, 0), M: 4*d* (½, 0, ½) and X atoms: 4*e* $(0, 0, z_X)$, where z_X are internal coordinates governing the M–X distances and the distortion of the MX_4 tetrahedra around M in the $[M_2X_2]$ blocks.

The calculations were carried out by means of the full-potential method with mixed basis APW+lo (LAPW) implemented in the WIEN2k suite of programs [28]. The generalized gradient correction (GGA) to exchange-correlation potential in the PBE form [29] was used. The plane-wave expansion was taken to $R_{MT} \times K_{MAX}$ equal to 7, and the *k* sampling with $10 \times 10 \times 10$ *k*-points in the Brillouin zone was used. The calculations were performed with full-lattice optimization including internal z_X coordinates. The self-consistent calculations were considered to be converged when the difference in the total energy of the crystal did not exceed 0.1 mRy and the difference in the total electronic charge did not exceed 0.001 e as calculated at consecutive steps.

3. Results and discussion

3.1. Structural properties

At the first step, the optimized atomic positions and the equilibrium structural parameters for the SrM_2X_2 phases are determined; the calculated values presented in Tables 1 and 2 are in reasonable agreement with the available experimental data [25–27,30].

Our results show that replacements in blocks $[Pd(Ni)_2Ge(As)_2]$ of the d metal atoms (Pd↔Ni) or p elements (Ge↔As) lead to *anisotropic deformations* of the crystal structure caused by strong anisotropy of inter-atomic bonds in "122" phases (see also Refs. [20,24]), but the type of such deformations will be quite different. Thus, going from $SrPd_2Ge_2$ to $SrNi_2Ge_2$, i.e. replacing a larger Pd atom ($R^{at}=1.37$ Å) by a smaller Ni atom ($R^{at}=1.24$ Å), the parameter *a* decreases (of about ~0.26 Å) whereas the inter-layer distance (parameter *c*) slightly grows. On the contrary, when going from $SrNi_2Ge_2$ to $SrNi_2As_2$, i.e. replacing larger As atom ($R^{at}=1.48$ Å) by a smaller Ge atom ($R^{at}=1.39$ Å), the parameter *a* slightly grows, whereas the parameter *c* decreases (at about 0.14 Å), see Table 1.

Thus, the results obtained reveal that various atomic replacements inside "122" phases can lead to essential anisotropic changes of their structural properties and are favorable for fine tuning of their geometry—in particular, in view of sensitivity of superconductivity to structural changes, see Refs. [31,32].

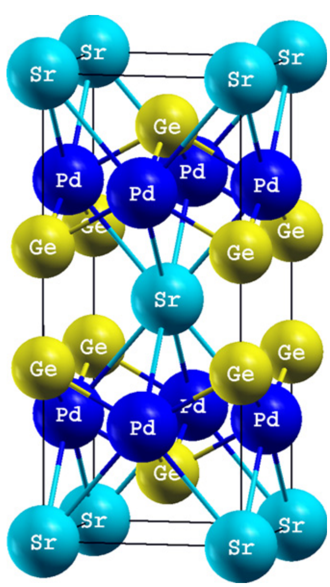

Fig. 1. (Color online) Crystal structure of tetragonal ($ThCr_2Si_2$-like) $SrPd_2Ge_2$ phase. $[Pd_2Ge_2]$ blocks and Sr atomic sheets are stacked along the *c*-axis.

3.2. Electronic properties

Figs. 2 and 3 show the band structures, Fermi surfaces, and total and atomic-resolved *l*-projected DOSs for the SrM_2X_2 phases as calculated for equilibrium geometries. We find that total energy calculations for magnetic (in assumption of ferromagnetic spin ordering) and non-magnetic (NM) states for these phases show that the NM state for all SrM_2X_2 phases is energetically most favorable.

We discuss the most important features of electronic structure for SrM_2X_2 phases, focusing on the near-Fermi region, Fig. 2. For AFe_2As_2 phases, the 2D-like Fe d_{xy}, $d_{x^2-y^2}$ bands, crossing the Fermi level (E_F) show low k_z dispersion. These bands form typical for FeAs SCs Fermi surfaces (FSs), which are composed from cylinder-like electron and hole pockets, directed along k_z, see reviews [2–4].

The examined SrM_2X_2 phases have the increased number of valence electrons (nve) as compared with FeAs-based materials

Table 2
The optimized lattice parameters (*a* and *c*, in Å) for $SrPd_2Ge_2$, $SrNi_2Ge_2$ and $SrNi_2As_2$ in comparison with available experiments.

Phase/ parameter	$SrPd_2Ge_2$	$SrNi_2Ge_2$	$SrNi_2As_2$
a	4.4588	4.1968	4.166
	(4.4088 [25])	(4.188 [26], 4.17 [27])	(4.137 [30])
c	10.3213	10.3595	10.502
	(10.1270 [25])	(10.254 [26], 10.25 [27])	(10.188 [30])
c/a	2.3148	2.4684	2.521
	(2.297 [8])	(2.448 [26], 2.458 [27])	(2.463 [30])

Available experimental data are given in parentheses.

Table 1
The optimized atomic positions and internal coordinates (z_X) for $SrPd_2Ge_2$, $SrNi_2Ge_2$ and $SrNi_2As_2$ in comparison with available experiments.

System (atomic position)	$SrPd_2Ge_2$	$SrNi_2Ge_2$	$SrNi_2As_2$
Sr (2a)	(0,0,0)	(0,0,0)	(0,0,0)
Pd(Ni) (4d)	(0,½,¼)	(0,½,¼)	(0,½,¼)
Ge(As) (4e)	(0,0,*z*); *z*=0.37030	(0,0,*z*); *z*=0.36007	(0,0,*z*); *z*=0.3621
	(*z*=0.37034 [25])	(*z*=0.362 [27])	(*z*=0.3634 [30])

Available experimental data are given in parentheses.