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Low-temperature electronic properties and band structures of LaTE_2Si_2 (TE=Fe, Co, Ag and Au)

K. Ciesielski, G. Chajewski, M. Samsel–Czekała, A. Hackemer, A.P. Pikul*, D. Kaczorowski

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P Nr 1410, 50-950 Wrocław 2, Poland

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ABSTRACT

Motivated by recent discovery of a non-Fermi liquid behavior and unconventional superconductivity in YFe_2Ge_2 we performed physical properties studies and fully relativistic band structure calculations for a few La-based silicides, namely $LaFe_2Si_2$, $LaCo_2Si_2$, $LaAg_2Si_2$ and $LaAu_2Si_2$. Electrical resistivity and heat capacity measurements revealed decreasing influence of *d*-electrons of the transition elements on the conduction electron scattering and the Sommerfeld coefficient with increasing the atomic number. Band structure calculations fully corroborated the experimental findings. No superconductivity was found in the investigated compounds down to 0.35 K.

1. Introduction

Ternary intermetallic phases with the stoichiometry 1:2:2 form a vast family of compounds, majority of which crystallizes in various derivatives of the tetragonal $BaAl_4$-type structure. Several magnetic *f*-electron systems from this group have attracted much attention due to their interesting physical properties, like complex magnetic ordering [1] or heavy–fermion superconductivity [2]. Nonmagnetic counterparts with full or empty *f*-shells have been hardly studied until very recently, when some nontrivial behaviors in a few of them have been revealed. For instance, $LaPt_2Si_2$ was found to exhibit charge–density–wave transition at $T^* = 112$ K followed by superconductivity below 1.7 K [3]. In turn, YIr_2Si_2 and $LaIr_2Si_2$ were shown to exhibit structural polymorphism significantly affecting their physical properties. Their high-temperature variants crystallize in the primitive tetragonal $CaBe_2Ge_2$-type structure (space group $P4/nmm$) and become superconducting below $T_c = 2.7$ K (YIr_2Si_2) and 1.6 K ($LaIr_2Si_2$), while the low-temperature polymorphs crystallize with the body-centered tetragonal $ThCr_2Si_2$-type unit cell (space group $I4/mmm$) and do not show any trace of superconductivity [4]. Most interestingly, YFe_2Ge_2 was reported to be an unconventional superconductor with $T_c = 1.8$ K and clear non-Fermi-liquid behavior in the specific heat in the normal state [5]. Theoretical and spectroscopic investigations pointed out that the unconventional properties of this germanide are mostly determined by 3*d*-electrons of iron [6–8].

Here, we report on the low-temperature electrical resistivity and thermodynamic properties of four La-based silicides, namely: $LaFe_2Si_2$, $LaCo_2Si_2$, $LaAg_2Si_2$ and $LaAu_2Si_2$. The experimental data are supplemented with the results of ab initio electronic band structure and Fermi surface calculations.

2. Material and methods

Polycrystalline samples of the LaTE_2Si_2 compounds with TE=Fe, Co, Ag and Au were synthesized by conventional arc melting the elemental constituents under protective argon atmosphere. Subsequently, the pellets were wrapped in molybdenum foil and annealed in evacuated silica tubes at 1273 K for two weeks. The crystal structure of the products was verified by powder X-ray diffraction (XRD) using X'pert Pro PANalytical diffractometer with Cu K_α radiation. The XRD patterns were analyzed using the Rietveld method implemented into the Fullprof software [9].

Magnetic measurements were performed from room temperature down to 2 K and in magnetic fields up to 5 T using a commercial Quantum Desing SQUID magnetometer. The electrical resistivity and the heat capacity were measured in temperature range 2–300 K and 0.35–10 K, respectively, using a Quantum Design PPMS platform.

The electronic band structures were calculated employing the fully relativistic version of the full-potential local-orbital (FPLO9) code [10]. The local density approximation (LDA) [11] of the exchange-correlation potential was included in the computations of non-magnetic states. In addition, self-consistent spin-polarized calculations were performed for $LaFe_2Si_2$ with both local-spin density approximation (LSDA) [11] and generalized gradient approximation (GGA) [12] of the exchange-correlation functional. The ferromagnetic (FM) states were considered with the ordering along the *c*-axis. The size of the selected

* Corresponding author.
E-mail address: A.Pikul@int.pan.wroc.pl (A.P. Pikul).

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Table 1
Refined basic unit cell parameters (a, b, z_{Si}) and physical characteristics of the LaTE_2Si_2 compounds from the fits of Eqs. (1) and (2) to the experimental data (see Figs. 1 and 2, respectively), together with the calculated parameters γ_b and N_F.

Compound	$LaFe_2Si_2$	$LaCo_2Si_2$	$LaAg_2Si_2$	$LaAu_2Si_2$
a (nm)	0.4056	0.4019	0.4292	0.4337
c (nm)	1.015	1.007	1.063	1.018
z_{Si}	0.380	0.380	0.378	0.390
ρ_0 ($\mu\Omega$ cm)	14.9	76.0	1.5	5.6
R ($\mu\Omega$ cm K^{-1})	0.283	1.154	0.096	0.081
Θ_R (K)	350	290	292	161
K ($\mu\Omega$ cm K^{-4})	7.6×10^{-7}	5.2×10^{-6}	7.7×10^{-8}	7.7×10^{-8}
γ (mJ K^{-2} mol^{-1})	22.0	11.2	4.7	4.4
ζ (mJ K^{-6} mol^{-1})	—	—	0.5	7.2
Θ_D (K)	202	201	162	155
γ_b (mJ K^{-2} mol^{-1})	11.6	10.7	3.4	3.3
N_F (states eV^{-1} f.u.$^{-1}$)	4.9	4.6	1.5	1.4

k-point meshes was $12 \times 12 \times 12$ (163 irreducible **k**-points) in the Brillouin zone. The band structures, total and partial densities of states (DOS's) and Fermi surfaces (FS's) were obtained. The partial DOS's were derived for different atomic sites or electron orbitals.

3. Results and discussion

The obtained XRD patterns were Rietveld-refined within the tetragonal $ThCr_2Si_2$-type unit cell with the lattice parameters and the positional parameters listed in Table 1. The results are close to those reported in the literature [13–15]. No foreign peaks due to secondary phase were noticed, hence confirming that the samples used in the experiments were single phases. The magnetic measurements confirmed Pauli paramagnetism of $LaFe_2Si_2$ [16]. Temperature independent paramagnetic behavior was revealed also for $LaCo_2Si_2$, while $LaAg_2Si_2$ and $LaAu_2Si_2$ were found to be weak diamagnets.

Fig. 1 shows the temperature dependencies of the electrical resistivity of the studied compounds. The overall shape of the $\rho(T)$ curves is characteristic of simple metals and follows the Bloch–

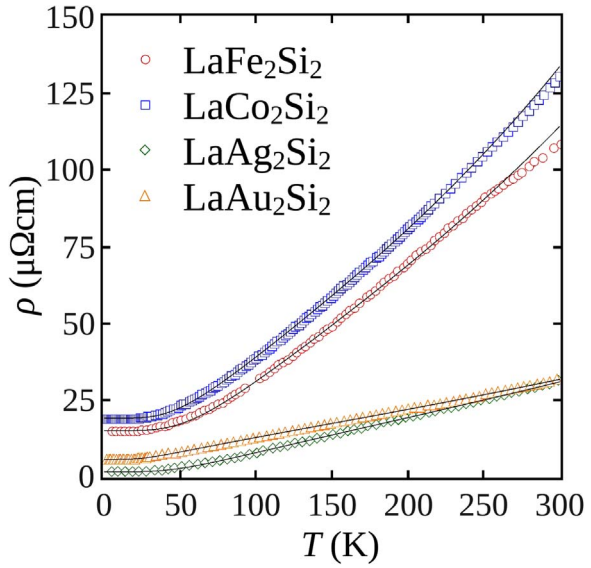

Fig. 1. Temperature variations of the electrical resistivity ρ of $LaFe_2Si_2$, $LaCo_2Si_2$, $LaAg_2Si_2$ and $LaAu_2Si_2$. Solid lines are fits of the Bloch–Grüneisen–Mott relation to the experimental data. For clarity, the values of the resistivity of $LaCo_2Si_2$ were divided by a factor of 4.

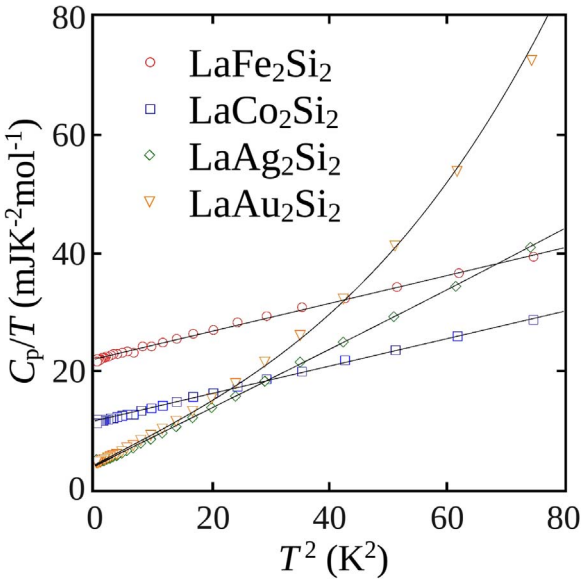

Fig. 2. Temperature dependencies of the specific heat of $LaFe_2Si_2$, $LaCo_2Si_2$, $LaAg_2Si_2$ and $LaAu_2Si_2$. Solid lines are fits of Eq. (2) to the experimental data.

Grüneisen–Mott formula [17]:

$$\rho = \rho_0 + R\left(\frac{T}{\Theta_R}\right)^5 \int_0^{\Theta_R/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} + KT^3 \quad (1)$$

where ρ_0 is the residual resistivity due to structural defects, R is a material constant describing electron–phonon interaction, Θ_R is a parameter describing a phonon spectrum (sometimes considered as an estimate of the Debye temperature), and the third term describes the interband $s - d$ scattering. Least-squares fitting Eq. (1) to the experimental data yielded the parameters gathered in Table 1. As can be noticed, with the exception of the Co-bearing phase both Θ_R and R decreases with increasing atomic number of the transition elements, which is in line with increasing atomic mass and a number of d-electrons of the TE atoms in the LaTE_2Si_2 series. The values of the fitting parameters obtained for $LaCo_2Si_2$ are significantly larger, possibly because of internal microcracks in the sample studied.

Temperature variations of the low-temperature specific heat C_p of the LaTE_2Si_2 compounds studied are plotted in Fig. 2 as C_p/T vs. T^2. The experimental curves are featureless, excluding the emergence of bulk superconductivity down to 0.35 K. In each case, $C_p(T)$ follows the low-temperature approximation of the Debye formula:

$$C_p = \gamma T + \beta T^3 + \zeta T^5 \quad (2)$$

where γ is the Sommerfeld coefficient and β is the phonon coefficient related to the Debye temperature via the formula:

$$\Theta_D = \sqrt[3]{rR\frac{12\pi^4}{5\beta}}, \quad (3)$$

where R is the universal gas constant and r is a number of atoms in the formula unit. The third term in Eq. (2) is a higher order term in the power series approximation of the Debye integral (see e.g. [18]). In the case of $LaFe_2Si_2$ and $LaCo_2Si_2$, the conventional low-temperature limit of the Debye law with only a T^3-term gave satisfactory results (i.e. the coefficient ζ was found to be negligible). However, for the systems with heavier transition elements, namely $LaAg_2Si_2$ and $LaAu_2Si_2$, it was necessary to apply the extended form of Eq. (2). The obtained fitting parameters are collected in Table 1. The values of γ and Θ_D derived for $LaFe_2Si_2$ are very close to those reported in the literature [19–22]. For the other compounds, no data allowing for such a comparison were published up to date.

As seen from Table 1, the electronic contribution to the specific heat