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# Experimental and first-principle study of $LuPd_2Si_2$ superconductor

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ABSTRACT

The $LuPd_2Si_2$ compound is a member of a large group of compounds crystallizing in the $ThCr_2Si_2$ tetragonal type of structure. The negative thermal expansion of the lattice parameter $c$ was determined by means of an x-ray diffraction experiment performed at different temperatures between 3 K and 300 K. Temperature of transition to a superconducting state was calculated and experimentally confirmed at 0.6 K. Comparison between results of theoretical calculations based on the local spin density approximation (LSDA) and the generalized gradient approximation methods (GGA) is given in the article.

## 1. Introduction

The ternary rare-earth compounds belonging to a 1-2-2 family are at the center of considerable attention due to the wide variety of magnetic properties and unusual behavior of transport properties. Especially, compounds based on Ce, Eu, or Yb are intensively studied due to their electronic structure properties which can give rise to phenomena like intermediate valence, unconventional superconductivity, heavy fermion properties and Kondo effect [1–5]. Compounds containing other rare-earth show complex magnetic phase diagrams [6,7]. The comparison between behavior of these compounds and isostructural compound based on nonmagnetic element can answer important questions about the interplay of magnetic, electronic and structural origin of the observed phenomena. The $LuPd_2Si_2$ compound crystallizes in $ThCr_2Si_2$ tetragonal structure adopting the I4/mmm space group (group no. 139). The $LuPd_2Si_2$ structure is naturally layered structure with rare-earth, transition metal and Si occupying 2a, 4d and 4e positions, respectively and can be described as alternating layers in sequence Lu-Pd-Si-Pd-Lu. $LuPd_2Si_2$ was previously reported to undergo a superconducting transition below 1 K [8]. There were reported lattice parameters $a = 0.4089$ nm and $c = 0.985$ nm and the critical superconducting temperature $T_c = 0.67$ K was determined by ac magnetic susceptibility measurement [8]. The further investigation of $LuPd_2Si_2$ by fully relativistic electronic structure calculations was presented in Ref. [9]. The authors obtained magnetic moment of 0.34 $\mu_B$/Lu. Inconsistencies concerning the energy position and hybridization of the fully occupied Lu-4f states in the later mentioned reference can be found. In the Ref [9] the local spin density approximation (LSDA) was used. In the present work we focus on electronic structure calculations of $LuPd_2Si_2$ and comparison of results of LSDA and the generalized gradient approximation methods (GGA). Experimental measurements of transport and magnetic properties were performed on polycrystalline sample of $LuPd_2Si_2$ and the obtained data are discussed with respect to the results of theoretical calculations. Furthermore, we present study of structural properties of $LuPd_2Si_2$. Knowledge of the crystal structure is extremely important for the complete understanding of the complex behavior of the studied compound. The evolution of lattice parameters of $LuPd_2Si_2$ can be particularly important for its comparison with that of isostructural valence fluctuating compounds where the changes in electronic structure can also lead to anomalous evolution of the unit cell parameters. We report a thorough study of thermal lattice expansion by means of a low-temperature x-ray powder diffraction in this paper. In addition, the hydrostatic-pressure effect on the superconductivity is presented.

## 2. Theoretical methods and experimental procedures

To study the density of electronic states (DOS) and the theoretical equilibrium volume of LuPd2Si2, the augmented plane wave plus local orbitals (APW + lo) method [10] and full potential local orbitals (FPLO) [11] based on density functional theory (DFT) have been employed. To obtain estimation of experimental equilibrium volume we used both the local spin density approximation (LSDA) [12] and generalized gradient approximation (GGA) [13–15] methods.

The polycrystalline sample was prepared from stoichiometric mixture of pure elements (3 N for Lu, 4 N for Pd and 6 N for Si) in a mono-

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arc furnace under protective Ar atmosphere. Analysis of the as cast sample revealed two foreign phases - one with composition $Pd_2Si$ and the other one was Lu-rich phase with composition Lu:Pd:Si (60:16:24). The differential scanning calorimetry (DSC) experiment performed on a piece of the obtained sample showed signatures of phase transition at 1603 K which corresponds to melting temperature of $Pd_2Si$ [16]. One part of the obtained ingot was wrapped in a Ta foil and sealed in a quartz tube with small residual pressure of Ar. The annealing was performed at 1323 K for one week. The composition and homogeneity was again studied by EDX and the disappearance of Lu rich foreign phase was confirmed. The $Pd_2Si$ impurity phase remained present in the sample and was detected by a very small DSC peak at 1603 K suggesting that the melting temperature of the main 1-2-2 phase lies above 1610 K which is the limit of our instrument (DSC Setaram). The crystal structure was investigated by means of x-ray diffraction in temperature range from room temperature down to 3 K. Low-temperature X-ray powder diffraction was performed using a refurbished Siemens D500 diffractometer, equipped with a low temperature option provided by a closed-cycle cryocooler (CCR, Sumitomo Heavy Industries). Cu-K$\alpha_{1,2}$ radiation was used and Bragg-Brentano geometry together with a linear detector to speed up the data recording [17]. The foreign $Pd_2Si$ phase was detectable in the diffraction pattern and the amount was determined to be below 3%. The obtained data were processed by the FullProf package [18]. Electrical resistivity measurement was performed by standard four-wire technique with lock-in detection in temperature range from 300 K to 0.38 K. The heat capacity was measured by using the relaxation method in the same temperature range. The sample environment was controlled by PPMS (Quantum Design) cryostat equipped with Helium-3 option and the 14 T superconducting magnet. The effect of pressure was studied by using the double-wall piston-cylinder pressure cell [19] with a nominal pressure of 3 GPa. The Daphne 7373 oil was used as a pressure transmitting medium [20,21]. The pressure was determined by a manganin wire and corrected for thermal expansion of the setup.

## 3. Results and discussion

The superconducting transition of $LuPd_2Si_2$ was confirmed by electrical resistivity measurement on polycrystalline sample, see Fig. 1. The superconducting transition temperature of $T_c = 0.58$ K was determined in zero magnetic field. This critical temperature is slightly lower than $T_c = 0.67$ K reported in literature [8] but it is still in reasonable agreement with the previous observation if we take into account sensitivity of $T_c$ to magnetic field with $dT_c/dH = -0.07$ K/mT, see Fig. 1. The pressure dependence of the critical temperature was obtained from the resistivity measurement under applied hydrostatic pressure up to 3 GPa and a linear decrease of critical temperature with increasing pressure, $dT_c/dP = -36$ mK/GPa, was determined.

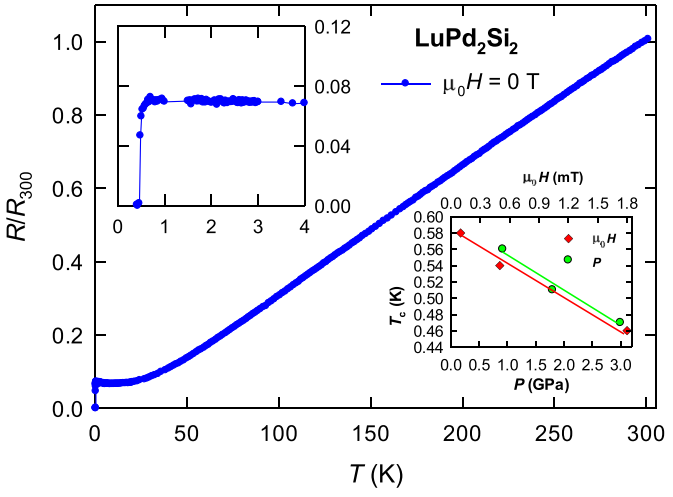


**Fig. 1.** Temperature dependence of electrical resistivity of $LuPd_2Si_2$. The effect of pressure and magnetic field is illustrated in the right inset. Pressures given in the inset are corrected for the effect of the pressure transmitting-medium thermal expansion.

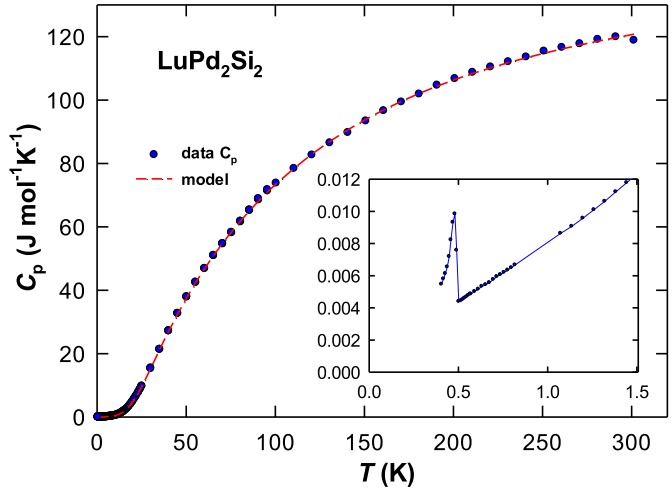


**Fig. 2.** Measured heat capacity data in broad temperature region and result of the model of heat capacity (red dashed line) as described in text. The superconducting transition can be observed as a sharp peak. The solid line in the inset is just guide to eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

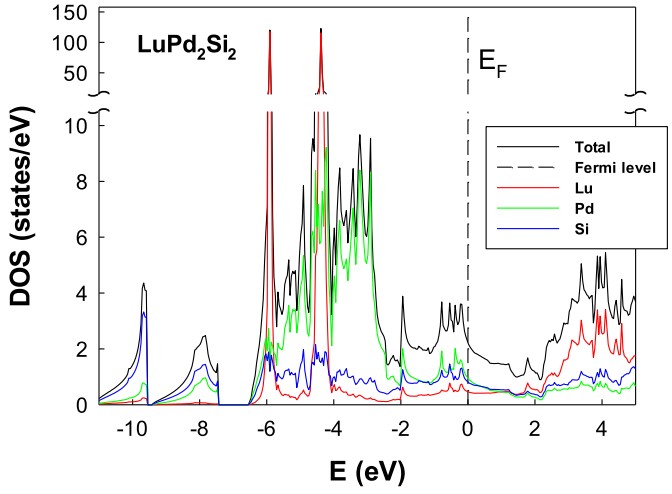


**Fig. 3.** The calculated DOS of the $LuPd_2Si_2$ compound. See text for details.

The heat capacity was measured in temperature range from 0.38 K up to 300 K. The data are plotted in Fig. 2 together with the result of fitting model. The data between 4 K and 300 K were treated by a combined contribution of acoustic and optical phonons and electronic specific heat [22]. The Debye model is used to describe three acoustic phonon branches and the contribution of optical phonon branches is calculated by the Einstein model. The optical phonon branches can be coupled to reduce the number of parameters. The electronic contribution of 8 mJ mol$^{-1}$. K$^{-2}$ was determined with respect to low temperature data and the value was fixed during the fitting procedure. The values of Debye, $\theta_D$, and Einstein, $T_E$, temperatures were randomly generated in the interval between 10 K and 800 K. We started with 100 different sets of random values of $\theta_D$ and $T_E$ and we let to converge the fitting for all the sets. Multiplicity of several Einstein temperatures were observed. The anharmonic corrections were zero but the Debye contribution anharmonic correction was $6.5 \times 10^{-5}$. The following parameters were obtained $\theta_D = 176$ K and $T_E = 145$ K, 423 K, 703 K, 108 K,