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Electronic structure of superconducting $Lu_2Ni_3Si_5$ and its reference compound $Y_2Ni_3Si_5$ by *ab initio* calculations

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ABSTRACT

Electronic structures of orthorhombic ternary nickel silicides: superconducting $Lu_2Ni_3Si_5$ and its non-superconducting counterpart, $Y_2Ni_3Si_5$, have been calculated employing the fully relativistic and full-potential local-orbital method within the density functional theory. Our investigations were focused particularly on the band structures and Fermi surfaces (FSs), being very similar for both ternaries. It appears that their FSs exist in four bands and contain electronlike and holelike three-dimensional sheets and small pockets, which suggests a presence of two- or even multi-band superconductivity (SC) in $Lu_2Ni_3Si_5$. The main difference between both systems is that only in $Lu_2Ni_3Si_5$ small electron FS pockets occur around the Γ point. It allows for arising BCS-like SC in this compound, as was deduced from previous heat-capacity measurements, while no sign of SC has been detected (at least down to 2 K) in $Y_2Ni_3Si_5$. In the latter system, a possible formation of a ferromagnetic ground state, which usually tends to destroy SC, has been excluded by our calculations.

1. Introduction

Wide interest in nickel-based (oxy)pnictide superconductors mainly of 1111, 122 and 344-type families, known in the literature, e.g. [1–3], containing the similar Ni–X atomic layers, where X is a pnictide, chalcogenide or boron atom, motivated us to investigate also other superconducting Ni-based materials possessing such layers with X = Si. Nickel-pnictide-like structures are usually strongly anisotropic, forming quasi-two-dimensional (Q2D) systems. They are built from positively charged layers of atoms of alkaline or rare-earth metals and negatively charged layers containing nickel and non-metallic atoms. Although in these families the superconducting transition temperatures, T_C, are rather low, usually below 5 K, they are widely investigated nowadays in analogy to the high-T_C iron-based rare-earth pnictides, like $SmFeAsO_{1-x}F_x$ and $Sr_{1-x}Sm_xFeAsF$, reaching the highest T_C of 55 K due to doping [4]. Interestingly, among Ni-based superconductors, contrary to Fe-based ones, rather three-dimensional (3D) rare-earth borocarbides, achieve T_C maximum of 16.5 K [5]. So far, a mechanism of high-temperature superconductivity (SC) has been not recognized. Therefore, a comparison of electronic structures of similar systems, based on nickel or iron atoms, might be crucial in understanding an SC phenomenon in such a class of materials.

The considered in this work family of ternary rare-earth nickel silicides adopts an orthorhombic structure of the $U_2Co_3Si_5$-type (*Ibam*, space group no. 72) containing the Ni–Si layers lying much closer to one another, along the c axis, than those in other nickel silicides, as e.g. $La_3Ni_4Si_4$ [6,7]. It is interesting that most of the $R_2Ni_3Si_5$-family members exhibit antiferromagnetic phase transitions at temperatures $T_N \leq 30$ K and the magnetic moments, originating only from the rare-earth atoms because the nickel atoms remain non-magnetically ordered (NMO) [8–14]. In antiferromagnetically ordered $(Pr;Dy;Ho)_2Ni_3Si_5$ systems, an existence of also short-range ferromagnetic (FM) correlations has been postulated, based on observations of an anomalous behavior of magnetoresistivity [15]. Up to now, among members of the $R_2Ni_3Si_5$ family, the superconductivity phenomenon has been detected only in $Lu_2Ni_3Si_5$ with $T_C = 2.1$ K, being metallic but NMO at least above the T_C [16]. Based on heat-capacity measurements, the SC mechanism in this material was interpreted as being rather weak-coupling BCS-like ($\Delta C/\gamma T = 1.1$ at $T = T_C$) [16]. Similarly to $Lu_2Ni_3Si_5$, the isostructural and isoelectronic $Y_2Ni_3Si_5$ system was found to be NMO (down to 4.2 K) and its electronic transport properties (measured down to 2 K), though showed also a metallic state, did not reveal any evidence of SC [17]. If the ground state of $Y_2Ni_3Si_5$ becomes, in fact, of the NMO kind, this compound may be considered as a candidate to be superconducting like $Lu_2Ni_3Si_5$. This

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expectation is inferred from an analogy to the family of tetragonal ternary iron silicides, in which only $(Lu;Y;Sc)_2Fe_3Si_5$, being just NMO members, exhibit SC [18]. Based on the analysis of heat-capacity measurements of $Lu_2Fe_3Si_5$, two-band SC having a weak-coupling BCS-like character was suggested [19].

Up to our best knowledge, no electronic-structure calculations results for both considered here ternaries, $Lu_2Ni_3Si_5$ and $Y_2Ni_3Si_5$, have been reported in the literature so far. Thus, in this paper, such results are presented for both compounds, with the main focus on their Fermi surfaces (FSs) analyzes at ambient and higher pressure from the point of view of possible SC mechanisms. Since as yet no experimental data have been available below 2.0 K, a possibility of a magnetically ordered ground state in $Y_2Ni_3Si_5$ was examined by us as well.

2. Computational methods

Electronic structure calculations of $(Lu;Y)_2Ni_3Si_5$ have been performed with a modern full-potential local-orbital (FPLO) method [20]. The Perdew–Wang form of the local (spin)-density approximation [L(S)DA] of exchange-correlation functional [21] was employed in both fully and scalar relativistic modes, the latter without an inclusion of the spin-orbit (SO) coupling. Experimental X-ray diffraction values of lattice parameters of the unit cell (u.c.) possessing the *Ibam* symmetry are as follows: $a = 0.9604$, $b = 1.1014$, $c = 0.5512$ nm for $Lu_2Ni_3Si_5$ [16] and $a = 0.95651$, $b = 1.11284$, $c = 0.56453$ nm for $Y_2Ni_3Si_5$ [22]. It should be mentioned that according to Ref. [16] the crystal structure of the Lu-based compound, probed on the powder sample, could not be assigned unambiguously and some slight distortion to the monoclinic variation (*C2/c*) of the orthorhombic (*Ibam*) structure could not be excluded. They were used as initial parameters in further optimization of the u.c. volumes at ambient and higher pressure by minimizing total energy but keeping the internal atomic coordinates (given below) fixed, which yielded some approximation of a pressure dependence of crystal and electronic structures. Here u.c. is equivalent to double formula units (f.u.). The same experimental atomic positions in u.c. as those obtained by the single-crystal X-ray data refinement for $Y_2Ni_3Si_5$ [22] were taken for both studied systems. This assumption is justified taking into account the fact that the isoelectronic Y and Lu atoms occupy equivalent positions in the crystal structure and the experimental atomic positions of $Y_2Ni_3Si_5$ and e.g. those of $Sm_2Ni_3Si_5$ [14] differ only negligibly, despite the considerable (compared to the pair of Y and Lu atoms) disparity in size between the Y and Sm atoms. The crystal structure is visualized in Fig. 1 where the used experimental atomic positions of $Y_2Ni_3Si_5$ [22] are as follows: Y (Lu) in (8j): (0.2632, 0.3691, 0); Ni(1) in (4b): (1/2, 0, 1/4); Ni(2) in (8j): (0.1123, 0.1342, 0); Si(1) in (8g): (0, 0.2663, 1/4); Si(2) in (8j): (0.3475, 0.1071, 0); Si(3) in (4a): (0, 0, 1/4). The following valence-basis sets were selected in our calculations: the Y: 4s4p; 5s5p4d; the Lu: 5s5p4f; 6s6p5d; the Ni: 3s3p; 4s4p3d, and the Si: 2s2p; 3s3p3d states. Total energy values of considered systems were converged with accuracy to ~1 meV for the $16 \times 16 \times 16$ (621 points) ***k***-point mesh in the non-equivalent part of the Brilouin zone (BZ). A possible FM ground state in $Y_2Ni_3Si_5$ was examined by standard spin-polarized, scalar relativistic self-consistent LSDA calculations. For this purpose, the fixed spin moment (FSM) method [23], implemented in the FPLO code, was utilized as well.

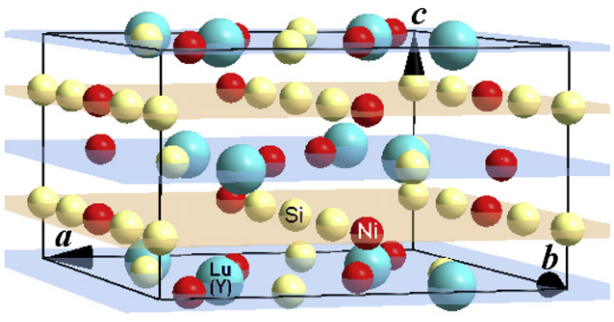

Fig. 1. Orthorhombic *Ibam* crystal unit cell of $(Y;Lu)_2Ni_3Si_5$ compounds of the $U_2Co_3Si_5$-type (no. 72).

3. Results and discussion

For both $(Lu;Y)_2Ni_3Si_5$ compounds, the theoretically optimized volumes of u.c., V_{calc}, amount to about 95.9% of their experimental volumes, V_{exp}. Results of electronic structure calculations, presented here, were obtained for the above V_{calc} and they do not differ considerably from those determined for V_{exp}. The total and partial DOSs of both studied systems, based on the fully relativistic approach, are plotted in Figs. 2 and 3. As seen in these figures, their overall shapes are similar for both compounds, differing mainly in the additional presence of two narrow peaks of the Lu 4f electron states. Our fully relativistic calculations for $Lu_2Ni_3Si_5$ indicate that these are the SO split Lu $4f_{5/2}$ and $4f_{7/2}$ peaks, located at 5.4 and 3.9 eV below the Fermi level (E_F), respectively (see upper inset to Fig. 2). As expected, based on the scalar relativistic calculations, one was able to get only one high peak of the 4f electrons occurring at about −4.5 eV (displayed in upper inset to Fig. 2). It is interesting to note that by employing *ab initio* calculations also in the scalar

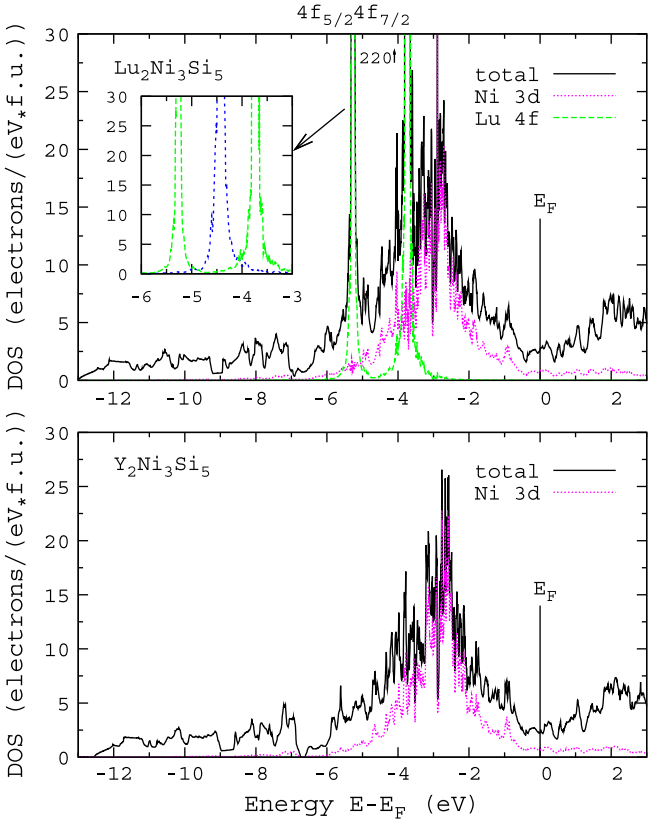

Fig. 2. Total and partial (per Ni 3d and Lu 4f electron orbitals) DOSs in $R_2Ni_3Si_5$ for R = Lu and Y, obtained in the fully relativistic mode. Upper inset shows the Lu $4f_{5/2}$ and $4f_{7/2}$ peaks on expanded scale. In the middle of this inset, there is hypothetical single peak of the Lu 4f electrons, yielded in the scalar relativistic mode (without SO splitting).