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Intermediate coupled superconductivity in yttrium intermetallics

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ABSTRACT

Non-magnetic YIn_3, $LaIn_3$ and $LuIn_3$ with a superconducting transition temperature T_c of 0.78, 0.71 and 0.24 K were investigated for superconductivity. Similarly, rare-earth compound $LaSn_3$ has been reported to exhibit superconductivity around 6.25 K, whereas the non-magnetic YSn_3 is a superconductor with T_c of 7 K. The substitution of 13th group In-atoms by 14th group Sn-atoms is seen to enhance T_c by nearly one order, although the lattice parameters increase by ~1.0% in YSn_3 compared to YIn_3 compound. It is observed from the ground state properties that the slight difference in the energy band structures of YIn_3, YIn_2Sn and YSn_3 gives rise to various complex Fermi surfaces which are multiply connected and exhibit vast differences. The Fermi level lies on a sharp peak in YSn_3 which has a higher density of states $N(E_F)$, whereas Fermi level lies on the shoulder of a sharp peak in YIn_3. The electron localization function (ELF) and difference charge density maps clearly illustrate the difference in the nature of bonding; the Y–Sn bonds are clearly more ionic (due to larger bond length) than Y–In bonds. These results are consistent with the Bader charges which show loss of charges from Y-atoms and a gain of charges by In/Sn atoms. The dynamical properties also clearly illustrate the difference in the nature of bonds in YX_3 intermetallics. A softening of the lowermost acoustic modes is observed in YIn_3, whereas all the modes in YSn_3 are observed to have positive frequencies which imply its greater stability. Since $\lambda_{el\text{-}ph} < 1$, both YIn_3 and YSn_3 compounds exhibit type I superconductivity according to BCS theory. However, the smaller $N(E_F)$ obtained from the density of states (DOS); the electron-phonon coupling constant $\lambda_{el\text{-}ph}$ obtained from the temperature dependent specific heat as well as the instability in phonon modes due to stronger Y–In and In–In bonds in YIn_3 may be the cause of lower T_c and filamentary nature of superconductivity. Insertion of Sn-atom in the YIn_3 lattice further consolidates the superconducting nature due to increase in $N(E_F)$ and γ (electronic component of specific heat), along with lowering of the frequency of imaginary modes from 5.6 THz to 1.5–0.6 THz. Thus T_c is directly related to the valence electron concentration and ternary YIn_2Sn may exhibit intermediate superconducting transition temperature.

1. Introduction

The field of potential superconductors has broadened vastly with the inclusion of early heavy fermions and high temperature superconductors which include magnetic ions. Heavy fermion superconductors such as $CeIn_3$ and light rare-earth compounds $LnSn_3$ (Ln = La-Gd) with cubic structures are found to exhibit conventional and unconventional superconductivity and have inspired new studies recently. Due to the ease of fabrication of nonmagnetic YIn_3 and YSn_3 compounds with the $AuCu_3$ structure, their superconducting properties have been explored to a much greater extent by experimental techniques along with investigations by *ab initio* methods. The Fermi surfaces of three related compounds $ScGa_3$, $RuGa_3$ and $LuIn_3$ were characterized by means of de Hass van Alphen (dHvA) technique. The effect of pressure on the FS and electronic structure of heavy fermion $ErGa_3$ compound was also studied experimentally [1,2]. The 1st principles fully relativistic linear-muffin-tin-orbital (LMTO) method was applied to study the electronic structure, FS and angular dependence of dHvA frequency in YIn_3, $LuIn_3$ and $YbIn_3$ binary intermetallics [3]. Electronic structure of related $REGa_3$ (RE = Er, Tm, Yb, Lu) intermetallics was investigated in LDA, GGA and warped muffin-tin approximation. The electronic structure was found to be sensitive to the Re-atoms due to the location of 4f-bands [4]. Similarity in the electronic structure of $LuGa_3$ suggested that $ScGa_3$ may also display ground state superconductivity. This was confirmed from temperature dependent specific heat and resistivity measurements down to 0.4 K [5]. The pressure dependent Fermi surfaces (FS) and electronic properties of isostructural 14th group $LaSn_3$ and YSn_3 were studied in the framework of DFT using the full potential linearized augmented

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plane wave (FPLAPW) method [6]. The optoelectronic and thermodynamic properties of $ScGa_3$ and $LuGa_3$ were studied by the FPLAPW method with various exchange potentials [7]. From the temperature dependent specific heat and lattice properties calculated by the FPLAPW method, $ScGa_3$ and $ScIn_3$ were found to exhibit weak intermediate coupled superconductivity [8]. In another study of $LaIn_3$ and $LaSn_3$ compounds, Bitter et al. reported the electron-spin-resonance (ESR) measurements in the La–In–Sn alloy system. They extracted the effective exchange interaction parameter to study the dependence of superconducting critical temperature as a function of Sn-atom substitution [9]. From the magnetic susceptibility, electrical resistivity and specific heat measurements of single crystals of isomorphic YSn_3, it was inferred that the compound was a type-II superconductor with T_c ~7 K. A high value of electron-phonon coupling constant $\lambda_{el\text{-}ph}$ was extracted from the specific heat measurements which placed YSn_3 compound in the strong-coupling regime [10,11]. Heavy fermion superconductors $CeIn_3$ and $CeMIn_5$ were found to exhibit high T_c. Due to the ease of fabricating high quality crystals of non-magnetic YIn_3, its resistivity, susceptibility and specific heat was measured down to liquid helium temperature by Johnson et al. [12]. This compound exhibits type I superconductivity with T_c~ 0.8 K. The BCS theory however yields a high value of λ~1.43, which places it in the strong-coupling range. Effect of pressure on the FS and elastic properties of AB_3 (A = Y, La; B = Pb, In, Tl) compounds was studied by the FPLAPW method. Topological changes were observed in all these compounds which may be related to the electron-phonon interactions [13]. The FPLAPW and planewave pseudo potential methods were used by Billington et al. [14] to calculate the ground state, phonon and electron-phonon coupling in YIn_3 compound. The authors concluded that el-ph coupling was capable of producing super conductivity in the compound. First principles calculations within various exchange-correlation functionals such as PBE-GGA and WC-GGA were carried out to study the elastic and mechanical properties for $ReSn_3$ (Re = Y, La, Ce) compounds [15]. The thermodynamical properties of YSn_3 compound have been determined in the framework of Eliashberg formalism and the critical temperature has been found to be equal to 6.52 K [16]. Temperature dependent thermal conductivity of $REIn_3$ compounds (RE = Y, Tb, Dy, Tm and Lu) was investigated between temperatures 4 and 300 K and external magnetic fields, where YIn_3 was used as a reference compound [17]. Electron spin resonance (ESR) experiment of Gd^{3+} doped YIn_3 was performed in order to confirm that electron-pairing is required for superconductivity mediated by magnetic interactions [18]. This experiment was performed to show that the spin relaxation of Gd^{3+} ions is due to exchange interaction between Gd^{3+} localized magnetic moments and conduction electrons (*ce*) processed via s-p-d type *ce* of YIn_3 at the Fermi level E_F.

From literature survey of various yttrium based compounds, it was observed that T_c is approximately 0.7 K for YIn_3 and increases to 7 K for YSn_3. A similar trend was observed in isomorphic $LaIn_{3-x}Sn$ alloy systems which are superconducting Pauli paramagnets. In the $LaIn_3$ compound, the superconducting critical temperature T_c~0.7 K showed an oscillatory dependence as a function of Sn substitution, presenting its highest value T_c~ 6.4 K for $LaSn_3$ end member. Recently, many of these binary systems have been studied extensively by means of dHvA technique as well as thermal conductivity and heat capacity measurements etc. to understand the nature of superconducting state. Since the YIn_3 and YSn_3 compounds are non-magnetic analogues of rare-earth compounds, these serve as optimum candidates for further study of the interplay between superconductivity, crystal structure and electronic structure. In this study, we benchmark our work through comparison with studies made by previous workers. The subtle differences in the density of states, electron localization function and Fermi surfaces have a direct bearing on the superconducting properties. The dynamical properties were investigated for the first time and provided an understanding of the phonon modes which give rise to structural instability thereby influencing the electron-phonon interactions. We also investigated the possibility of superconductivity in hypothetical YGa_3 and ternary YIn_2Sn compounds.

2. Methodology

Two computational methods were used in a complimentary manner. The calculation of structural, electronic and transport properties of YX_3 (X = Ga, In, Sn) intermetallics was carried out by self-consistent scheme by solving the Kohn–Sham equations. The full potential linearized augmented plane wave (FP-LAPW) method was applied in the framework of the density functional theory (DFT) along with exchange–correlation (XC) potentials such as Wu–Cohen (WC) and Perdew–Burke–Erazerhof (PBESol) in the generalized gradient approximation (GGA) using Wien2k code [19]. The calculations were performed with 165 k-points for YIn_3, YSn_3 and YGa_3 and 147 k-points for YIn_2Sn. The iteration was halted when the difference charge density was less than 0.0001e ao^{-3} between steps as convergence criterion. The core cut-off energy which defines the separation of core and valence states was chosen as −6.0 Ry. The transport properties were also calculated by applying the BoltzTrap code [20] interfaced with Wien2K.

In addition, for the calculations of the dynamical properties, we have employed the Vienna *ab initio* simulation package (VASP) in projector augmented wave (PAW) formalism [21]. The exchange and correlation was described in the form of PBE in GGA. The electronic wave functions were expanded in a plane-wave basis with an energy cut-off of 250.92 eV. The Brillioun zone (BZ) sampling was done with a Monkhorst-Pack point grid of $3 \times 3 \times 3$. The PHONON software [22] uses the force constants provided by VASP code.

3. Results and discussion

3.1. Crystal structure

The experimental lattice constants for YIn_3 and YSn_3 were obtained from Ref. [14] and Ref. [10] respectively. The optimized lattice parameters, volume, pressure and energy of convergence are presented in Table 1(a). The Y-atoms are positioned at (0, 0, 0) and Ga/In/Sn-atoms are positioned at (1/2, 1/2, 0). The YIn_2Sn compound is created by substituting In-atom by Sn-atom in YIn_3. The optimized lattice parameters calculated by FP-LAPW method are found to deviate from experimental values for the different exchange correlations (XC) by 0.82% for Wu–Cohen (WC) and 0.96% for PBEsol. The deviation is minimum (0.42%) for the PBE implemented in PAW method. A similar deviation of lattice parameters is observed in the case of the YSn_3 compound also. Detailed structural optimization of the unit cell as a function of external pressure has been performed by minimizing the total energy. The total energy of the crystal is minimized with respect to its volume and the minimum energy is found to be −42,065.85, −42,657.50, −43,840 and −18,432.25 Ry corresponding to YIn_3, YIn_2Sn, YSn_3 and YGa_3 respectively. The calculated pressure corresponding to the minimum volume was 69.13, 55.039, 79.17 and 100.82 GPa for YIn_3, YIn_2Sn, YSn_3 and YGa_3 are respectively. The volume vs. energy curves of YX_3 compounds have been presented in Fig. 1(a–d), and their crystal structures are shown in the inset.

The Y–Y bond length is 4.55 Å in YIn_3 which increases to 4.68 Å in YSn_3 and has intermediate value of 4.58 Å in YIn_2Sn; the Y–In bond length is 3.21 Å in YIn_3; Y–Sn bondlength is 3.27 Å in YSn_3, an increase of 1.86% in the bondlength is observed with increase in a single valence electron in Sn-atom. The input parameters