Physical properties of SrSn$_4$ single crystals

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Abstract

We present detailed thermodynamic and transport measurements on single crystals of the recently discovered binary intermetallic superconductor, SrSn$_4$. We find this material to be a slightly anisotropic three-dimensional, strongly coupled, possibly multiband, superconductor. Hydrostatic pressure causes a decrease in the superconducting transition temperature at the rate of $\approx -0.068 \text{ K kbar}^{-1}$. Band structure calculations are consistent with experimental data on the Sommerfeld coefficient and upper superconducting critical field anisotropy, and suggest a complex, multi-sheet Fermi surface formed by four bands.

(Some figures may appear in colour only in the online journal)

1. Introduction

Recent discoveries of non-oxide superconductors [1–4] with respectably high transition temperatures, $T_c$, and pairing mechanisms more complex than an isotropic, single-band, phonon-mediated one, have revitalized interest in intermetallic superconductors and promoted detailed studies of relatively simple binary and ternary materials, in particular those containing alkaline earths or light elements, that did not get enough attention in the past due to their complex synthesis, air sensitivity or were just overlooked.

The existence of a binary SrSn$_4$ phase was suggested about 30 years ago [5] but only recently [6] was the crystal structure solved and superconductivity ($T_c = 4.8 \text{ K}$) discovered. Thus SrSn$_4$ is the most recent addition to the alkaline earth stannides group of superconductors (for SrSn$_3$, BaSn$_3$ and BaSn$_5$ the superconducting transition temperatures are $\approx 5.4 \text{ K}$ [7], $\approx 2.4 \text{ K}$ [8] and $\approx 4.4 \text{ K}$ [9], respectively). SrSn$_4$ crystallizes in the orthorhombic structure ($Cmcm$ space group) with a unique Sr site and three different Sn sites. Of the physical properties, only low temperature and low field magnetization measured on a polycrystalline sample have been reported so far [6].

In this work we report the growth of single crystals of SrSn$_4$ and measurements of their thermodynamic and transport properties. Both the superconducting and normal states were characterized. The relevant results are compared with the band structure calculations.

2. Methods

Single crystals of SrSn$_4$ were produced by traditional solution-growth methods [10, 11]. Elemental Sr and Sn were placed in a 2 ml alumina crucible (with the ratio of 3.5:96.5). A second, catch crucible, containing silica wool was placed on the top of the growth crucible and sealed in a silica ampoule under approximately 1/3 atmosphere of argon gas. It should be noted that the packing and assembly of the growth ampoule was performed in a glovebox with nitrogen atmosphere. The sealed ampoule was placed in a 2 ml alumina crucible (with the ratio of 3.5:96.5). A second, catch crucible, containing silica wool was placed on the top of the growth crucible and sealed in a silica ampoule under approximately 1/3 atmosphere of argon gas. It should be noted that the packing and assembly of the growth ampoule was performed in a glovebox with nitrogen atmosphere. The sealed ampoule was heated up to 800 $^\circ \text{C}$ over several hours, then cooled to 370 $^\circ \text{C}$ and slowly cooled to 260 $^\circ \text{C}$ over 36 h. At this temperature, the crucible was removed from the furnace and the remaining liquid was decanted. The crystals grow as elongated blades or rods of a few mm length and sub-mm in the other two dimensions. The crystals are air-sensitive and have to be kept in a nitrogen glovebox. An effort was made to minimize the exposure to air in the process of handling and shaping the samples for the thermodynamic and transport measurements.
Figure 1. Comparison of the x-ray patterns taken on non-oxidized and oxidized powdered SrSn$_4$ single crystals. Peaks that belong to the SrSn$_4$ are labeled with their $h$ $k$ $l$ values. Note: the only differences between the two runs were (i) removal of Kapton film and (ii) 7 h exposure to air. Note: second-phase Sn peaks (from small amounts of residual Sn flux) are essentially unchanged by exposure to air.

Powder x-ray diffraction data on both non-oxidized and oxidized samples were collected by a Rigaku Miniflex diffractometer with Cu Kα radiation at room temperature. The diffraction pattern of the non-oxidized SrSn$_4$ was taken from the powder of SrSn$_4$ single crystals that were ground in a glovebox. The sample powder was sealed by Kapton film during the measurement to protect it from oxidation. The same powder was used for the oxidized x-ray diffraction after a 7 h exposure to air.

Temperature- and magnetic-field-dependent dc magnetization was measured using a Quantum Design MPMS-5 SQUID magnetometer. Electrical resistance was measured in a Quantum Design PPMS instrument using a conventional four-probe geometry. Platinum wires were attached to the sample using EpoTek H20E silver epoxy with the current flowing approximately along the longest dimension of the crystal ($a$ axis). The epoxy was cured in air at 120°C for ~20 min. This procedure resulted in some surface oxidation, but seems to preserve the structural integrity and electrical current continuity for the resistance samples. Heat capacity was measured in a PPMS instrument using a relaxation technique. Low field dc magnetization under pressures up to ~10 kbar was measured in MPMS-5 using a commercial, HMD, Be–Cu piston–cylinder pressure cell [12] with Daphne oil 7373 as a pressure medium and superconducting Pb as a low temperature pressure gauge [13].

3. Results and discussion

Powder x-ray diffraction (figure 1) on the non-oxidized sample confirms that the synthesized crystals are SrSn$_4$ with $Cmcm$ structure. The obtained lattice parameters are $a = 4.625(2)$ Å, $b = 17.384(6)$ Å and $c = 7.077(3)$ Å, consistent with the literature data [6]. A few lines from residual Sn flux are also visible. In contrast, the diffraction peaks of SrSn$_4$ all disappear in the oxidized sample’s diffraction pattern, leaving only Sn peaks, with their intensities remaining basically unchanged (figure 1). These results imply that the oxidation of the powdered SrSn$_4$ results in a phase that is too small or disordered to diffract.

Temperature-dependent resistivity data for SrSn$_4$ are presented in figure 2. Since the sample was of somewhat irregular shape, the data are presented normalized to the room temperature value. The room temperature resistivity, to within a factor of two, is approximately 200 $\mu$cm. The resistivity data show metallic ($d\rho/dT > 0$) behavior with rather high residual resistivity ratio, $\text{RRR} = \rho(300 \text{ K})/\rho(5 \text{ K}) \approx 70$. The superconducting transition, with an onset at $\sim 4.9$ K, is clearly seen in the data.

Figure 2. The temperature-dependent, normalized resistivity of SrSn$_4$. Inset: low temperature data showing the superconducting transition.

Anisotropic temperature-dependent susceptibility, $M/H$, of SrSn$_4$.

Figure 3. Anisotropic temperature-dependent susceptibility, $M/H$, of SrSn$_4$.
or ferromagnetic contribution that saturates by $\sim$5 kOe at $\sim\times10^{-4} \mu_B/\text{f.u.}$ value. The temperature dependence of the susceptibility is somewhat surprising. The high temperature part of the anisotropic $M/H(T)$ in principle can be fitted with a modified Curie–Weiss law, $\chi = \chi_0 + C/(T - \Theta)$, resulting in a rather large, $0.7$–$0.9 \mu_B$, effective moment and large, negative, of the order of $-200$ K, values of $\Theta$. At this point we have doubts that such a local-moment-like picture has any merit. More work is required to determine if this temperature dependence is intrinsic and what is the mechanism behind it.

Superconductivity with the onset of $\sim4.8$ K is clearly seen in the low field zero-field-cooled (ZFC) susceptibility data, figures 4 and 5 (no corrections for the demagnetization factor were employed). To infer an anisotropic upper superconducting critical field for SrSn$_4$, a set of low field ZFC susceptibility measurements were performed (see figures 4 and 5). A criterion of $M = 0$ was chosen for the upper critical field. Alternatively, anisotropic $H_{c2}(T)$ can be evaluated from the shifts of resistively measured superconducting transitions in different applied magnetic fields (figure 6). Onset and offset criteria are used for the resistivity data (figure 6(a)). The resulting anisotropic $H_{c2}(T)$ curves are shown in figure 7. As is often the case, the $T_{\text{onset}}$ criterion agrees quite well with the $T_{\text{offset}}$ criterion for magnetization. Albeit different measurements and criteria give somewhat different $H_{c2}(T)$ curves, several features are observed in all of them. A distinct upward curvature is clearly seen for both orientations (this upturn is particularly sharp in onset resistivity data). This feature might be a signature of multiband superconductivity [14]. The upper critical field of SrSn$_4$ is rather small, clearly below 10 kOe at $T = 0$. The anisotropy of $H_{c2}$ is rather small, it does not exceed $\sim1.5$. $H_{c2}(T)$ curves from magnetization and offset resistive data are similar. Taken together these data suggest that this material might have complex superconductivity and/or a superconducting $H$–$T$ phase diagram. It has to be noticed that $T_c$ and the superconducting critical fields found for SrSn$_4$ in this work are significantly different from that for elemental Sn used as flux ($T_c(Sn) \approx 3.7$ K, and $H_c(Sn, T = 0) = 305$ Oe), which rules out traces of Sn flux in the crystals as the source of the superconducting behavior [15].

The low temperature heat capacity of SrSn$_4$ is shown in figure 8. A 10 kOe applied field is enough to completely suppress superconductivity (figure 7) without changing the normal state properties. From the low temperature, in-field, heat capacity data, the Sommerfeld coefficient for SrSn$_4$ is estimated to be $\gamma \approx 9.7$ mJ mol$^{-1}$ K$^{-2}$ and the Debye temperature $\Theta \approx 170$ K. The superconducting transition is clearly seen in zero-field heat capacity data. The jump at $T_c$ is $\Delta C_p/T_c \approx 20.8$ mJ mol$^{-1}$ K$^{-2}$ which corresponds to $\Delta C_p/\gamma T_c \approx 2.1$. This value is higher than the canonical 1.43 value expected for an isotropic weakly coupled Bardeen–Cooper–Schriffer (BCS) superconductor and suggests that SrSn$_4$ is a strongly coupled
Figure 6. Low temperature resistivity of SrSn$_4$ measured at 0, 50, 100, 200, 300, 400, 500, 600, 800, 1000, 2000 and 3000 Oe. (a) $H \parallel b$ and (b) $H \parallel ac$. Criteria for $T_{\text{onset}}$ and $T_{\text{offset}}$ are shown for the $H = 300$ Oe, $H \parallel b$ data.

Figure 7. Anisotropic upper critical field of SrSn$_4$ from magnetization and magnetotransport measurements.

Figure 8. Low temperature heat capacity of SrSn$_4$ plotted as $C_p$ versus $T$ in zero and 10 kOe ($H \parallel b$) applied field. Upper left inset: the same data plotted as $C_p$ versus $T^2$, dashed line—extrapolation of the low temperature linear region of the 10 kOe data. Lower right inset: $H = 0$ $C_p(T)$ data plotted on a log–log scale, the dashed line corresponds to $C_p \propto T^3$.

Figure 9. Pressure dependence of the superconducting transition temperature of SrSn$_4$. Dashed line—linear fit. Inset—low field magnetization under pressure, the arrow points in the direction of increasing pressure.

Finally, the $C_p(T)$ behavior in the superconducting state (figure 8, lower right inset) appears to be non-exponential and reasonably well described by the $C_p \propto T^3$ function. If intrinsic, such dependence might point to deviations from isotropic single-band superconductivity for this material. We add a word of caution here that lower temperature heat capacity measurements are required to better assess the nature of the superconducting state in SrSn$_4$.

The superconducting transition temperature of SrSn$_4$ linearly decreases under pressure up to ~8 kbar (figure 9). The pressure derivative $dT_c/dP = -0.068 \pm 0.007$ K kbar$^{-1}$, is rather small, similar in sign and order of magnitude to those measured for a number of elemental and binary superconductors [17]. Such pressure dependence is possibly the result of rather weak dependence of the density of states on energy near the Fermi level as well as possibly opposing changes to $T_c$ caused by a shift in the phonon spectrum by hydrostatic pressure.
The electronic structure calculation has been done within generalized gradient approximations of density functional theory using the QUANTUM ESPRESSO package [18]. We have employed a plane-wave basis set and ultrasoft pseudo-potential [19] and the Perdew and Wang [20] exchange–correlation functional. The Brillouin zone (BZ) summations were carried out over a $16 \times 16 \times 8$ BZ grid with Gaussian boarding 0.02 Ryd in a self-consistent calculation and summation over tetrahedra for electronic density of states calculation. The plane-wave energy cutoff at 30 Ryd allows an accuracy of 0.2 mRyd/atom. The calculated density of states (DOS) is presented in figure 10. Similar to the results published in [6, 21], the Fermi level ($E_F$) is located near the edge of a local maximum and close to a local minimum. However, the local minimum is less pronounced compared to linear muffin-tin orbital (LMTO) results [6, 21]. The value of DOS at $E_F$ ($\approx 5$ St/eV cell) is pretty high and the corresponding $\gamma_{band} \approx 5.8$ mJ mol$^{-1}$ K$^{-2}$. Comparison with the experimental value, $\gamma_{exp} = (1 + \lambda)\gamma_{band}$, yields the value of the enhancement factor (due to electron–electroton–electron–phonon interactions) $\lambda \approx 0.7$, that appears to be comparable to the enhancement observed in alkali metals due to electron–phonon interactions [22]. The almost equal distribution of total DOS between all atoms in the compound points to strong hybridization of valence electrons (that might contribute to the value of $\lambda$). A detailed analysis of the character of electrons bonds has been provided in [6].

According to the calculations, a Fermi surface (FS) of SrSn$_4$ is formed by multiple sheets formed by four bands (figure 11). The FS topology is complex: bands 4 and 7 give contribution in the form of a number of rather small, distorted, ellipsoids, whereas bands 5 and 6 contribute to the FS in the form of multiply connected ‘monsters’. There appears to be no dominating low-dimensional, cylindrical, FS parts. The small $H_{c2}$ anisotropy is consistent with this three-dimensional FS. Similarly, no profound anisotropy in the electrical transport is expected.

### 4. Summary

Detailed thermodynamic and transport measurements were performed on single crystals of SrSn$_4$ with $RRR \approx 70$. The normal-state magnetic susceptibility is paramagnetic and slightly anisotropic. SrSn$_4$ can be characterized as a strongly coupled three-dimensional superconductor with $T_c \approx 4.8$ K and the upper critical field of the order of 2 kOe. The anisotropy of $H_{c2}$ does not exceed 1.5 and is slightly temperature-dependent. $T_c$ decreases slowly under hydrostatic pressure up to $\sim 10$ kbar. The heat capacity and $H_{c2}(T)$ data suggest that superconductivity in this material may be more complex than isotropic BCS. Band structure calculations of the DOS at $E_F$ are consistent with experimental observations, suggesting the strong hybridization of valence electrons and yielding a three-dimensional FS with multiple sheets originating from four bands.

Since SrSn$_4$ crystals have high RRR and easily accessible $T_c$, detailed studies of the symmetry of the superconducting state by low temperature thermal transport and/or penetration depth measurements could be of interest.

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References

[1] Nagarajan R, Mazumdar C, Hossain Z, Dhar S K, Gopalakrishnan K V, Gupta L C, Godart C, Padalia B D and Vijayaraghavan R 1994 Phys. Rev. Lett. 72 274
[2] Cava R J et al 1994 Nature 367 252
[3] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 Nature 410 63
[4] Rotter M, Tege M and Johrendt D 2008 Phys. Rev. Lett. 101 107006
[5] Marshall D and Chang Y A 1981 J. Less-Common Met. 78 139
[6] Hoffmann S and Fässler T F 2003 Inorg. Chem. 42 8748
[7] Fässler T F and Hoffmann S 2000 Z. Anorg. Allg. Chem. 626 106
[8] Fässler T F and Kronseder C 1997 Angew. Chem. Int. Edn Engl. 36 2683
[9] Fässler T F, Hoffmann S and Kronseder C 2001 Z. Anorg. Allg. Chem. 620 2486
[10] Canfield P C and Fisk Z 1992 Phil. Mag. B 65 1117
[11] Canfield Paul 2010 Properties and Applications of Complex Intermetallics (Book Series on Complex Metallic Alloys vol 2) ed E Berlin-Ferreé (New Jersey: World Scientific) p 93
[12] www.qdusa.com/products/high-pressure-cell-mpms.html
[13] Eiiling A and Schilling J S 1981 J. Phys. F: Metal Phys. 11 623
[14] Shulga S V, Drechsler S-L, Fuchs G, Müller K-H, Winzer K, Heinecke M and Krug K 1998 Phys. Rev. Lett. 80 1730
[15] Finnemore D K and Mapother D E 1965 Phys. Rev. 140 A507
[16] Carbotte J P 1990 Rev. Mod. Phys. 62 1027
[17] Brandt N B and Ginzburg N I 1965 Usp. Fiz. Nauk 85 485
[18] Brandt N B and Ginzburg N I 1965 Sov. Phys.–Usp. 8 202 (Engl. transl.)
[19] Giannozzi P et al 2009 J. Phys.: Condens. Matter 21 395502
[20] Vanderbilt D 1990 Phys. Rev. B 41 7892
[21] Perdew J P and Wang Y 1992 Phys. Rev. B 45 13244
[22] Grimvall G 1981 The Electron–Phonon Interaction in Metals (Amsterdam: North-Holland)
[23] Kokalj A 1999 J. Mol. Graph. Modell. 17 176