8-21-2012

Physical properties of single crystalline BaSn5

Xiao Lin
Iowa State University and Ames Laboratory

Sergey L. Bud’ko
Iowa State University and Ames Laboratory, budko@ameslab.gov

Paul C. Canfield
Iowa State University and Ames Laboratory, canfield@ameslab.gov

Follow this and additional works at: https://lib.dr.iastate.edu/physastro_pubs

Part of the Condensed Matter Physics Commons

The complete bibliographic information for this item can be found at https://lib.dr.iastate.edu/physastro_pubs/682. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.

This Article is brought to you for free and open access by the Physics and Astronomy at Iowa State University Digital Repository. It has been accepted for inclusion in Physics and Astronomy Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Physical properties of single crystalline BaSn5

Abstract
We present a comprehensive study of the binary intermetallic superconductor, BaSn5. High-quality single crystalline BaSn5 was grown out of a Sn flux. Detailed thermodynamic and transport measurements were performed to study BaSn5's normal and superconducting state properties. This material appears to be a strongly coupled, multiband superconductor. $H_c^2(T)$ is almost isotropic. De Haas–van Alphen oscillations were observed and two effective masses were estimated from the FFT spectra. Hydrostatic pressure causes a decrease in the superconducting transition temperature at the rate of $\approx -0.053 \pm 0.001$ K/kbar.

Keywords
single crystals, superconducting, thermodynamic, transport properties

Disciplines
Condensed Matter Physics

Comments
Physical properties of single crystalline $\text{BaSn}_5$

Xiao Lin, Sergey L. Bud'ko & Paul C. Canfield

To cite this article: Xiao Lin, Sergey L. Bud'ko & Paul C. Canfield (2012) Physical properties of single crystalline $\text{BaSn}_5$, Philosophical Magazine, 92:24, 3006-3014, DOI: 10.1080/14786435.2012.682180

To link to this article: https://doi.org/10.1080/14786435.2012.682180

Published online: 04 May 2012.
Physical properties of single crystalline BaSn₅

Xiao Lin*, Sergey L. Bud’ko and Paul C. Canfield

Department of Physics and Astronomy and Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA

(Received 26 January 2012; final version received 20 March 2012)

We present a comprehensive study of the binary intermetallic superconductor, BaSn₅. High-quality single crystalline BaSn₅ was grown out of a Sn flux. Detailed thermodynamic and transport measurements were performed to study BaSn₅’s normal and superconducting state properties. This material appears to be a strongly coupled, multiband superconductor. \( H_c^2(T) \) is almost isotropic. De Haas–van Alphen oscillations were observed and two effective masses were estimated from the FFT spectra. Hydrostatic pressure causes a decrease in the superconducting transition temperature at the rate of \( \approx -0.053 \pm 0.001 \) K/kbar.

Keywords: single crystals; superconducting; thermodynamic and transport properties

1. Introduction

To search for new superconductors, one of many ways is to look for compounds that share similar features with the already reported superconductors. On the one hand, BaSn₅ has a similar band dispersion near the Fermi level (\( E_F \)) as A15 type superconductors, such as V₃Si and Nb₃Sn [1]. On the other hand, BaSn₅ forms in the \( P\bar{6}/mnm \) structure, a variant of the AlB₂ structure, the prototype of MgB₂ which superconducts at \( 40 \) K [2–5].

The first study of BaSn₅ can be traced back to 1979 [6], however, only recently has its structure been solved [1]. As one of the alkaline earth stannide group of superconductors (for SrSn₄, SrSn₃, BaSn₃) the superconducting transition temperatures are \( \sim 4.8 \) K [7,8], \( \sim 5.4 \) K [9] and \( \sim 2.4 \) K [10] respectively), BaSn₅’s superconducting transition temperature is reported to be \( \sim 4.4 \) K [1]. So far, only its low-temperature and low-field magnetization has been characterized on polycrystalline samples [1].

In this article we report the growth of single crystalline BaSn₅, and the measurement of its thermodynamic and transport properties. Both the superconducting and normal states are characterized. We also present the effect of pressure on the superconducting properties of BaSn₅, and the observation of low-temperature de Haas–van Alphen oscillations.

*Corresponding author. Email: xiaolin@iastate.edu

ISSN 1478–6435 print/ISSN 1478–6443 online
The work as part of Xiao Lin, Sergey L. Bud’ko and Paul C. Canfield’s official duties as Federal Government Contractors is published by permission of the Ames Laboratory, US Department Of Energy, under Contract Number(s) FA9550-09-1-0603 and DE-AC02-OTCH 11358. The US Government retains for itself, and others acting on its behalf, a paid-up, non-exclusive, and irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

http://dx.doi.org/10.1080/14786435.2012.682180
http://www.tandfonline.com
2. Experimental details

Single crystals of BaSn$_5$ were grown out of excess Sn by the high-temperature solution technique [11]. Elemental Ba and Sn with an atomic ratio of Ba$_8$Sn$_92$ were placed in a 2 ml alumina crucible. A second catch crucible stuffed with silica wool was placed on the top of the growth crucible. Both crucibles were sealed in a silica ampoule under approximately $1/3$ atmosphere of high-purity argon gas. To prevent oxidization of the growth materials, the packing and assembly of the ampoule was performed in a glovebox with a nitrogen atmosphere. This ampoule was heated up to 700°C, then cooled to 425°C, followed by a slow cool over a period of 40 hours to 270°C, at which temperature the excess flux was decanted from the crystals. Crystals of BaSn$_5$ grown in this manner form in rod-like shapes of a few mm in length and sub-mm in the other two dimensions. Due to the samples’ air-sensitivity, crystals were kept in the glovebox, and efforts were made to minimize their exposure during measurement.

Powder X-ray diffraction data on both non-oxidized and oxidized samples were collected by a Rigaku Miniflex diffractometer with Cu-K$_\alpha$ radiation at room temperature. The diffraction pattern of the non-oxidized BaSn$_5$ was taken from the powder of BaSn$_5$ single crystals which was ground in the glovebox. The sample powder was sealed by Kapton film during the measurement to protect it from oxidization. To study the oxidation effect, a second X-ray diffraction was performed on the same powder after removal of the Kapton film and a seven-hour exposure to the air. The lattice constants of non-oxidized BaSn$_5$ were statistically determined by measurements of multiple samples with Si ($\alpha = 5.4301$ Å) as an internal standard.

Temperature- and magnetic-field dependent dc magnetization data were measured in a Quantum Design MPMS-5 SQUID magnetometer. The ac resistance was measured via a standard four-probe method in a Quantum Design PPMS instrument with the ACT option. Platinum wires were attached to the sample using Dupont 4929 silver paint with the current approximately flowing along the longest dimension (the crystal’s $c$-axis). Resistance as a function of temperature was measured at different magnetic fields with the field’s direction parallel to the $c$-axis and $ab$-plane, respectively. A relaxation technique was applied in the heat capacity measurements in a PPMS instrument. For the measurement of the low-field dc magnetization under pressure, a commercial HMD Be–Cu piston–cylinder pressure cell [12] was used. The highest pressure reached $\sim 10$ kbar with Daphne oil 7373 as a pressure medium and superconducting Pb as a low-temperature pressure gauge [13].

3. Results and discussion

Figure 1 presents a comparison of powder X-ray diffraction on both non-oxidized and oxidized sample. The diffraction pattern from the non-oxidized sample confirms that the synthesized crystals are BaSn$_5$ with the $P6/mmm$ structure. The obtained lattice parameters are $\alpha = 5.368(4)$ Å, $c = 7.097(4)$ Å, consistent with the reported data [1]. Together with BaSn$_5$’s diffraction peaks, several peaks from the Sn flux residue are also visible in the diffraction pattern. In contrast, after a seven-hour exposure to air, the same specimen lost all its diffraction peaks of BaSn$_5$. As shown in Figure 1, only Sn’s diffraction peaks survived, with their intensities
essentially unchanged. The disappearance of BaSn₅ under the powder X-ray diffraction is probably due to the oxidization of BaSn₅, resulting in phases that are too small or too disordered to diffract. Similar phenomena were also observed in the powder X-ray diffraction data of non-oxidized and oxidized single crystalline SrSn₄ [8].

The zero-field, in-plane resistivity of BaSn₅ as a function of temperature is presented in Figure 2. Due to the sample’s irregular shape in cross-section and its air-sensitivity, its resistivity is normalized with respect to the room temperature value. To within a factor of 25%, the room temperature resistivity reaches approximately 100 μΩcm. In the higher temperature region, the resistivity manifests typical metallic behavior, increasing linearly as the temperature rises. The very substantial residual resistivity ratio (RRR) = ρ(305 K)/ρ(5.0 K) ~ 1200 indicates that the crystals grow with a very low number of impurities/defects (a conclusion further supported by the

Figure 1. Comparison of the X-ray patterns taken on non-oxidized and oxidized powdered BaSn₅ single crystals. Peaks that belong to BaSn₅ are labeled with their h k l values. Note: The only differences between the two runs were (i) removal of the Kapton film and (ii) seven hours exposure to air.

Figure 2. The temperature-dependent, normalized resistivity of BaSn₅. Inset: low-temperature data showing the superconducting transition.
observation of quantum oscillations, discussed below). The inset to Figure 2 shows the low-temperature resistivity and a sharp transition to the superconducting state with offset at about 4.4 K, which is consistent with the literature data [1].

The temperature-dependent dc magnetic susceptibility, $M/H$, with the magnetic field parallel to the c-axis and ab-plane is shown in Figure 3. For an applied field of 50 kOe, the normal state of BaSn$_5$ exhibits diamagnetic behavior in both directions, and essentially does not change with temperature in the higher temperature region. Small anisotropy can be detected above 20 K, with absolute value of $|(M/H)_{ab}| > |(M/H)_c|$. However, in the low-temperature region, a dramatic enhancement of the diamagnetic feature, especially with the field parallel to the c-axis, is clearly seen in the inset to Figure 3. These sudden changes in $M/H$ are most likely brought about by de Haas–van Alphen oscillations and are shown in the upper inset to Figure 4.

To study de Haas–van Alphen oscillations in BaSn$_5$, the dc magnetization as a function of the applied magnetic field at several different temperatures was
measured (Figure 4). However, due to the sample’s air-sensitivity and irregular shape in the ab-plane, only studies with the field parallel to the c-axis are included in this work. The oscillations in the magnetization can be observed at multiple temperatures, superimposed on the nearly constant magnetic background. The upper inset of Figure 4 gives an example of this oscillatory behavior as a function of the inverse field up to 70 kOe at 1.85 K. A fast Fourier transform (FFT) was used to convert the oscillations to their Fourier spectra in Figure 4. Due to the limitation of the signal to noise ratio, only two peaks can be resolved from the spectra with frequencies of 1.16 MG (α) and 1.59 MG (β). Figure 4 also represents the evolution of the spectra with respect to temperature. It can be clearly seen that the amplitudes of the spectra gradually attenuate and finally fade away at about 15 K. For a certain frequency $F$, the amplitude of the oscillation in the magnetization $M$ is given by the Lifshitz–Kosevitch (LK) equation [14]:

$$M = -2.602 \times 10^{-6} \left( \frac{2\pi}{HA'} \right)^{1/2} \times \frac{GFT \exp(-\alpha p x/H)}{p^{3/2} \sinh(-\alpha p T/H)} \times \sin \left[ \frac{(2\pi p F)}{H} - \frac{1}{2} \pm \frac{\pi}{4} \right]$$

where $\alpha = 1.47(m/m_0) \times 10^3$ G/K, $A''$ is the second derivative of the cross-sectional area of the Fermi surface with respect to the wavevector along the direction of the applied field, $G$ is the reduction factor arising from the electron spin, $\rho$ is the number of the harmonic of the oscillation, and $x$ is the Dingle temperature. Thus, the temperature dependence of the amplitude ($A$) of frequency $\alpha, \beta$, plotted in the lower inset to Figure 4, can be used to determine the effective mass of the orbits via the LK formula, described above. From the slope of ln($A/T$) plotted as a function of temperature, the effective masses were found to be $m_\alpha \approx 0.09 m_0$ and $m_\beta \approx 0.13 m_0$, where $m_0$ is the bare electron mass. However, for further understanding of the oscillations and the topology of the Fermi surface, the angular dependence of the spectra as well as detailed calculations of the band structure and the Fermi surfaces of BaSn$_5$ are needed.

The zero-field-cooled (ZFC) susceptibilities measured at a set of different low fields are presented in Figure 5 (no corrections for the demagnetization factor were employed). At 25 Oe, a sharp superconducting transition is clearly seen with the
onset of $\approx 4.4 \text{ K}$. To infer an anisotropic upper superconducting critical field for BaSn$_5$, the first data point that deviates from the normal state is chosen as the criterion of the superconducting transition. Alternatively, anisotropic $H_{c2}(T)$ can be evaluated from the shifts of the resistively measured superconducting transitions in different applied magnetic fields (Figure 6). $R = 0$ is chosen as the $T_{R=0}$ criterion in the resistivity data. Multiple $M(T)$ and $R(T)$ measurements were carried out on different samples, and the data were consistent with each other. The resulting anisotropic $H_{c2}(T)$ curves are shown in Figure 7, in which $H_{c2}(T)$ obtained from the magnetization data agrees with $H_{c2}(T)$ obtained from the resistivity data quite well. Linear extrapolations yielded an upper critical field of $\sim 550 \text{ Oe}$ at $T = 0 \text{ K}$ from $M(T)$ measurement, and $H_{c2}(T = 0) \approx 950 \text{ Oe}$ from $R(T)$ data. Both measurements clearly show that BaSn$_5$ maintains a rather small upper critical field. Despite of the differences in the $H_{c2}$ values, both $M(T)$ and $R(T)$ support the conclusion that BaSn$_5$ shows almost isotropic behavior in its superconducting state as seen in Figure 7.

Figure 6. (a) Low-temperature resistance of BaSn$_5$ measured at 0, 50, 100, 250, 500 and 750 Oe with $H \parallel \langle ab \rangle$. (b) Low-temperature resistance of BaSn$_5$ measured at 0, 50, 100, 200, 300, 400, 500 and 750 Oe with $H \parallel c$. Criteria for $T_{R=0}$ are shown for the $H = 0$, $H \parallel \langle ab \rangle$ data.

Figure 7. The upper critical field of BaSn$_5$ from magnetization and magnetotransport measurements.
It should be noticed that $T_c$ and the superconducting critical fields obtained for BaSn$_5$ in this work are different from that for elemental Sn used as the flux ($T_c$(Sn) $\approx$ 3.7 K, and $H_{c2}$(Sn, $T = 0$) = 305 Oe), which rules out traces of Sn flux in the crystals as the source of the superconducting behavior.

The low-temperature heat capacity of BaSn$_5$ was measured in both the zero and applied magnetic field (Figure 8). It is clearly seen that the superconductivity is completely suppressed in 10 kOe without changing its normal state properties. A clear jump at about 4.4 K in the zero-field heat capacity data is associated with the superconducting transition, which gives $\Delta C_p/T_c \approx 16.7$ mJ/mol K$^2$. The lower left inset to Figure 8 shows the low-temperature (down to 0.4 K), in-field (20 kOe), heat capacity data, the Sommerfeld coefficient for BaSn$_5$ is estimated to be $\gamma \approx 10.8$ mJ/mol K$^2$, and the Debye temperature $\Theta_D \approx 182.5$ K. Thus, $\Delta C_p/\gamma T_c$ can be estimated to be about 1.55. This value is slightly higher than the canonical 1.43 value expected for an isotropic weakly coupled BCS superconductor and suggests that BaSn$_5$ might be a strongly coupled superconductor [15]. Finally, the $C_p(T)$ behavior in the superconducting state (Figure 8, upper right inset) appears to be non-exponential and reasonably well described by the function $C_p \propto T^{2.8}$. If intrinsic, such a dependence might point to deviations from isotropic single band superconductivity for this material.

The superconducting transition temperature of BaSn$_5$ linearly decreases under pressure up to $\sim$8 kbar (Figure 9). The pressure derivative $dT_c/dP \approx -0.053 \pm 0.001$ K/kbar, is rather small, similar in sign and order of magnitude to those measured for a number of elemental and binary superconductors [16]. Such a pressure dependence is possibly the result of a rather weak dependence of the density of states on the 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.

![Figure 8. Low-temperature heat capacity of BaSn$_5$ plotted as $C_p(T)$ versus $T$ in a zero and 10 kOe ($H || (ab)$) applied field. Lower left inset: low-temperature heat capacity of BaSn$_5$ plotted as $C_p(T)$ versus $T^2$ in a zero and 20 kOe ($H || (ab)$) applied field, solid line – extrapolation of the low-temperature linear region of the 20 kOe data. Upper right inset: zero-field $C_p(T)$ data plotted on a log–log scale; the solid line corresponds to $C_p \propto T^{2.8}$.](image)
4. Summary

In this article we presented the synthesis of high-quality single crystalline BaSn$_5$, as well as detailed studies of its thermodynamic and transport properties. BaSn$_5$ manifests metallic behavior in its normal state with (RRR) $\sim$ 1200. Its normal-state magnetic susceptibility is diamagnetic and slightly anisotropic. De Haas–van Alphen oscillations were observed at low temperatures and high fields with the applied magnetic fields parallel to the $c$-axis; two effective masses were resolved via FFT. BaSn$_5$ superconducts at $\sim$4.4 K with the upper critical field not exceeding 1 kOe. $H_{c2}$ shows almost isotropic behavior. $T_c$ decreases slowly under hydrostatic pressure up to 10 kbar. The heat capacity data suggest that superconductivity in BaSn$_5$ may be more complex than isotropic BCS.

Since both Haas–van Alphen oscillations and a superconducting state are observed for these high-quality BaSn$_5$ single crystals, detailed study of the angular dependence of the oscillatory behavior, the Fermi topology and the symmetry of the superconducting state could be of interest.

Acknowledgements

This work was carried out at the Iowa State University and supported by AFOSR-MURI grant No. FA9550-09-1-0603 (X. Lin and P.C. Canfield). Part of this work was performed at Ames Laboratory, US DOE, under contract No. DE-AC02-07CH 11358 (S.L. Bud’ko).

References