Type-II superconductivity in W₅Si₃-type Nb₅Sn₂Al

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Abstract
We report the discovery of superconductivity (SC) in the ternary aluminide Nb₅Sn₂Al, which crystallizes in the W₅Si₃-type structure with one-dimensional Nb chains along the c-axis. It is found that the compound has a multiband nature and becomes a weakly coupled, type-II superconductor below 2.0 K. The bulk nature of SC is confirmed by the single heat jump, whose temperature dependence shows apparent deviation from a single isotropic gap behavior. The lower and upper critical fields are estimated to be 2.0 mT and 0.3 T, respectively. From these values, we derive the penetration depth, coherence length and Ginzburg–Landau parameter to be 516 nm, 32.8 nm and 15.6, respectively. In contrast, the isostructural compound Ti₅Sn₂Al does not superconduct above 0.5 K. A comparison of these results with other W₅Si₃-type superconductors suggests that $T_c$ of these compounds correlates with the average number of valence electrons per atom.

Keywords: superconductivity, ternary aluminide, W₅Si₃-type structure

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

1. Introduction

Some structural types have been shown to favor the occurrence of superconductivity (SC) in intermetallic compounds [1]. A well-known example is cubic A15 materials with the general formula $A_2B_3$, in which nearly 50 superconductors were found and the highest $T_c$ reaches above 20 K [2]. Recently, the $A_2B_3$ compounds and their derivatives emerge as another fertile ground for SC [3–16]. These materials mainly crystallize in three different structural types, namely, tetragonal Cr₂B₂-type [17], W₅Si₃-type [18], and hexagonal Mn₃Si₃-type [19]. In particular, the W₅Si₃ and A15 types are similar in that they both consist of one-dimensional chains of the A atoms, which could give rise to a large density of states at the Fermi level $[N(E_F)]$ [20]. So far, except for W₅Si₃ itself [9], superconductors of this structural type include Nb₅X₃ (X = Si, Ge and Ga) [3–5], Nb₅Sn₂Ga [7], Ta₂Ga₃Sn [8], Hf₅Sb₂₃Ru₀.₅ [13], and Zr₅Sb₂₄Ru₀.₆ [14]. The exploration and study of a new material will help to identify the factors that govern $T_c$ in these materials.

Ternary aluminides Nb₅Sn₂Al and Ti₅Sn₂Al were first synthesized in the 1990s and found to adopt the W₅Si₃-type structure [21]. However, to our knowledge, their physical properties have not been investigated to date. In this paper, we present measurements of resistivity, Hall coefficient, magnetic susceptibility and specific heat on high-quality polycrystalline samples of Nb₅Sn₂Al and Ti₅Sn₂Al. We show that Nb₅Sn₂Al is a type-II superconductor with $T_c$ of 2.0 K, and the behavior of its specific heat jump is inconsistent with the Bardeen–Cooper–Schrieffer (BCS) prediction for a single isotropic gap. Nevertheless, the isostructural Ti₅Sn₂Al with remains normal down to 0.5 K, albeit with a larger
The structure of M₅Sn₂Al is sketched in

3.1. Crystal structure and chemical composition

These samples were measured with an energy-dispersive x-ray radiation at room temperature. The chemical compositions of Sommerfeld coefficient. We compare these results with other W₅Si₃-type superconductors and discuss the dependence of their Tc on the valence electron count.

2. Experimental

Polycrystalline M₅Sn₂Al (M = Nb, Ti) samples were synthesized by using a solid state reaction method, similar to the previous report [21]. High purity powders of M (99.99%), Sn (99.999%) and Al (99.999%) with the stoichiometric ratio of 5:2:1 were homogenized and pressed into pellets in an argon-filled glove-box. The pellets were then loaded in an alumina crucible, which was sealed in a tantalum (Ta) tube. The Ta tube was protected in a argon-filled sealed quartz tube, which was heated to 900°C–1000°C in a muffle furnace. After maintaining for 10 d, the quartz tube was quenched into cold water. The reaction was repeated for several times with intermediate grinding to ensure sample homogeneity.

The purity of the resulting M₅Sn₂Al samples was checked by powder x-ray diffraction (XRD) using a PANalytical x-ray diffractometer with a monochromatic Cu-Kα1 radiation at room temperature. The chemical compositions of these samples were measured with an energy-dispersive x-ray (EDX) spectrometer (Model Octane Plus). The spectra were collected on different locations of each sample, and the Al content was not included in the analysis due to contribution from Al sample holders. For consistency reasons, all the physical property measurements were performed on samples derived from the same pellet. A part of the pellet was cut into regular-shaped samples for transport and specific heat measurements, and the remaining part was crushed into powders. The electrical resistivity was measured using a standard four-probe method. Resistivity, Hall coefficient and specific heat measurements down to 1.8 K were performed on a Quantum Design PPMS-9 Dynacool. Measurements of resistivity and specific heat down to 0.5 K were carried out on a Quantum Design PPMS-9 Evercool II. The two sets of specific heat data agree well within 5% in the overlapped temperature range. The dc magnetization was measured on crushed powders with a commercial SQUID magnetometer (Quantum Design MPMS3).

3. Results

3.1. Crystal structure and chemical composition

The structure of M₅Sn₂Al is sketched in figures 1(a) and (b). All the atoms are distributed orderly in the lattice, and there are two distinct crystallographic sites for the M atoms, namely M(1) at 16k site and M(2) at 4b site. Notably, these atoms form linear and zigzag chains along the c-axis, respectively. For Nb₅Sn₂Al, this one-dimensional arrangement of Nb atoms is reminiscent of that observed in Nb₅Sn. Figure 1(c) shows the XRD patterns of the Nb₅Sn₂Al and Ti₅Sn₂Al samples at room temperature, together with structural refinement profiles using the GSAS program.

![Figure 1](image_url)

Figure 1. Schematic structure of M₅Sn₂Al projected perpendicular (a) and parallel (b) to the M atom chains. (c) Powder x-ray diffraction patterns and their refinement profiles at room temperature for Nb₅Sn₂Al and Ti₅Sn₂Al. The asterisks mark the impurity phases in the Ti₅Sn₂Al sample.

The observed and calculated diffraction patterns show a good agreement for both cases, demonstrating that they adopt the tetragonal W₅Si₃-type structure. As can be seen in table 1, the refined lattice parameters are a = 10.638 Å, c = 5.225 Å for Nb₅Sn₂Al and a = 10.558 Å, c = 5.262 Å for Ti₅Sn₂Al, which are in good agreement with the previous report [21]. It is also noted that, for Ti₅Sn₂Al, there exists additional diffraction peaks due to unknown impurities, whose maximum intensity is around one tenth that of the main phase. This suggests that the impurity phases occupy ~10% of the sample volume. On the other hand, EDX measurements yield the Nb:Sn molar ratio of 5:2.06(6) and Ti:Sn ratio of 5:2.09 (3) for the Nb₅Sn₂Al and Ti₅Sn₂Al samples, respectively. These results indicate that both compounds are stoichiometric within the experimental error. In addition, a Ti:Sn ratio in the range of 5:2.55–2.80 is observed in a small part of the Ti₅Sn₂Al sample, which is presumably ascribed to the impurities detected in XRD.
3.2. Resistivity and Hall coefficient

Figure 2(a) shows the temperature dependence of resistivity for Nb$_5$Sn$_2$Al and Ti$_5$Sn$_2$Al. For both samples, the resistivity shows a weak metallic behavior with a concave curvature, similar to that observed in other $A_5B_3$ compounds [10–12, 15]. Actually, the data of Nb$_5$Sn$_2$Al is an almost rigid upward shift of that of Ti$_5$Sn$_2$Al, pointing to essentially the same temperature-dependent electron scattering mechanism for the two samples. However, their low temperature behavior is quite different. As can be seen in the inset of figure 2(a), when cooling below 2.5 K, the resistivity of Nb$_5$Sn$_2$Al drops rapidly to zero, evidencing a superconducting transition. By contrast, for Ti$_5$Sn$_2$Al, the decrease in resistivity tends to saturate and no SC is observed down to 0.5 K.

Figure 2(b) shows the temperature dependence of $1/\rho_{H}$ for the two samples, where $e$ is the electron charge and $R_H$ is the low-field Hall coefficient. The $R_H$ of Nb$_5$Sn$_2$Al is negative at room temperature and becomes positive below 200 K. A similar sign reversal in $R_H$ is observed for Ti$_5$Sn$_2$Al, but its $R_H$ changes back to negative again at $\sim$100 K. These results provide clear evidence that these materials are multiband systems with both electrons and holes. Nevertheless, at temperatures below 50 K, $R_H$ is nearly temperature independent and the Hall resistivity is linear with magnetic field (see the inset of figure 2(b)) for both samples. Hence it appears that, in this temperature range, their electrical transport is dominated by a single type of carriers. Assuming a one-band model, the hole and electron densities are estimated to be $1.3 \times 10^{22}$ cm$^{-3}$ and $1.5 \times 10^{22}$ cm$^{-3}$ for Nb$_5$Sn$_2$Al and Ti$_5$Sn$_2$Al, respectively.

Table 1. Refined structural parameters of M$_5$Sn$_2$Al (M = Nb, Ti). Here $a$ and $c$ are the lattice parameters, $V$ the unit cell volume, $R_{wp}$ and $R_p$ the weighted and unweighted $R$ factors.

| Atoms | Site | $x$ | $y$ | $z$ |
|-------|------|-----|-----|-----|
| $M1$  | 16k  | 0.073 08 | 0.213 4 | 0   |
| $M2$  | 4b   | 0      | 0.5  | 0.25 |
| Sn    | 8h   | 0.168 3 | 0.668 3 | 0   |
| Al    | 4a   | 0      | 0.0  | 0.25 |

The occurrence of SC in Nb$_5$Sn$_2$Al is corroborated by the magnetic susceptibility results of powder samples shown in figure 3. Here the demagnetization effect is taken into consideration assuming that the powders consist of cubic-shaped grains with the demagnetization factor $N_d = 0.3$. A strong diamagnetic signal is observed in both field-cooling (FC) and zero-field cooling (ZFC) data. In addition, a divergence is seen between the ZFC and FC curves, which is characteristic of a type-II superconducting behavior. The linear extrapolation of the initial ZFC diamagnetic transition intersects with the baseline at 2.0 K (see the inset of figure 3), which coincides with the onset of zero resistivity. In light of this coincidence, we determine $T_c$ as 2.0 K for Nb$_5$Sn$_2$Al. At 0.4 K, the ZFC and FC data correspond to shielding and Meissner effects.
fractions of 85% and 22%, respectively, and hence clearly indicate bulk SC.

### 3.4. Specific heat

Figure 4(a) shows the low temperature specific heat data for Nb₅Sn₂Al and Ti₅Sn₂Al. A strong anomaly is observed in Nb₅Sn₂Al near its Tc, which further confirms the bulk nature of SC. On the other hand, its normal-state data can be well described by the Debye model C_p/T = γ + βT², where γ and β are the Sommerfeld and phonon specific heat coefficients, respectively. The fit yields γ = 19.0 mJ mol⁻¹ K⁻² and β = 0.396 mJ mol⁻¹ K⁻⁴. The Debye temperature Θ_D is then calculated as Θ_D = (12π²NR/5β)¹/² = 340 K, where N = 8 and R is the molar gas constant 8.314 J mol⁻¹ K⁻¹. Applying the same analysis to the data of Ti₅Sn₂Al gives γ = 31.5 mJ mol⁻¹ K⁻², β = 0.270 mJ mol⁻¹ K⁻⁴, and Θ_D = 386 K. Compared with Nb₅Sn₂Al, the larger Θ_D of Ti₅Sn₂Al is as expected, but its larger γ value is somewhat surprising.

Figure 4(b) shows the normalized electronic specific heat of Nb₅Sn₂Al at zero field after subtraction of the phonon contribution, plotted at a function of reduced temperature T/Tc. One can see that the normalized specific heat jump Dc/γTc ~0.86 is considerably smaller than the BCS value of 1.43 [22]. Furthermore, the temperature dependence of the specific heat jump shows a significant deviation from the BCS theory, especially in the low temperature region. Note that an extrapolation of Dc/γT to 0 K yields a negative value. This, together with the absence of additional XRD peaks from impurities (see figure 1(c)), suggests that the sample has a superconducting volume fraction close to 100%. It therefore appears that the small specific heat jump is of intrinsic origin, which points to the presence of multiple gaps as in MgB₂ [23] and Lu₂Fe₃Si₅ [24], or even gap nodes. Nevertheless, the C_p/γT data at 0.5 K is still as large as 50% of its normal-state value, and hence to distinguish these scenarios, C_p/γT measurements down to mK range would be needed.

Assuming that SC in Nb₅Sn₂Al is mediated by electron–phonon coupling, the corresponding constant, λ_p, can be estimated by using the inverted McMillan formula [25]

\[
λ_p = \frac{1.04 + μ^*\ln(Θ_D/1.45T_c)}{(1 - 0.62μ^*)\ln(Θ_D/1.45T_c) - 1.04},
\]

where μ^* is the Coulomb repulsion pseudopotential. Taking an empirical μ^* value of 0.13, we obtain λ_p = 0.46, which implies weak coupling SC in Nb₅Sn₂Al. This is consistent with the low value of ΔDc/γTc.

### 3.5. Critical fields and superconducting parameters

Figure 5(a) shows the isothermal magnetization curves at various temperatures for Nb₅Sn₂Al. The effective lower critical field Bc₁,eff at each temperature is defined as the value at which the curve deviates from its initial linear behavior. The resulting Bc₁,eff is plotted as a function of temperature in figure 5(b), and the extrapolation of the data to zero temperature yields Bc₁,eff(0) = 1.4 mT [26]. After correction for the demagnetization factor, we obtain the zero-temperature lower critical field Bc₁(0) = Bc₁,eff(0)/(1 - NGL) = 2.0 mT. Figure 5(c) shows the temperature dependence of resistivity for Nb₅Sn₂Al under various magnetic fields. With increasing field, the resistive transition is gradually suppressed to lower temperatures, as expected. Following the same criterion as shown above (see section 3.2), we determine Tc for each field as the temperature at which zero resistivity is achieved, and plot the data in figure 5(d). Extrapolation of the upper critical field Bc₂ to zero temperature, using the Wathamer–Helfand–Hohenberg (WHH) theory [27], gives Bc₂(0) = 0.3 T.

With Bc₁(0) and Bc₂(0) determined, we can estimate various superconducting parameters of Nb₅Sn₂Al. The Ginzburg–Landau (GL) coherence length ξGL(0) as ξGL(0) = (Φ₀/2πBc₂(0))¹/² = 32.8 nm, where Φ₀ = 2.07 × 10⁻¹⁵ Wb is the flux quantum. Then from the equations Bc₁(0)/Bc₂(0) = (lnNGL + 0.5)/(2ξGL²) [28] and Bc₁(0) = (Φ₀/4πξGL²eff(lnNGL + 0.5), ξGL = 15.6 and λeff = 516 nm are obtained.
the superconducting transition temperature, arrow marks the zero-temperature upper critical temperature. The solid line denotes the initial linear behavior and the arrow marks the deviation from this linearity at 0.4 K. Figure 5. (a) Field dependence of magnetization curves for the Nb5Sn2Al sample measured after zero-field cooling to various temperatures. The solid line denotes the initial linear behavior and the arrow marks the deviation from this linearity at 0.4 K. (b) Temperature dependence of the effective lower critical field \(B_{c2}(0)\). The solid line is a fit to the data using the local dirty limit formula. The arrow marks the zero-temperature upper critical field \(B_{c1}(0)\) after correction for the demagnetization factor. (c) Temperature dependence of resistivity for the Nb5Sn2Al sample under various magnetic fields up to 80 mT in increment of 10 mT. (d) The upper critical field \(B_{c2}\) plotted as a function of temperature for Nb5Sn2Al. The solid line is a WHH fit to the data.

Figure 6. The superconducting transition temperature \(T_c\) plotted as a function of the average number of valence electrons per atom ratio for all known ‘W5Si3’-type superconductors. The dashed lines are guides to the eyes.

Matthias [29], \(T_c\) of intermetallic superconductors is expected to exhibit two maxima at \(e/\alpha\) close to 5 and 7 [29]. Indeed, as can be seen from figure 6, most of the ‘W5Si3’-type superconductors have \(e/\alpha\) in the range between 4.25 and 4.625, although \(T_c\) is generally higher for superconductors containing group IVB elements than those containing group VB elements. Furthermore, in the latter case, a \(T_c\) maximum is found at \(e/\alpha \sim 4.5\), which is slightly lower than the empirical value of 4.7 [29]. These results suggest that this family of superconductors follows the Matthias rule and their \(T_c\) is mainly controlled by the band filling rather than \(N(E_F)\). In this respect, the absence of SC in Ti5Sn2Al can be explained since its \(e/\alpha\) of 3.875 appears to fall below the lower bound for SC. On the other hand, the \(e/\alpha\) of W5Si3 exceeds the above range and reaches 5.25, hinting at the existence of another \(T_c\) maximum at higher valence electron content.

Finally, we note that, despite similar Nb atom chains, the \(T_c\) of Nb5Sn2Al is nearly one order of magnitude smaller than that of Nb3Sn. This corroborates the previous notion that the presence of these one-dimensional chains is not a sufficient condition for achieving high \(T_c\) [4, 5]. Instead, it is pointed out that the \(\lambda_{ph}\) value of Nb5Sn2Al is only about one-third that of Nb3Sn [30], which highlights the importance of electron–phonon interaction in enhancing \(T_c\).

5. Conclusion

In summary, we have studied the transport, magnetic and thermodynamic properties of isostructural Nb5Sn2Al and Ti5Sn2Al. The results demonstrate that Nb5Sn2Al is a type-II superconductor with a bulk \(T_c\) of 2.0 K and a non-BCS gap, while Ti5Sn2Al remains metallic down to 0.5 K. Surprisingly, compared with Nb5Sn2Al, Ti5Sn2Al has an even larger Sommerfeld coefficient, suggesting that the absence of SC is not due to a reduction in \(N(E_F)\). Nevertheless, these results are in line with the empirical rule based on the average number of valence electrons per atom, and at the value of \(\sim 4.5\) a \(T_c\).
maximum is found for the ‘W$_2$Si$_3$’-type superconductors. Further studies to increase the number of valence electrons and electron–phonon coupling, which may result in higher $T_c$, are highly desirable in future.

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