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Ta₅GeB₂: New T₂ superconductor phase

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ABSTRACT

We report superconductivity at T_c ~3.8 K in the new ternary phase Ta₅GeB₂. Bulk superconductivity is confirmed by magnetization, electrical resistivity and heat capacity measurements, the results showing conventional bulk superconductivity. Ta₅GeB₂ is a further example of a stoichiometric T₂ phase with Cr₅B₃ prototype structure.

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1. Introduction

M₅Si₃B and M₅Ge₃B (where M is a transition metal) are well known through a variety of physical properties with potential for application at high temperatures [1–3] as well as being an interesting class of materials for more fundamental investigations regarding, for example, superconductivity. Nb₅Si₃ and Nb₅Ge₃ are known to superconduct at 0.7 K [4] and 0.5 K [5] respectively which with doping with small radii elements such as B, N or C have T_c's enhanced to 7.8 K for Nb₅Si₃ and 15.3 K [6] for Nb₅Ge₃ [7]. In this case, the superconducting properties are related to a high temperature phase (with a prototype Mn₅Si₃ with hexagonal symmetry) that is stabilized by the interstitial doping mentioned previously.

The Nb–Si–B ternary system also shows that it is possible to stabilize another phase, the so called T₂ phase, by substitution of Si for B. Samples with composition Nb₅Si_{3–x}B_x show maximum solubility for x = 1 (Nb₅Si₂B) [8]. Interestingly, Nb₅Si_{3–x}B_x was found to be superconducting at certain B doping and it was the first Cr₅B₃ prototype structure phase to be found as a superconductor. Many others compounds with the same prototype structure (Cr₅B₃) were found to be superconductors as well, such as W₅SiB₂, (W, Ta)₅SiB₂ and Mo₅SiB₂ [9–11]. In Mo₅SiB₂ the T₂ phase is stoichiometric, and

its superconducting properties emerge with just one critical temperature. However, it is common to find other boron-silicide compounds that have the T₂ phase with a solubility limit of Si for B without nucleation of secondary phases and that it is possible to observe that the critical temperature is strongly dependent on the substitution level of Si.

Recent reports propose the existence of stoichiometric phases in the binary system Ta–Ge such as Ta₃Ge, Ta₅Ge₃, [12–15]. Ta₃Ge, for instance, can assume two different prototype structures, α-Ta₃Ge and β-Ta₃Ge. α-Ta₃Ge is stable below 1550 °C and has the Ni₃P prototype structure with tetragonal symmetry [13], while β-Ta₃Ge is stable above 1550 °C and in spite of also having also tetragonal symmetry has the Ti₃P prototype structure [14]. Another interesting phase is Ta₅Ge₃, also known to exhibit two different crystal structures, one stable at high temperatures in the W₅Si₃ prototype with tetragonal symmetry and another stable at room temperature in the Mn₅Si₃ structure with hexagonal symmetry [16]. However when B is add to this system, the new Ta–Ge–B ternary shows two different equilibrium phases with composition of Ta₅Ge₃B and Ta₅Ge₂B at 700 °C [17]. The first one consists of a Mn₅Si₃ prototype with interstitial doping of B, the doping causing this phase to be stable at room temperature. The second one is the so called T₂ phase with Cr₅B₃ prototype structure that is stabilized by substituting Ge for B at the 8 h Wyckoff position. Here we report results of resistivity, magnetization and specific heat as function of temperature that confirms the existence of superconductivity in

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Ta₅GeB₂ as another example of the T₂ phase with Cr₅B₃ prototype structure.

2. Experimental procedure

Polycrystalline samples of Ta₅Ge_{3-x}B_x with $0.2 \leq x \leq 1.0$ were prepared by solid state reaction. High purity powders of Ta, Ge and B were weighted in stoichiometric amounts, homogenized, pressed into pellets, sealed in a quartz ampoule under Ar atmosphere, heat treated at 1200 °C for 100 h and finally quenched in ice water. Another heat treatment at 1800 °C for 24 h was necessary to achieve a single phase sample within the X-ray diffraction resolution. This treatment was carried out in a resistive furnace (tubular Ta heating element) under argon. X-ray powder diffraction patterns were performed at room temperature with 40 kV–30 mA, Cu-K α radiation, and Ni filter. The 2 θ data were collected from 10 to 90° using a step of 0.05°. X-ray diffraction data were analyzed using Rietveld refinement with the software PowderCell [18] Vesta Crystallography [19] and GSAS [20].

Physical properties were obtained using a commercial VSM-PPMS EverCool II from Quantum Design. Magnetization as a function of temperature was determined with zero field cooling (ZFC) and field cooling (FC) in an applied magnetic field of 50 Oe. Electrical resistivity as a function of temperature was measured using the standard four-probe method from 1.8 to 300 K. Here, we define the superconducting transition temperature (T_C) as the temperatures corresponding to a 2% resistivity drop, a 1% magnetization drop in the ZFC measurements and a 1% heat capacity anomaly start from normal state. These measurements were done both without and in applied magnetic field in order to estimate the upper critical field. Specific heat of a polished flat sample with Ta₅GeB₂ composition was measured in the range of 2 K–20 K.

3. Results

Fig. 1 shows the X-ray diffraction pattern of a sample annealed at 1800 °C for 24 h, along with the results of the Rietveld refinement and simulated structure.

The refinement was stable and converged fast. The parameter goodness-of-fit (χ^2) and weighted-profile reliability factor (R_{wp}) were 1.838 and 8.68% respectively, reasonable values for a reliable X-ray diffraction refinement. The peaks observed in 36.4 (in overlap with a peak of the T₂ phase), 40.9 and 63° (pointed out by stars in the Fig. 1) were indexed as Ta₃Ge phase published elsewhere [12] (space group 86 and Ni₃P prototype structure). A sample with this composition was prepared in order to investigate if this phase could give rise to the superconductivity observed and regarding the low temperature properties this compound is found to be a Pauli-paramagnetic (data not shown). The difference between the experimental data and the refinement is shown by the blue line in Fig. 1(a). The refinement was performed by starting with the structure published for the Ta₅Ge₃ as α -Ta₅Ge_{0.5} [16] (Fig. 1(b) shows the simulated), however, some significant differences in the intensity between the observed and calculated X-ray diffraction patterns were only diminished by considering that B atoms were occupying the 8 h Wyckoff position (Fig. 1(c) shows the simulated structure). It is important to mention that neutron diffraction would be necessary to confirm that the B atoms are truly in these sites. The published data for Ta₅Ge₃ $a = b = 6.599$ Å, $c = 12.01$ Å for the lattice parameters and space group I4/mcm (140). Our results for the same space group are $a = b = 6.239$ Å, $c = 11.578$ Å for the lattice parameters and with B atoms in the 8 h Wyckoff position one expects to see smaller lattice parameters since the B ionic radius is smaller than the Ge ionic radius. It is important to mention that this was the only composition where single phase tetragonal T₂ phase

Fig. 1. (a) X-ray diffraction data. (b) Simulated structure of Ta₅Ge₃ and (c) simulated structure considering B atoms substituting Ge atoms of the 8 h Wyckoff position.

with Cr₅B₃ prototype structure were observed. This behavior also occurs in the Mo–Si–B system [11]. These results suggest that this is another example of a stoichiometric T₂ phase. In Nb–Si–B system the solubility range of the substitution of Si for B is relatively large [6].

Magnetization as a function of temperature is shown in Fig. 2.

Fig. 2 displays a superconducting transition close to 3.8 K in the ZFC and FC regimes and the inset shows the M vs H dependence at 2.0 K with the typical signature of type II superconductivity. The estimated superconducting volume by ZFC curve is around 80% which strongly suggests a bulk superconducting state. Resistivity as a function of temperature measurements also shows a

Fig. 2. Magnetization as a function of temperature in the ZFC and FC regimes showing the superconducting critical temperature close to 3.8 K. The inset shows the M vs H at 2.0 K suggesting a type II superconductor.

superconducting transition with onset temperature close to 3.8 K which is consistent with magnetization measurements as shows Fig. 3.

Fig. 3(b) shows the offset temperature ($R = 0$) around 3.5 K, attesting to the excellent quality of the polycrystalline sample obtained after annealing at 1800 °C. Also shown is the resistivity as a function of temperature in different applied magnetic fields. The shift of the transition temperature as a function of applied magnetic field is typical of a real superconducting state. We used the mid-point of the transition as a criterion to define H_{c2} and used this data in applying the so called WHH theory [21]. Using Eq. (1) it is possible to estimate the upper critical field at zero K.

$$H_{c2} = -0.693 \left(\frac{dH}{dT} \right)_{T_c} T_c \quad (1)$$

Fig. 4 shows the H_{c2} phase diagram and the results after applying the WHH theory. Experimental data is shown as hollow circles and the calculated data as the red line.

In this diagram the upper critical field at zero Kelvin is 5190 Oe which is consistent with the M vs H measurement showed in Fig. 2. The coherence length estimate from the upper critical field at zero Kelvin is about 25.2 nm. These results strongly suggest that this compound is a new bulk superconductor with T_c close to 3.8 K.

The jump close to 3.8 K is clear evidence of bulk superconductivity in this material. The Sommerfeld coefficient (γ) suggests a high density state at Fermi level. The linear fit at low temperature regime gives $\beta = 0.36975$ (mJ/molK⁴), the coefficient of the phonon contribution. From this one estimates the Debye temperature of $\Theta_D = 348$ K. The subtraction of the phonon contribution to the specific heat allows us to separate the electronic contribution. This is shown in the inset to Fig. 5 where the jump close to 3.8 K is clearly seen and which is consistent with all measurements shown in this paper. The jump size, $\Delta C/\gamma T_c$, is about 1.4, consistent with weak coupling BCS (1.43).

Fig. 3. (a) Normalized resistivity as a function of temperature showing the superconducting critical temperature close to 3.8 K which is consistent with observed in magnetization measurements. (b) Low temperature resistance data with applied magnetic field.

Fig. 4. H_{c2} vs T suggests H_{c2} of 5190 Oe at 0 K, estimated from WHH theory in the dirty limit.

Fig. 5. (a) C_p/T vs T^2 shows a clear jump close to 3.8K which is consistent with other measurements. (b) The electronic contribution to heat capacity confirming unambiguously bulk behavior in this material.

The electronic contribution in the superconductor state (below of T_c) also allows us to estimate the superconductor gap using the logarithmic plot shown in Fig. 6.

The linear fitting observed in Fig. 6 suggests that this material follows BCS behavior. In this case we can use the BCS prediction for the superconducting state below T_c given by:

Fig. 6. $\ln(C_e)$ vs T_c/T in the superconductor state below T_c . The nice linear fit is consistent with a BCS superconductor.

$$\frac{C_e}{\gamma T_c} = 8.5e^{\frac{0.82\Delta_0}{k_B T}} \quad (2)$$

From the fit we get an energy gap (Δ_0) of 0.968 meV for $T \rightarrow 0$ and $2\Delta_0/k_B T_c \sim 3.45$, which is the characteristic of weak coupling BCS superconductors. Finally, these results present a new superconductor in the Cr_5B_3 (T_2 phase) prototype series of Mo_5SiB_2 , $\text{Nb}_5\text{Si}_{3-x}\text{B}_x$, and W_5SiB_2 .

4. Conclusions

The systematic synthesis study of Ta_5GeB_2 with Cr_5B_3 prototype structure (so-called T_2 phase) presented in this article finds this compound to be a new superconductor in this family. Our results demonstrate that this material is a BCS superconductor with $T_C \sim 3.8$ K with coherence length $\xi_0 \sim 25.2$ nm, $\theta_D \sim 348$ K and gap $\Delta_0 \sim$

0.968 meV.

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