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Evidence of multiband behavior in a new superconductor $Ta_{0.8}Zr_{0.2}B$ with FeB-prototype structure.

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Abstract

We present results that show a relation between crystalline structure and superconductivity in the $Ta_{1-x}Zr_xB$ system. The substitution of Ta for Zr atoms induces a crystal structure change from CrB- to FeB-prototype structure in which superconductivity is present with higher superconducting critical temperature T_c. The interrelation between T_c and Zr content shows a dome-like behavior with maximum T_c at x = 0.2. In this sample, bulk superconductivity was observed and characterized by magnetization, electrical resistivity and specific heat measurements, all consistent with a superconducting critical temperature close to 7.8 K. The upper and lower critical field diagrams have no usual behavior which may be connected to a multiband scenario.

Introduction

In the most recent assessment of the Ta-B system, five compounds are considered to be stable: TaB_2, Ta_3B_4, TaB, Ta_3B_2 and Ta_2B [1]. Among them, superconductivity has been reported for TaB and Ta_2B with superconducting critical temperatures of 4.0 and 3.12 K, respectively [2-4]. Besides that, there is the case of TaB_2, found non-superconducting in earlier experiments [5] and more recently a superconducting transition was observed in the vicinity of 9.5 K [6]. The binary TaB crystallizes in the orthorhombic CrB-prototype structure with space group *Cmcm*. Failamani *et al.* reported that the substitution of Ta atmos for Ti, Zr and Hf in TaB was able to stabilize an orthorhombic FeB-prototype structure (space group Pnma) with general formula $Ta_{1-x}RM_xB$ [7]. More recently, Silva et al. have shown that the TaB with FeB-prototype phase, is stable in the Ta-B binary system [8], the FeB-prototype phase crystallizes from the melt but is not stable at low temperatures. It has been shown that $Ta_{0.7}Hf_{0.3}B$ is a new superconducting material with T_c close to 6.7 K, (x = 0.3 being the phase composition with the highest T_c) and presents a strong signature of multiband superconductivity [9], based on Hall effect data and heat capacity measurements. Although the main motivation to investigate refractory metals borides has been their application at temperatures above 1000°C in extreme environments [10, 11], superconductivity is frequently observed in these phases. Within this context, this work presents results of a systematic experimental study on the effect of Zr substitutions for Ta in the $Ta_{1-x}Zr_xB$ (x = 0.1 to 0.3) compound. This material is another example of multiband superconductors in the $Ta_{1-x}RM_xB$ phase family, showing a maximum critical temperature of ~ 7.8 K at $Ta_{0.7}Zr_{0.2}B$ stoichiometry.

Experimental Procedure.

Polycrystalline samples of $Ta_{1-x}Zr_xB$ (with $0.1 \leq x \leq 0.3$, ranging from 0.05) were synthesized by arc melting pieces of high-purity Zr, Ta and B on a water-cooled Cu hearth in high purity Ar atmosphere and using Ti sponge as getter. The weight loss during the arc melting was negligible (<0,2%). Crystallographic characterization was performed using powder samples in a PANalytical model Empyrean diffractometer with Cu K_α radiation. The phases were identified using crystallographic information reported in the literature [7, 12], and the lattice parameters were determined by Rietveld refinement using PANalytical software HighScore Plus. Magnetization, electrical resistivity and heat capacity were measured using Quantum Design VSM-PPMS EverCool II equipment. Magnetization as a function of temperature was measured in Zero Field Cooled (ZFC) and Field Cooled (FC) regime under 20 Oe. Magnetization as a function of applied magnetic field was measured at 2.5 K. Electrical resistivity as a function of temperature was determined using the standard four point geometry between 2.0 and 300 K, both with and without applied magnetic field in order to estimate the upper critical field at zero Kelvin. The specific heat measurements was performed on polished flat samples by the relaxation method.

Results and Discussion.

Figure 1 shows both experimental and refined X-ray diffraction patterns for a sample of $Ta_{0.8}Zr_{0.2}B$ nominal composition. An excellent fit between the experimental and simulated diffraction patterns is observed using FeB as prototype, indicating that the sample is X-ray due to the secondary FeB prototype structure as in reference 7. This secondary phase is richer in Zr and it is not superconductor phase. The lattice parameters obtained after Rietveld refinement are a = 6.140 Å, b = 3.159 Å and c = 4.620 Å. X-ray samples were obtained for compositions between 0.1 ≤ x ≤ 0.3.

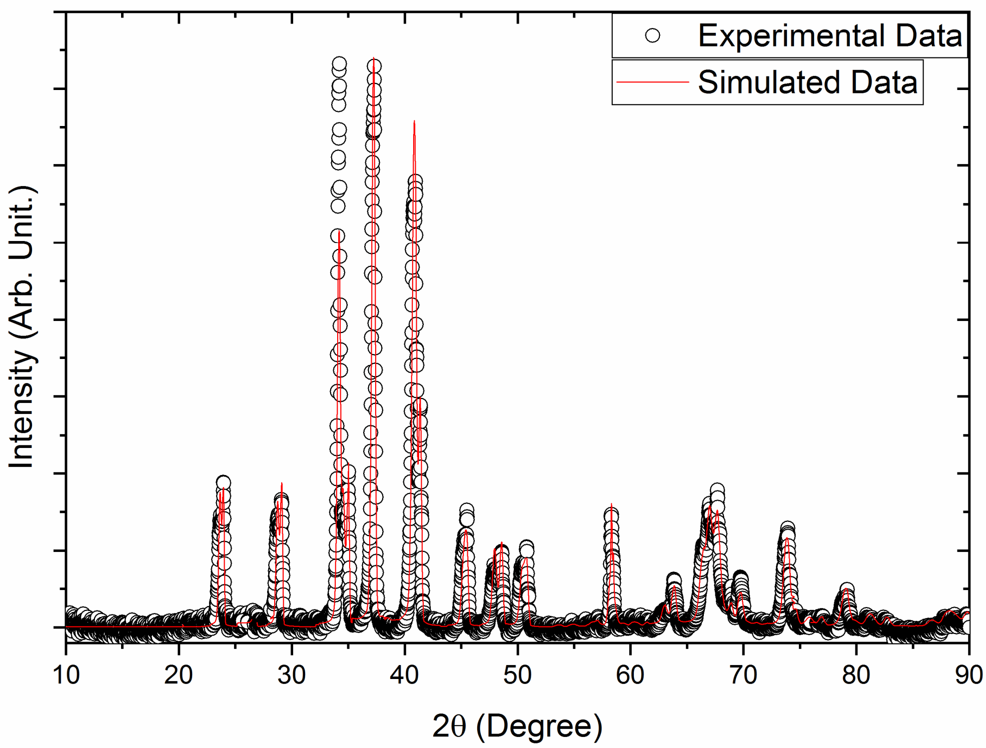


Figure 1 - X-ray diffraction pattern of $Ta_{0.8}Zr_{0.2}B$ showing good agreement between experimental and simulated data.

All the samples presented a single phase pattern in the range of 0.1 ≤ x ≤ 0.3, but here we focus on the results for the sample with highest T_c, $Ta_{0.8}Zr_{0.2}B$, whose X-ray diffraction pattern is shown in Figure 1. The magnetization as function of temperature in the ZFC and FC regimes for this composition is displayed in Figure 2.

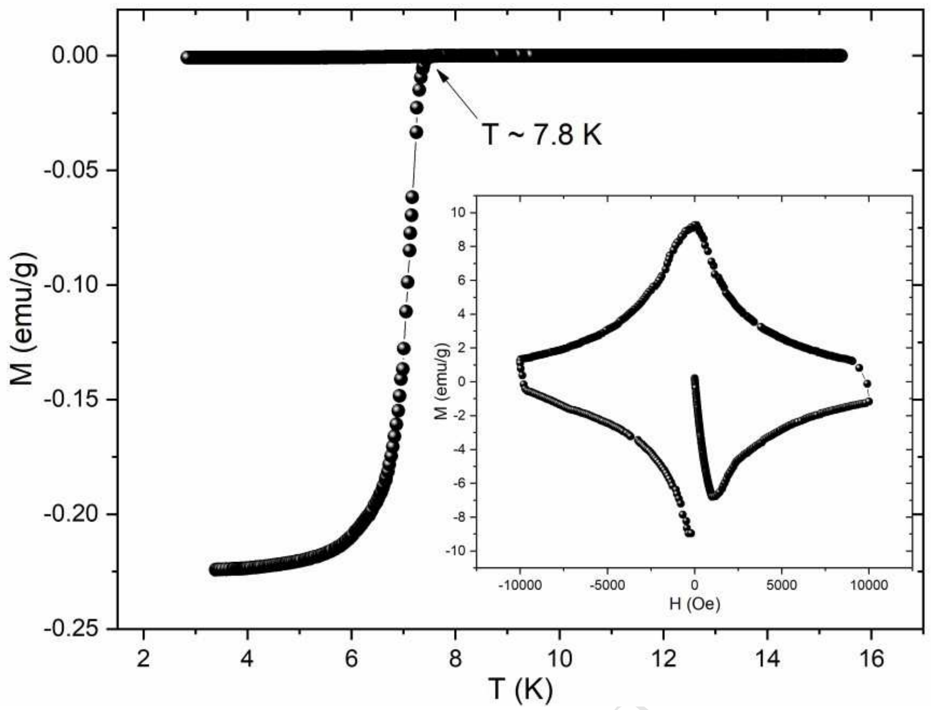


Figure 2 - M versus T for sample of composition $Ta_{0.8}Zr_{0.2}B$ showing a superconducting transition close to 7.8 K. The inset shows the M versus H dependence at 2.5 K, which suggests type II superconductivity

A sharp superconducting transition with critical temperature at near 7.8 K can be observed in this Figure. The estimated superconducting fraction from the magnitude of the magnetization signal is around 95%. The inset shows the M vs H behavior at T = 2.5 K, which reveals a type-II superconductor with a relatively high upper critical field. The critical temperatures as a function of Zr concentration for $Ta_{1-x}Zr_xB$ are shown in Figure 3.

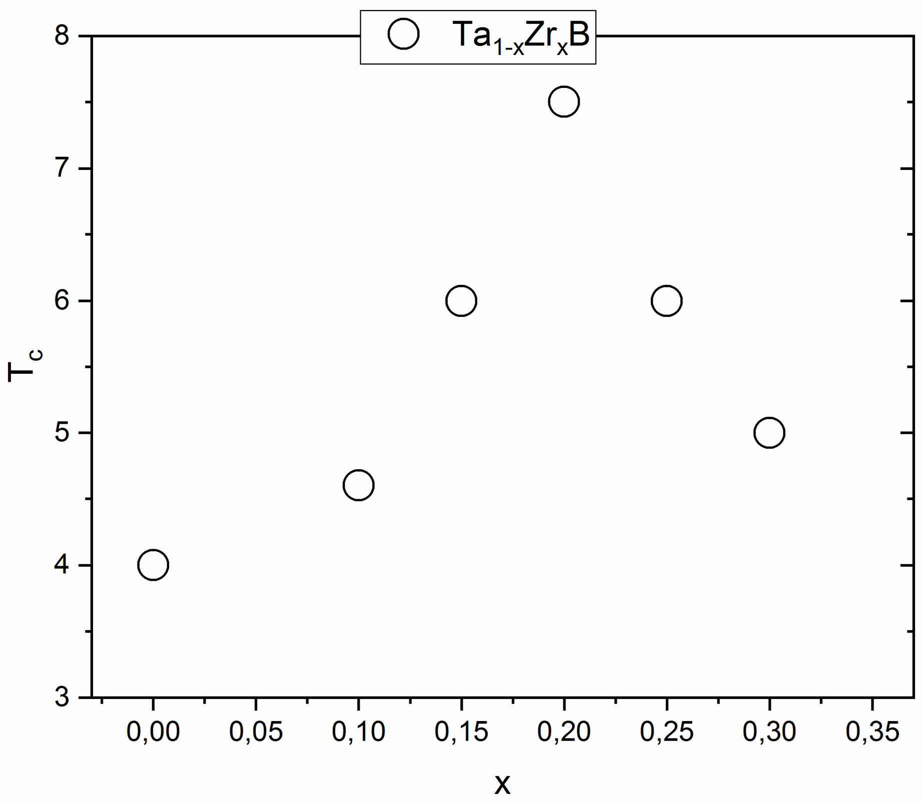


Figure 3 – T_c as a function of Zr content showing a dome with the maximum T_c close to x = 0.20.

In this Figure a dome-like behavior is seen with a maximum critical temperature reached with x =0.2. However, the first point (x= 0) refers to undoped TaB which possess a CrB-prototype structure and, therefore, different from the samples Zr-doped samples with FeB-prototype structure. This dome-like behavior was also observed for the $Ta_{1-x}Hf_xB$ compounds [8] and, therefore, seems to be a characteristic behavior of the FeB-prototype phase stabilized with either Hf or Zr.

The electrical resistivity as a function of temperature in absence of magnetic field is shown in Figure 4. A sharp transition (ΔT_c < 0.5 K) with onset temperature close to 7.8 K can be observed. The transition width is smaller than 0.5 K, revealing a high quality polycrystalline sample. This result is totally consistent with the magnetization measurement. The inset in Figure 4 shows the electrical resistivity in applied magnetic field up to 8.0 T.

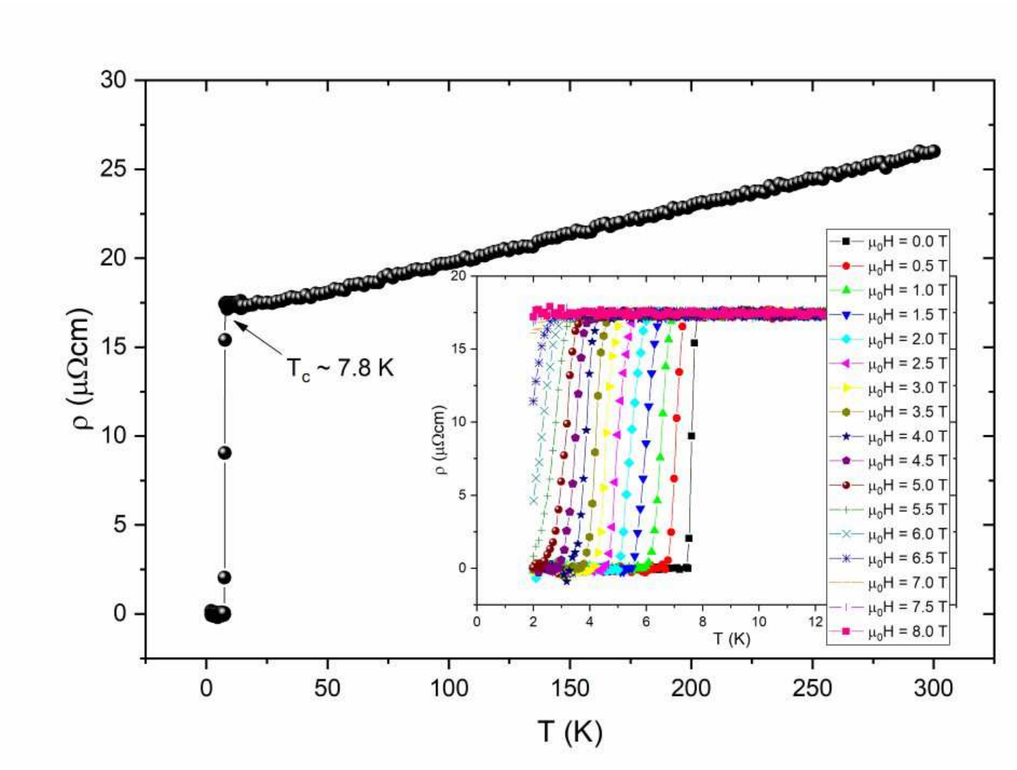


Figure 4 – Resistivity versus temperature for the sample $Ta_{0,8}Zr_{0,2}B$ showing the sharp transition with onset close to 7.8 K. Inset shows resistance in applied magnetic field between 0 and 8.0 T.

The μ_oH_{c2} versus reduced temperature ($t_r = T/T_c$) phase diagram can be built using the mid-point of the transition as a criterion for T_c. The upper critical field at zero temperature can be estimated using the WHH formula in the dirty limit [13],

$$\mu_oH_{c2(0)} = -0.693T_c(d\mu_oH_c/dT)_{T=T_c} \quad (1)$$

Using this equation the upper critical magnetic field at zero Kelvin ($\mu_oH_{c2(0)}$) was estimated to be ~ 5.5 T. Figure 5 displays a clear deviation of the experimental data (red dashed line), indicating that the empirical quadratic conventional relation, [$\mu_oH_{c2(T)} = \mu_oH_{c2(0)}(1-t_r^2)$], cannot be applied for this material. It indicates that this material is not a single gap superconductor. Indeed, other multiband superconductors also display similar divergence. For example, the multiband $LaFeAsO_{0.89}F_{0.11}$ phase, exhibits this divergence in the upper critical field [14]. Many others examples can be found in the literature, $LuNi_2B_2C$ [15] and YNi_2B_2C [16]

among others [17-19]. Micnas *et al.* [20] suggest that another equation better describes a superconductor with more than one gap:

$$\mu_o H_{c2(T)}=\mu_o H_{c2(0)}(1-t^{1.5})^{1.5} \tag{2}$$

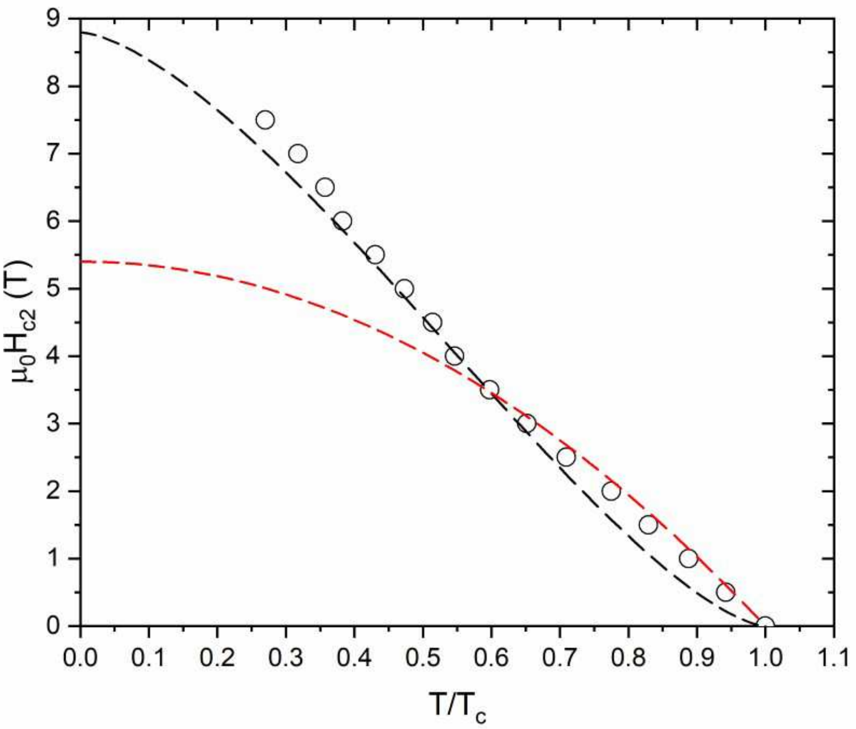
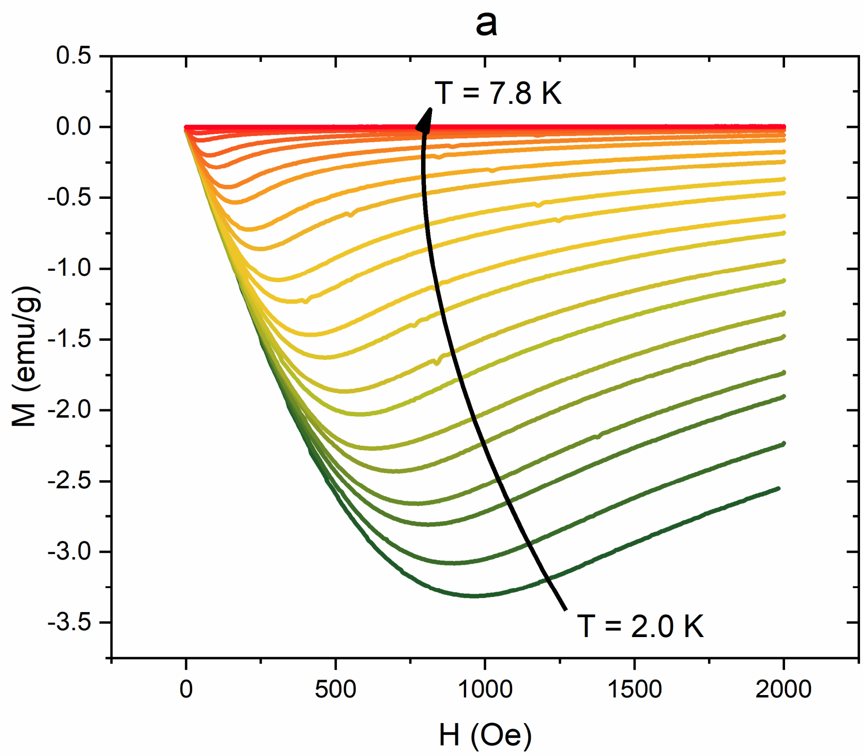
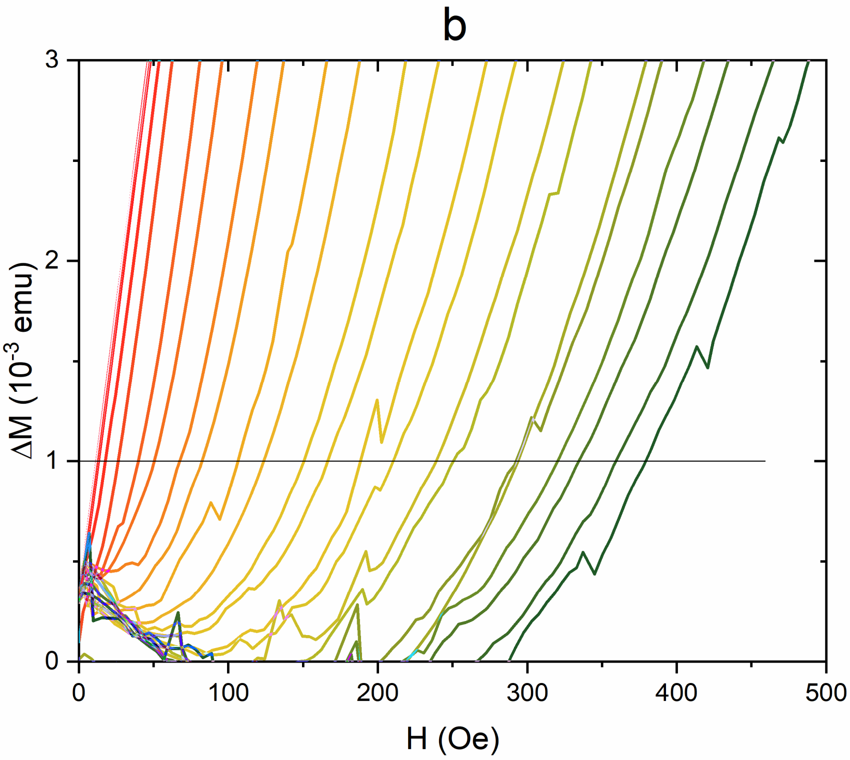


Figure 5 – μ_0H_{c2} versus reduced temperature (t) (black symbols). Red dashed line is the fit estimated by WHH theory [11]. Dashed black line is the fit using the equation suggested by Micnas et al. [18] for a superconductor with two gaps.

In Figure 5, the experimental points seems to fit very well with this equation (black dashed line), and the upper critical field value in zero Kelvin could be estimated to be around 8.8 T. Thus, these results suggest that this material may be another example of a boride multiband superconductor. Another deviation from conventional single band behavior occurs lower critical magnetic field phase diagram. In order to verify the existence of this in $Ta_{0.8}Zr_{0.2}B$, M vs H was measured at several temperatures between 2.0 and 7.8 K as shown in Figure 6 (a). Figure 6 (b) shows ΔM vs H, H_{c1} being defined using $\Delta M = 10^{-3}$ as a criterion and plotted against t_r in Figure 6 (c). The existence of two gaps in this superconductor can be observed, which is similar to those of other superconducting materials recognized as multiband superconductors.


a
T = 7.8 K
T = 2.0 K
M (emu/g)
H (Oe)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
0
500
1000
1500
2000


b
ΔM (10^{-3} emu)
H (Oe)
3
2
1
0
0
100
200
300
400
500

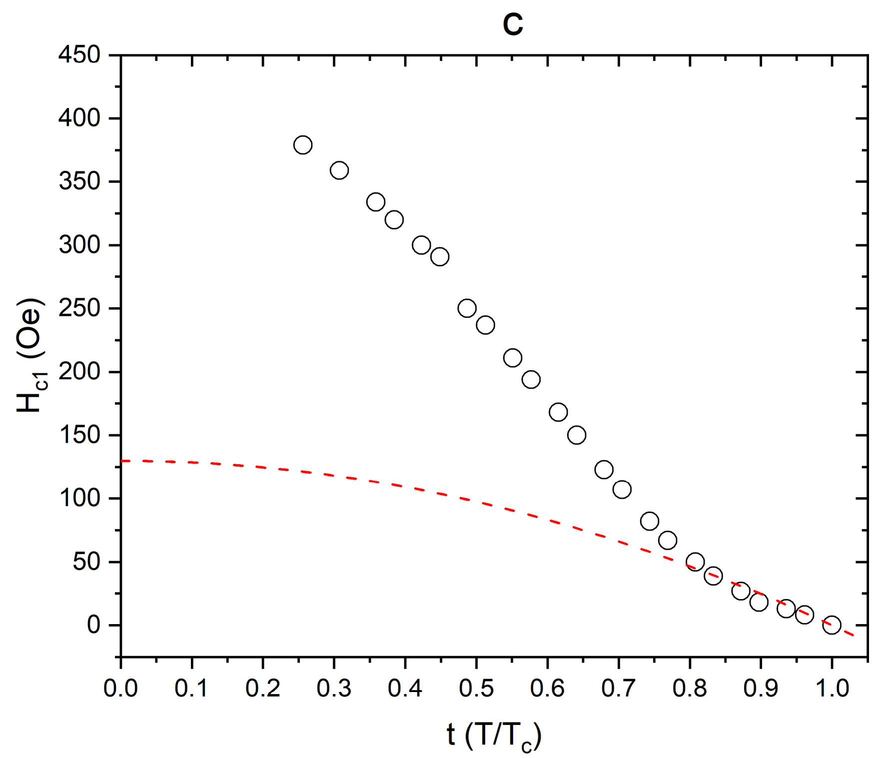


Figure 6 - a – M versus H at different temperatures, with isotherms between 1.8 K and 7.8 K. b - ΔM vs H and the H_{c1} was defined using $\Delta M = 10^{-3}$ as criterion for lower critical field definition. c – H_{c1} versus t (T/Tc) (black symbols). Dashed red line is fit estimated by the conventional single band superconductor.

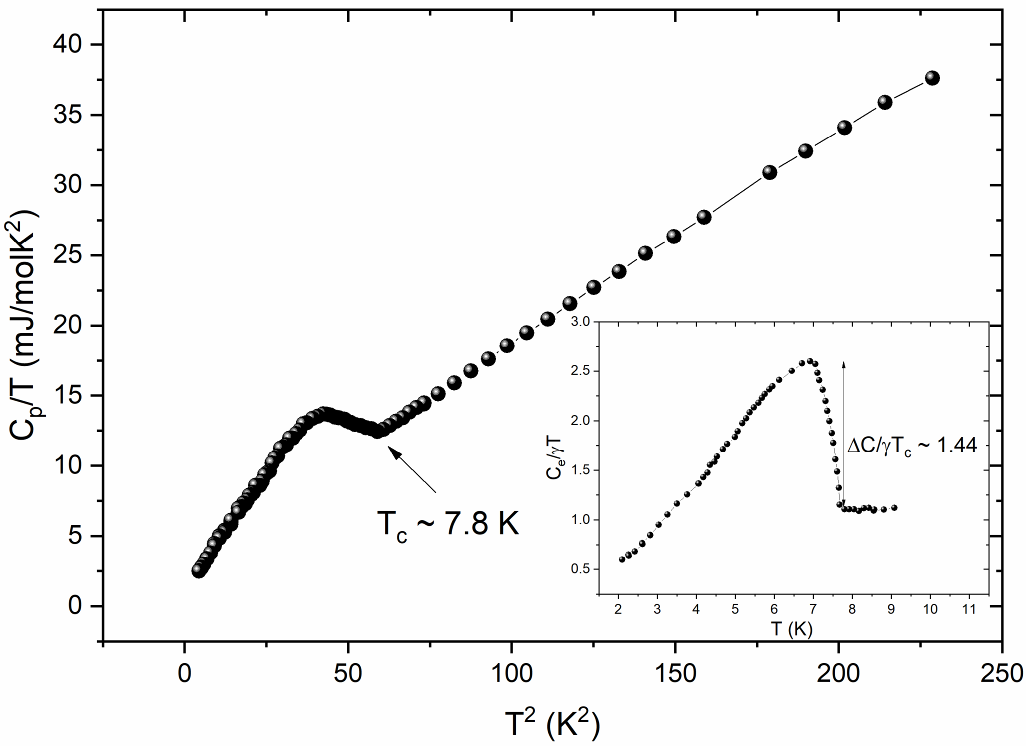


Figure 7 - Cp/T versus T showing the superconducting anomaly at ~ 7.8 K. Inset shows electronic contribution to specific heat, which reveals that the ΔC/γTc value is close to the BCS prediction.

In Figure 7 a clear jump around 7.8 K can be observed in the specific heat measurement, indicating that this material is unambiguously a new bulk superconductor. This is consistent with the conclusions derived from the results of the present investigation using other measurement techniques (magnetization and resistivity). Using the Debye approach at low temperatures, given by $C_p/T = \gamma + \beta T^2$, the values of $\gamma \sim 3.067$ mJ/molK^2 and $\beta \sim 0.1511$ mJ/molK^4 are obtained. From this β value, the Debye temperature $\theta_D \sim 295$ K is estimated, which is slightly smaller than that obtained for $Ta_{0.7}Hf_{0.3}B$, $\theta_D \sim 325.93$ K) [8], suggesting different phonon spectra for these two compounds of the same family. The γ value is proportional to the Density of States at the Fermi Level. In this case, the γ value for $Ta_{0.8}Zr_{0.2}B$ suggests a higher Density of States than that for $Ta_{0.7}Hf_{0.3}B$ ($\gamma \sim 2.0$ mJ/molK^2) [8]. The subtraction of the phonon contribution allows us to evaluate the electronic contribution for this material. The inset of Figure 7 shows just the electronic contribution for specific heat. An analysis of the jump yields $\Delta C/\gamma_n T_c \sim 1.44$, which is close to that predicted by BCS, and indicates that the superconducting gap is in the weak-coupling limit. The exponential behavior of the electronic specific heat suggests an excess entropy, which indicates that another gap can be opened at lower temperatures, confirming that $Ta_{0.8}Zr_{0.2}B$ is another example of multiband superconductor.

Conclusion

This article presents a systematic study of Zr substitutions for Ta in $Ta_{1-x}Zr_xB$. The results show that Zr additions to TaB change its crystal structure from CrB-prototype to FeB-prototype in $Ta_{1-x}Zr_xB$ with composition range $0.1 \leq x \leq 0.3$. The FeB-prototype structure displays superconducting behavior with a maximum in the superconducting critical temperature close to 7.8 K for x=0.2 nominal composition. The present set of results shows that this new superconductor phase can be understood in a multiband scenario through anomalies observed in the upper and lower critical fields and the heat capacity.

Acknowledgments

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Hightlight

- This paper show that Zr additions to TaB change its crystal structure from CrB-prototype to FeB-prototype in Ta1-xZrxB with composition range 0.1 ≤ x ≤ 0.3
- Ta1-xZrxB has been found to be a new superconductor at 7.8 K.
- Magnetization, specfic-heat and electrical resistivity measurements points to a multiband superconducting state.