Superconductivity in the Th$_{0.93}$Zr$_{0.07}$B$_{12}$ compound with UB$_{12}$ prototype structure

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A R T I C L E   I N F O

Article history:
Received 17 April 2015
Received in revised form 11 July 2015
Accepted 13 July 2015
Available online 15 July 2015
Communicated by L. Chivelber

Keywords:
Superconductivity
ThB$_{12}$ system
New superconductors

A B S T R A C T

In this work, we report superconductivity at 5.5 K in the new pseudo-ternary Th$_{0.93}$Zr$_{0.07}$B$_{12}$ compound. We show clearly evidence that appropriate amounts of Zr substitution at the Th site induce the stabilization of the UB$_{12}$ prototype structure at ambient pressure. The superconducting bulk properties of Th$_{0.93}$Zr$_{0.07}$B$_{12}$ are confirmed by means of magnetization, electronic transport properties and specific heat measurements. The $H-T$ phase diagrams based on magnetization and magnetoresistance measurements yield $\mu_0H_\text{c1}(0) = 6$ mT and $\mu_0H_\text{c2}(0) = 98$ mT and allow us to estimate the coherence length $\xi_0 \sim 57.9$ nm and the penetration depth $\lambda_L \sim 234$ nm at zero kelvin.

1. Introduction

The M–boron (M = lanthanides, actinides, and transition metals) binary systems host a few stoichiometric phases which crystallize in the UB$_{12}$ prototype structure. At ambient pressure growth conditions, it is well known that this structure can be obtained with seven lanthanide elements ([Tb–Lu]B$_{12}$) [1–4], three actinide members (UB$_{12}$, NpB$_{12}$, and PuB$_{12}$) [5–7], and three transition metals (YB$_{12}$, ZrB$_{12}$, and ScB$_{12}$) [8–10]. These compounds have attracted a lot of scientific efforts due to their extraordinary range of electronic, magnetic and structural properties. For instance, HoB$_{12}$, ErB$_{12}$, and TmB$_{12}$ compounds exhibit antiferromagnetic ordering, with Nel temperatures of 7.38, 6.65, and 3.28 K, respectively [11–14]; UB$_{12}$ shows Pauli paramagnetism [15]; and YB$_{12}$, ZrB$_{12}$, ScB$_{12}$, and LuB$_{12}$ have been addressed as superconducting materials [16–20].

In spite of this, several phases, such as ThB$_{12}$, with UB$_{12}$ structure have been also obtained by using external hydrostatic pressure [21]. Since this work is the only one reporting the ThB$_{12}$ phase existence, a lot of questions about its electronic and magnetic properties remain unclear.

Based on the mentioned above, in this work we report the influence of Zr doping in the ThB$_{12}$ system. We show clear evidence that 7% of Zr substitution is already able to stabilize the ThB$_{12}$ structure, under normal pressure conditions. Superconductivity was found to appear in this system with a maximum $T_c$ (~5.5 K) close to the Th$_{0.93}$Zr$_{0.07}$B$_{12}$ composition. From the penetration depth and coherence length values, the Ginzburg–Landau (GL) parameter ($\kappa$) was found to be 4.04. In addition, heat capacity measurements indicated a conventional superconductivity in this compound.

2. Experimental procedure

The samples were prepared from stoichiometric amounts of Th, Zr and B pieces (high purity >99.999%) which were melted on a water cooled Cu hearth in an arc furnace with high electrical current and elevated heat extraction, under high purity argon atmosphere and using a Ti sponge getter. The samples were flipped over and remelted 5 times to ensure good homogeneity. Due to the low vapor pressure of the constituent elements at the melting temperature, the weight loss during the arc melting was negligible (<0.5%). X-ray powder diffractograms were obtained in a Panalytical diffractometer model Empyrean with detector PIXcel1D using CuK$\alpha$ radiation. The lattice parameters were determined by using the PowderCell software and simulation as well [22]. Magnetic data were obtained using a high sensitivity VSM-SQUID magnetometer from Quantum Design. The temperature dependence was obtained using a zero field cooling (ZFC) and field cooling (FC) sweeps with an applied DC magnetic field of 10 Oe. The M ver-
sus H measurement was performed at 2.0 K. Electrical resistivity measurements were made between 2.0 and 300 K with a conventional four probe method using an AC current bridge of 1000 μA in the PPMS-9T equipment. The resistivity data were obtained at zero field and at several applied magnetic fields in order to estimate the upper critical field. The specific heat of a piece cut from the sample was measured in the range of 1.8–10 K with a calorimeter in the PPMS (Quantum Design) using the relaxation method.

3. Results

The upper panel of Fig. 1 shows the X-ray powder diffraction pattern for the sample with Th0.93Zr0.07B12 composition. Majority of the peaks can be indexed using the UB12 prototype structure, which belongs to the cubic Fm-3m space group with lattice parameter $a = 7.465$ Å [12]. To confirm this assumption, Fig. 1 also shows the simulated X-ray for the ThB12 structure (see lower panel). An excellent agreement is found between the experimental result and the simulated structure. Based on this, one can infer that the substitution of 7% of Th by Zr is able to stabilize the UB12 structure in the Th–B system, at ambient pressure conditions. In the inset we show the ThB12 crystal structure in which the blue spheres are Th and the yellow ones are B. The broadening is due to the size of the grain in our sample. Actually the grain size is relatively small because these samples come from melting process (as cast sample).

Surprisingly, this stable structure shows superconducting behavior, as can be seen in Fig. 2(a), which shows the magnetization as a function of temperature in the zero-field cooled (ZFC) and field cooled (FC) regimes sweeps with an applied field of 10 Oe. This figure displays a clear diamagnetic transition at 5.5 K. The hysteresis between ZFC and FC regimes indicates that Th0.93Zr0.07B12 has weak flux pinning centers. Without correcting for the demagnetization or sample size effects, we estimate the superconducting volume fraction (ZFC) in this sample to be around 80.0% of perfect diamagnetism, indicative of possible bulk superconductivity.

Fig. 2(b) shows the resistivity as a function of temperature at zero magnetic field for a Th0.93Zr0.07B12 polycrystalline sample. The sharp transition reflects the good quality of our polycrystalline sample. The onset of the superconducting transition at ~5.5 K can be better seen in the inset of Fig. 2(b) which shows very good agreement with the magnetization measurement shown in Fig. 2(a).

In order to estimate the lower critical field, the field dependence of the magnetization (M vs. H) was measured from 1.8 to 6.0 K as shown in Fig. 3(a). The values of $H_{c1}$ were determined by examining the point of deviation from the linear slope of the magnetization curve, using $\Delta M = 10^{-3}$ emu as a criterion for the difference between the Meissner line and magnetization signal (see Fig. 3(b)) [23].

From the data of Fig. 3(b), we are able to construct the $\mu_0 H_{c1}$ versus temperature diagram displayed in Fig. 4. The lower critical field as a function of the reduced temperature can be described in terms of a monotonic curve with a quadratic dependence dictated by the empirical function: $H_{c1}(T) = H_{c1}(0)(1 - t^2)$, where $t = T/T_c$. The fit of our data to this expression (solid red line) suggests that the vortex penetration in this material can be well described by BCS theory. By extrapolating the fit to zero Kelvin, we find that $\mu_0 H_{c1}$ is approximately 6 mT at zero temperature. Using this value ($\mu_0 H_{c1} \sim 6$ mT), it is possible to estimate the penetration depth using the formula $\lambda = \frac{\pi}{kT}$, where the $\lambda$ parameter is the penetration depth $\lambda \sim 234$ nm, at zero Kelvin.

In order to estimate the upper critical field, Fig. 5(a) shows the normalized resistance as a function of magnetic field for a Th0.93Zr0.07B12 polycrystalline sample. The resistance was normalized by the resistance value in the normal state to better determine the upper critical field ($H_{c2}$). As it can be seen in Fig. 5(a) the onset of superconductivity shifts to lower temperatures gradually with increasing magnetic field. The magnetoresistance behavior suggests a relatively small upper critical field ($H_{c2}$), consistent with the $M$ vs. $T$ and $M$ vs. $H$ curves. Using a criterion of 50% of normal state resistance, the estimated $H_{c2}$–$T$ phase diagram shown in Fig. 5(b) was constructed. The results shown in Fig. 5(b) we can estimate the upper critical field at zero temperature ($\mu_0 H_{c2}(0)$) using the WHH formula [24] in the limit of short electronic mean-free path (dirty limit). $\mu_0 H_{c2}(0) = -0.693(dH_{c2}/dT)_{T=0}$ T_c. The zero temperature $H_{c2}$ value of ~98 mT was determined by extrapolating the red line to 0 K.

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**Fig. 1.** (Color online.) Experimental (upper) and simulated (lower) X-ray diffractions. In the inset we show the ThB12 crystal structure in which the blue spheres are Th and the yellow ones are B.

**Fig. 2.** (a) Magnetization as a function of temperature in the ZFC and FC regimes. A clear superconducting transition is observed close to 5.5 K. (b) Resistivity as a function of temperature at zero magnetic field. In the inset, one can see clearly the sharp superconducting transition at 5.5 K.
The upper critical field estimate from WHH (Fig. 5b) allows an estimation of the coherence length by using the Ginzburg-Landau (GL) formula: \( \mu_0 H_{c2} (0) = \frac{\phi_0}{2 \pi \xi_0^2} \), which yields \( \xi_0 \approx 57.9 \text{ nm} \). The penetration depth and coherence length give the GL parameter (\( \kappa \)) through the expression \( \kappa = \frac{\phi_0}{\pi \lambda_0^2} \approx 4.04 \). Although this value (\( \kappa = 4.04 \)) is much bigger than critical value (\( \kappa_c = (1/2)^{1/2} \)), conventionally used to classify superconductors as type-I or type-II, it is still low compared to the \( \kappa \) value typically obtained for type-II superconductors. For example, the Zr0.96V0.04B2 compound is a type-II superconductor and shows \( \kappa \sim 100 \) [25].

Recently, theoretical studies have shown the existence of a very special superconductor type, which can have \( \kappa \) value in the vicinity of the theoretical limit value called “Bogomolny regime” [26], i.e., \( \kappa_c \). In this regime, it is admitted that in the superconductor topological excitations are stable and vortices can attract one another at long range but repel at shorter ranges, and, therefore, should form clusters in low magnetic fields [27,28], these superconductors are currently classified as type-1.5 [28] or type-II/I [29,30]. More recently, Vagov et al. [31] showed that below \( T_c \), in the \( \kappa \times T \) phase diagram, there exists a critical range of \( T \) and \( \kappa \) parameters where the degeneracy of the superconducting state at \( T_c \), that is at Bogomolny critical point, is lifted into a sequence of novel topological equilibria and based on this they defined a new class of superconducting materials, “the critical superconductors”, that generalizes the types II/I and type-1.5. Based on this reasoning and the low-\( \kappa \) value obtained, we can suggest that the Th0.93Zr0.07B12 compound can be one more example of this nonconventional type-II superconductor. Corroborating to this, the related ZrB12 compound has been also addressed as a type-II superconductor [29]. This material has \( \kappa = 0.65 \) and crosses over from type-I to type-II superconductivity close to 4 K with decreasing temperature. This assumption is very exciting, but specific heat and vortex imaging studies on single crystals should be done in order to confirm the type-II/I character of the Th0.93Zr0.07B12 compound. It will also be interesting to have band structure calculation in order to guide the search of new compounds with the suggested behavior.

The bulk phase transition from the normal to the superconducting state in the Th0.93Zr0.07B12 sample was also verified by specific heat measurements at low temperatures. A clear superconducting transition is observed in the \( C_p/T \) versus \( T^2 \) curve, presented in Fig. 6, where the critical temperature is observed close to 5.5 K, consistent with the resistivity and magnetization measurements. The normal state data can be fit to the expression \( C_p = \gamma + \beta T^3 \) by using a least-square analysis which yields \( \gamma = 17.1 \) (mJ/molK2) and \( \beta = 0.22 \) (mJ/molK4). This \( \beta \) value yields the Debye temperature \( \Theta_D \sim 486 \) K. The value of the Sommerfeld coefficient suggests high density of states at the Fermi level. By subtracting the phonon contribution, we are able to evaluate separately the electronic contribution to the specific-heat, plotted as \( C_e/T \) vs. \( T \) in the inset of
4. Conclusion

In this paper, we show that 7% of Zr is able to stabilize the ThB12 phase, with UB12 type structure at ambient pressure. We also report that this phase becomes superconducting below 5.5 K with the parameters $\mu_0 H_c(0) = 6$ mT, $\mu_0 H_c(0) = 98$ mT, $\delta_1 \sim 57.9$ nm and $\delta_2 \sim 234$ nm, at zero Kelvin. The heat capacity data agree with BCS theory which could indicate conventional superconducting behavior in this material.

Acknowledgement

This material is based upon work supported by the FAPESP (2011/05961-3, 2014/01581-0, 2013/20181-0), NAP-USP, FAPEMIG, CNPq (448041/2014-6, 300821/2012-3) and CAPES (CAPES/CNPq PVE A10/2013), to which the authors wish to express their thanks. We would like also thank A. Shanenko and A. Vagov for stimulating discussions.

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