Ta$_{1-x}$Hf$_x$B: a new FeB-prototype superconductor

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1. Introduction

The Ta–B binary system (Okamoto et al [1]) presents five stoichiometric phases, TaB$_2$, Ta$_3$B$_4$, TaB, Ta$_3$B$_2$ and Ta$_2$B. These well-known high temperature materials have special applications under extreme environmental conditions [2, 3]. In addition, recent investigations on the Ta rich side of this system suggest the existence of a new unidentified high-temperature phase [4]. Although these materials have been extensively studied, we can find only a few results on superconductivity in this system. Superconductivity has been reported for TaB and Ta$_2$B with critical temperatures of 4.0 and 3.12 K, respectively [5–7].

Here, we report the effect of Hf doping in the TaB system. TaB crystallizes in the orthorhombic CrB prototype structure (Cmcm space group) with lattice parameters $a = 3.27$ Å, $b = 8.66$ Å, and $c = 3.15$ Å [8]. We show clearly evidence that appropriate amounts of Hf substitution at the Ta site induce the stabilization of the FeB prototype structure in the ternary Ta$_{1-x}$Hf$_x$B system. Superconductivity appears in these alloys with a maximum $T_c$ ($\sim 6.7$ K) for the Ta$_{0.7}$Hf$_{0.3}$B compound. For this composition, the Hall signal has a temperature dependence which can be related to more than one electron velocity on the Fermi surface and the specific heat at low temperature deviates from the conventional exponential temperature dependence. These results are not expected at low fields within single-band BCS theory.

Multiband superconductivity has been observed in some superconducting materials such as MgB$_2$ and YNi$_2$B$_2$C [9–13]. In fact, MgB$_2$ is the clearest example and the most studied multiband superconductor. It has been confirmed by experimental techniques, such as high-resolution angle-resolved photoemission spectroscopy (ARPES) [9] and directional point-contact spectroscopy [10]. Based on these studies, our results suggest that the Ta$_{0.7}$Hf$_{0.3}$B compound is a new multiband superconducting boride.
high purity elements Ta, Hf, and B were melted on a water cooled Cu hearth in an arc-furnace in an Ar atmosphere using a Ti sponge getter. The samples were flipped and re-melted 5 times to ensure good homogeneity. The weight loss during the arc melting was negligible (<0.3%). After melting, the samples were sealed in a special furnace and treated at 2000 °C for 8 h under an argon atmosphere. Powder x-ray diffraction (XRD) patterns were obtained using a Rigaku MultiFlex diffractometer which provides Cu Kα radiation. The lattice parameters were determined by using the PowderCell software and simulation as well [14].

Physical properties were investigated using a commercial VSM-PPMS EverCool II and also a VSM-SQUID magnetometer both from Quantum Design. Magnetization as a function of temperature was determined using zero field cooling (ZFC) and field cooling (FC) regimes, under an applied magnetic field of 20 Oe. In order to estimate the lower critical field, M versus H was measured from 1.8 to 6 K. Electrical resistivity as a function of temperature was measured using the standard four-probe method from 1.8 to 300 K. These measurements were performed both without and in an applied magnetic field in order to estimate the upper critical field. The specific heat of a polished flat sample with Ta0.7Hf0.3B composition was measured in the range of 0.45–20 K using a He3 system.

Here, we define the superconducting transition temperature (Tc) as the temperature corresponding to a 2% resistivity drop, a 1% magnetization drop in the ZFC measurements and a 1% heat capacity anomaly start from normal state.

To measure the Hall voltage, the sample was cut into a square with ~4 mm sides and ~0.5 mm thickness. The electrical contacts were placed on the corners of the sample. Low resistance contacts (~0.1 Ω) were prepared by sputtering gold. Magnetoresistive properties measurements were carried out in a in a commercial VSM-PPMS EverCool II with a 9 T magnet by using an adapted van der Pauw method with permutation of the voltage and current contacts (details about these measurements can be found in reference [15]).

3. Results and discussion

X-ray diffraction patterns for melted samples of Ta1−xHfxB with x up to 0.05 (not shown here) present the coexistence of diffraction peaks arising from two different orthorhombic symmetries. Most of the peaks can be indexed using the CrB prototype which is related to the TaB phase, and some peaks are also related to the FeB prototype (space group Pnma). We can also observe that the intensities of the diffraction peaks related to the TaB phase with the CrB prototype structure decrease with increasing Hf level. As x reaches values bigger than 0.05, only peaks associated with FeB symmetry remain and are still stable up to x = 0.40. These results indicate unambiguously that increasing the doped Hf concentration in Ta1−xHfxB can stabilize the orthorhombic FeB prototype structure in this system. Figure 1 shows a comparison between a simulated and experimental diffraction pattern for a polycrystalline sample of Ta0.7Hf0.3B.

The excellent agreement between experiment and simulation strongly suggests that Hf substitution in Ta1−xHfxB can stabilize the FeB prototype structure in this system. Rietveld refinement indicates lattice parameters equal to a = 6.2462 Å, b = 3.1513 Å and c = 4.7496 Å, at this substitution level. In this prototype structure, B occupies 4c at (0.13, 0.25, 0.3) and Ta/Hf share 4c at (0.325, 0.25, 0.615). The inset shows a schematic view of the crystal structure where the yellow spheres represent Ta or Hf atoms and the green spheres represent B atoms. Based on these results, we can say that Hf can stabilize a new boride compound not reported in the literature so far.

Excellent agreement between experimental and simulated FeB structure was also observed for compositions between 0.1 ≤ x ≤ 0.4. In samples with x higher than 0.4, secondary phases can be observed coexisting with the FeB type structure, which indicates that x = 0.4 is the solubility limit for Hf substitution at the Ta site. In the 0.05 ≤ x ≤ 0.4 range Ta1−xHfxB can be interpreted as a ternary compound.

It is well known that TaB binary compounds, with a CrB type structure, show superconductivity below ~4.0 K [5]. When 10% of Ta atoms are replaced by Hf the FeB prototype structure is stabilized and the superconducting critical temperature goes up to 5.7 K, as verified by magnetization measurements. Tc increases as the Hf content increases and reaches a maximum close to the Ta0.7Hf0.3B composition. A summary of our magnetization measurements is present in figure 2(a) which shows Tc as a function of Hf level (x–Tc phase diagram). We can clearly see a dome behavior with a maximum Tc close to x = 0.30. Thus, we will concentrate our discussion on this composition. Figure 2(b) shows a sharp superconducting transition close to 6.7 K for a sample of Ta0.7Hf0.3B. The inset shows M versus H at 1.8 K, displaying type II superconductivity. The shield observed in the Meissner state allows us to estimate a superconducting volume close to 55%, since the susceptibility value for perfect

Figure 1. Comparison between simulated and experimental XRD for a polycrystalline sample of Ta0.7Hf0.3B. The inset shows a schematic view of the FeB prototype structure, where green spheres represent B atoms and yellow spheres Ta or Hf atoms.
diamagnetism is $-1/4\pi$ (CGS system). These results strongly suggest bulk superconductivity in this new boride material with Ta$_{0.7}$Hf$_{0.3}$B composition.

Figure 3 shows resistivity as a function of temperature at zero magnetic field for a Ta$_{0.7}$Hf$_{0.3}$B polycrystalline sample. The sharp transition reflects the good quality of our sample. The onset of the superconducting transition is estimated to be 6.7 K and zero resistivity is reached at 6.2 K. This 0.5 K difference shows very good agreement with the magnetization measurements shown in figure 2(b). This can be explained by a high density of defects caused by the quenching procedure at high temperature and also the distortion in the lattice due to the chemical doping. The residual resistivity ratio value, $\text{RRR} = 1.3$, supports this explanation.

The inset of figure 3 displays the dependence of the superconducting critical temperature on the applied magnetic field, showing a shift of the critical temperature typical of superconducting behavior. The magnetoresistance behavior suggests a relatively high upper critical field ($\mu_0 H_c^2$). A $\mu_0 H_c^2 - T$ phase diagram was constructed using a criterion of $\mu_0 H_c^2 \sim 10.5$ T. The Hall voltage as a function of temperature at an applied magnetic field of 7.0 T (left axis). Carrier density is of order $10^{22}$ cm$^{-3}$ suggesting that electrons are the majority carrier (right axis).
50% of normal state resistance, as shown in figure 4(a). The upper critical field at zero temperature ($\mu_0 H_c(0)$) can be estimated using the Werthamer–Helfand–Hohenberg (WHH) formula [16] in the limit of short electronic mean-free path (dirty limit).

$$\mu_0 H_c(0) = -0.693 T_c \left( \frac{d\mu_0 H_c}{dT} \right)_{T\rightarrow T_c}. \quad (1)$$

The curve estimated by the WHH formula allows us to determine a $\mu_0 H_c(0)$ value of $\sim 10.5$ T (see red line in figure 4(a)). This value is consistent with resistivity measurements where zero resistance can be observed even at a 7.0 T applied magnetic field (see figure 3).

Focusing on the normal state properties of Ta$_{0.7}$Hf$_{0.3}$B, figure 4(b) shows Hall voltage as a function of temperature. The Hall signal has a temperature dependence which can be related to more than one electron velocity on the Fermi surface, suggesting two different scattering times. According to this theory [17], the longitudinal conductivity is governed by the transport scattering time $\tau$ proportional to $1/T$, while the Hall conductivity follows $1/T^2$ since the Hall relaxation rate is proportional to $1/T^2$. In fact, this behavior is also observed in MgB$_2$ thin films which are recognized as classical multiband compounds [18, 19]. The carrier density of $10^{22}$ cm$^{-3}$ in Ta$_{0.7}$Hf$_{0.3}$B suggests a relatively high density of states at the Fermi level. The voltage signal suggests that the majority carriers are electrons.

Finally, specific heat measurements are shown in figure 5(a) for Ta$_{0.7}$Hf$_{0.3}$B. A jump (anomaly) in $C_p/T$ versus $T$ appears close to 6.7 K as we found from resistivity and magnetization measurements (figures 2 and 3). The sharp specific heat anomaly indicates bulk superconducting behavior, consistent with the superconducting volume estimated from magnetization measurements. As expected, below $T_C$ the specific heat signal must decrease exponentially and reaches zero at zero Kelvin, according to thermodynamic predictions. In spite of this, our results suggest that the specific heat has a finite saturation at low temperature in $C_p/T$ versus $T$ (figure 5(a)).

In order to separate the phononic contribution, we have used the Debye approximation at low temperature given by $C_p/T = \gamma + \beta T^2$, which yields $\gamma = 2.0$ mJ mol$^{-1}$ K$^{-2}$ and $\beta = 0.11$ 222 (mJ mol$^{-1}$ K$^{-4}$). Using the $\beta$ value we can calculate a Debye temperature $\Theta_D \sim 325.93$ K. Subtracting the phonon contribution allows us to evaluate separately the electronic contribution to the specific-heat, plotted as $C_e/T$ versus $T$ in figure 5(b). An analysis of the jump yields $\Delta C_e/\gamma_o T_c \sim 1.11$ which is somewhat close to the BCS prediction (1.43), indicating that this gap is in the weak-coupling limit. Surprisingly, an unexpected upturn emerges at $T \sim 1.4$ K in the $C_e/T$ versus $T$ data. In fact, similar behavior has been reported and attributed to either Schottky contributions or magnetic impurities [20, 21]. However, Ta$_{0.7}$Hf$_{0.3}$B has no Schottky contributions and also has no magnetic impurities. Thus, this unexpected upturn may relate to a second superconducting gap and can be explained using the multiband scenario. Based on this, our results suggest that the Ta$_{0.7}$Hf$_{0.3}$B compound is a new multiband superconducting boride, but further measurements at lower temperatures should be performed to look for the signature of a second gap.

4. Conclusion

In this paper, the physical properties of a new superconducting ternary system Ta$_{1-x}$Hf$_x$B were explored. We show that substitution of Ta by Hf ions can stabilize the orthorhombic FeB prototype structure in these compounds. Superconductivity arises in this system with a maximum $T_c \sim 6.7$ K near the composition Ta$_{0.7}$Hf$_{0.3}$B. The heat capacity data deviate from conventional BCS theory, which could indicate some unconventional superconducting behavior in this material, possibly related to multiband effects in Ta$_{0.7}$Hf$_{0.3}$B. Additionally, the Hall constant has strong temperature dependence, similar to that seen in multiband MgB$_2$, suggesting that this compound is a new example of a multiband superconducting boride.
Acknowledgments

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.

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