Th$_2$NiC$_2$: a low density of states superconductor

A J S Machado$^{1,2}$, T Grant$^1$ and Z Fisk$^1$

$^1$ Department of Physics and Astronomy, University at Irvine, Irvine, CA 92697, USA
$^2$ Escola de Engenharia de Lorena, Universidade de São Paulo, PO Box 116, Lorena, SP, Brazil

E-mail: jefferson@demar.eel.usp.br

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Abstract

The metallic carbides exhibit many novel prototypes of crystalline structure. Among these compounds Th$_2$NiC$_2$ was reported in 1991 as a new carbide which crystallizes in the U$_2$IrC$_2$ prototype structure. In this work we report a reinvestigation of the synthesis of this compound. We find that Th$_2$NiC$_2$ is a new superconductor. Our results suggest that this phase is stable only at high temperatures in the system Th–Ni–C. The substitution of Th by Sc stabilizes the phase and improves the superconducting properties. The highest superconducting critical temperature occurs at 11.2 K with nominal composition Th$_{1.8}$Sc$_{0.2}$NiC$_2$. The electronic coefficient determined by specific heat measurements is close to zero. This unusual result can be explained by covalent bonding in the compound.

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

1. Introduction

One of the highlights of solid state chemistry in recent years has been the discovery of diverse types of transition metal carbides which exhibit many novel prototype structures [1–3]. An important characteristic of these special carbides is the presence of single and/or multiple metal–carbon bonds. In past years a variety of solid state structures [1–3]. Among these carbides is the presence of single and/or multiple metal–carbon bonds. In past years a variety of non-metals transition metal carbides that have been characterized are found to contain related types of metal–carbon bonds, as indicated by their interatomic distances. The other element, other than carbon or a transition metal, is generally a highly electropositive multivalent metal such as lanthanide (Ln), yttrium, uranium or thorium. The complete ionization of the electropositive metal to the stable ions Ln$^{3+}$, Y$^{3+}$ or Th$^{4+}$ leads to a negatively charged transition metal subnetwork, which can be considered as organometallic net. There are many ternary compounds crystallizing in many different prototype structures but of particular interest in this paper is the U$_2$IrC$_2$ prototype structure, also known as Na$_2$HgO$_2$. This prototype has a relatively simple body centered tetragonal crystal structure which was first determined for U$_2$IrC$_2$ [4]. Moss et al [5] reported the discovery of two new compounds Th$_2$NiC$_2$ and Th$_2$NixC$_5$. The Th$_2$NiC$_2$ compound crystallizes in the tetragonal symmetry with space group I4/mmm and prototype structure U$_2$IrC$_2$, with lattice parameters $a = 3.75$ Å and $c = 12.35$ Å. The carbide Th$_2$NiC$_2$ contains isolated linear C–Ni–C units in which the carbon atoms are only singly bonded to the nickel atom so that the C$^{2-}$ ligand is isoelectronic with an F$^-$ ligand. The isolated linear [C–Ni–C]$^{2-}$ anions with 26 valence electrons has Ni–C distance of about 1.93 Å, which is suggestive of Ni–C single bonding [1, 6]. In this compound each nickel atom has the 14 electrons required to fill seven orbital cylindrical spd$^5$ manifolds [1]. So assignment of the usual +4 and −4 oxidation states to the Th and isolated carbon atoms, respectively, in Th$_2$NiC$_2$ leads to the formal oxidation state of zero for the nickel, which corresponds to a d$^{10}$ metal configuration. Uranium platinum metal carbides U$_2$TC$_2$ ($T$ = Ru, Os, Rh, Ir and Pt) also crystallize in the same prototype structure as Th$_2$NiC$_2$ [7]. In this family of uranium platinum metal carbides the U$_2$PtC$_2$ represents a superconducting [8] nearly-heavy-fermion system which has been investigated intensively [9–12]. The Th$_2$NiC$_2$ and U$_2$PtC$_2$ are electronically similar and in this work we present results which indicate that Th$_2$NiC$_2$ is a superconducting material with a superconducting critical temperature close to 8.5 K. The partial substitution of T by Sc decreases the lattice parameters and increases the superconducting critical temperature from 8.5 up to 11.2 K.
Figure 1. X-ray diffraction pattern of the Th$_2$NiC$_2$ as-cast sample. We can observe three phases in equilibrium: the Th$_2$NiC$_2$ with monoclinic symmetry and $\gamma$-ThC$_2$ with cubic symmetry. The inset shows a schematic unit cell where red spheres represent Th atoms, blue represents Ni atoms and black spheres represent carbon atoms.

2. Experimental procedure

The samples of nominal composition Th$_2$NiC$_2$ and Th$_{x}$Sc$_{1-x}$NiC$_2$ ($x = 0.0, 0.1, 0.2$ and $0.3$) were made by arc-melting together the high purity elements, taken in the appropriate amounts, in a Zr-gettered arc furnace on a water-cooled Cu hearth under high purity argon. The samples were remelted five times to ensure good homogeneity. Due to the low vapor pressure of these constituent elements at their melting temperatures, the weight losses during arc-melting were negligible ($<0.5$%). A microcomputer-controlled diffractometer equipped with a copper target for Cu K$_\alpha$ ($\lambda = 1.54056$ Å) radiation was used to obtain the powder x-ray diffraction patterns. The lattice parameters were determined using the PowderCell software [13]. Magnetic data was obtained using a commercial VSM-SQUID from Quantum Design. The temperature dependence of magnetization was obtained using zero-field-cooling (ZFC) and field-cooling (FC) conditions, under an applied magnetic field of 50 Oe. After both ZFC and FC measurements, $M$ versus $H$ data was acquired at 1.8 K. Electrical resistivity measurements were performed between 1.8 and 300 K using a conventional four-probe system. The samples were irregular in shape and gold wires were spot-welded to the samples and served as the voltage and current leads. These measurements were carried out with and without an applied magnetic field in order to estimate the upper critical field, using a PPMS apparatus (Quantum Design). The heat capacity (relaxation method) of a piece cut from one sample was determined in the 1.8–10 K range using a calorimetric probe inserted in the PPMS apparatus.

3. Results and discussion

Figure 1 shows the x-ray diffraction pattern of the as-cast Th$_2$NiC$_2$. The majority peaks can be indexed to the tetragonal structure belonging to the space group $I4/mmm$ and prototype structure U$_2$IrC$_2$. The lattice parameters $a = 3.748$ Å and $c = 12.349$ Å are consistent with values reported in the literature [7]. The inset shows a schematic unit cell where the red spheres represent Th atoms, blue represents Ni atoms and black spheres represent carbon atoms.

Figure 2. Magnetization as a function of temperature of the sample presented in figure 1. The difference between ZFC and FC strongly suggests superconductivity with critical temperature close to 8.5 K. The inset shows the $M$ versus $H$ curve which clearly demonstrated type II superconducting behavior.
Sc being much smaller than Th [17–19]. We verified this possibility, making compositions with 0.1, 0.2 and 0.3 of Sc content in the nominal composition Th$_{2-x}$Sc$_x$NiC$_2$. For Th$_{1.9}$Sc$_{0.1}$NiC$_2$ composition, the x-ray results show Th$_2$NiC$_2$ and $\alpha$-ThC$_2$ with monoclinic symmetries in equilibrium. This result suggests that, at this level of substitution of Th by Sc, the phase of interest is stabilized. The magnetization versus temperature, shows that for this composition the critical temperature increases, from 8.5 K of the pure compound to 10.0 K (see figure 3). Furthermore, the compound is more stable in air than the pure compound (without Sc). This sample survives being exposed in air for about three months. Indeed the other compositions mentioned above also form in this structure. However, for nominal composition of scandium with $x > 0.3$ the superconductivity disappears and there arises a ferromagnetic behavior, where the secondary phase (unidentified) appears to be responsible for the magnetic behavior. The dependence of the superconducting critical temperature on Sc content is shown in figure 4, where we see dome-like behavior. The highest superconducting critical temperature occurs at a composition Th$_{1.8}$Sc$_{0.2}$NiC$_2$. We chose this composition to complete the characterization. Figure 5 shown x-ray results for this composition (Th$_{1.8}$Sc$_{0.2}$NiC$_2$), where we observe that the sample appears more single phase than pure compound presented in figure 1. There is only a monoclinic dicarbide in equilibrium with Th$_2$NiC$_2$, as occurs for the other compositions for which the critical temperature behavior is shown in figure 4. This result strongly suggests that Sc stabilizes the tetragonal phase with the U$_2$IrC$_2$ prototype structure. The inset of this figure shows the behavior of the lattice parameter with Sc doping. The systematic decrease of the lattice parameter is consistent with the fact that Sc is smaller than Th. The critical temperature is about 11.2 K, as shown in figure 6. The difference in results between ZFC and FC conditions indicates a type II superconductor and points to a weak Meissner effect due to strong flux pinning. The $M(T)$ is independent of $T$ in the normal state, indicative of a Pauli paramagnetism. The type II behavior is clear in the inset of this figure, which shows $M$ versus $H$ data at 1.8 K, and from which can be determined the lower critical field value ($H_{c1}$). The lower critical field ($H_{c1}$) was estimated through the deviation from linearity in the $M$ versus $H$ curve. Using the linear behavior in the Meissner effect the estimated $H_{c1}$ is about 171 Oe. With this estimate it is possible to define the penetration depth through the formula $H_{c1} = \frac{\Phi_0}{2\pi\lambda L}$, where the $\lambda_L$ parameter represents the penetration depth which yields $\lambda_L \sim 138$ nm at 1.8 K.

The resistance as a function of temperature showed, unambiguously, the sharp superconducting transition close to 11.2 K (figure 7), which is consistent with the result of figure 6. The inset displays the shifting of the critical temperature with applied magnetic field. We show resistance instead of resistivity because the shape of the sample is completely irregular, making the determination of the
Within the same weak-coupling BCS theory this gives an upper critical field of 20.65 T, which is much higher than $\mu_0H_{c2}(0)$ in the absence of Pauli paramagnetism (11.6 T). Hence pair breaking in Th$_{1.8}$Sc$_0.2$NiC$_2$ is most probably determined by orbital fields. The fitting in figure 8 data allows an estimation of the coherence length through the Ginzburg–Landau (GL) formula, $\mu_0H_{c2}(0) = \frac{\phi_0}{2\pi\xi_0}$, which yields $\xi_0 \sim 5.3$ nm. At 1.8 K the coherence length estimated from figure 8 is about 5.4 nm, while the penetration depth is about 138 nm. These values yield a GL $\kappa(1.8) \sim 26$, which is much higher than $\frac{1}{\sqrt{2}}$. This $\kappa$ is consistent with the behavior of a type II superconductor, as seen in the $M$ versus $H$ curve (inset of figure 6).

The specific heat measurements show a rather small jump close to 11.0 K (figure 9). The inset shows the $C/T$ against $T^2$ where we can observe the normal state specific heat which can be fitted to the expression $C_n = \gamma T + \beta T^3$ by a least-squares analysis. This fitting yields the value $\gamma \approx 0.02$ (mJ mol$^{-1}$ K$^{-2}$) and $\beta \approx 0.271$ (mJ mol$^{-1}$ K$^{-4}$). This $\beta$ value corresponds to a Debye temperature of $\Theta_D \sim 330$ K. The $\gamma$ value represents the Sommerfeld coefficient per mole formula unit and is proportional to the density of states at the Fermi level. This value is surprisingly suggesting almost no electrons at the Fermi level. This small value of the Sommerfeld coefficient is consistent with the small jump observed at the superconducting critical temperature. If we consider a weak coupled BCS superconductor, the jump in specific heat at $T_c$ is $\Delta C/\gamma T_c = 1.43$, which implies $\Delta C \sim 0.32$ mJ mol$^{-1}$ K$^{-1}$. This value is close to the noise level of a commercial Quantum Design Physical Properties Measurement System. For phonon-mediated superconductivity, superconducting critical temperature ($T_c$) is given approximately by $T_c = (\Theta_D/1.45) \exp[-1.04(1 + \lambda)/\lambda]$. Taking the Debye temperature estimated from figure 9 (330 K), $\lambda$ is approximately 0.5, which is in the weak electron–phonon coupling regime. However, the strong covalent bond between Ni and C could give a large value
of \( \langle \omega^2 \rangle \), which represents the characteristic phonon frequency averaged over the phonon spectrum. This important parameter could play an important role in the mechanism of the superconductivity in this material. Indeed other materials also present low density of the states at the Fermi level where the jump in specific heat is very hard to see. As an example, we can mention diamond doped with boron which exhibits a superconducting critical temperature close to 4.0 K. In this material the authors were not able to observe a jump in specific heat due to a pretty low Sommerfeld coefficient [21]. Another example is superconductivity in the perovskite phase BaPb\(_{1-x}\)Bi\(_x\)O\(_3\), which can exhibit superconductivity at 11.1 K [22]. Although the authors were not able to explain why they did not observe a jump in the specific heat measurement, the Sommerfeld coefficient is too low as also occurs in our sample. But it is surprising that this compound has very low density of states at the Fermi level when compared with U\(_2\)PtC\(_2\), which crystallizes in the same prototype structure and displays a \( \gamma \) value of approximately 75 mJ mol\(^{-1}\) K\(^{-2}\), almost a heavy-fermion material. In our results on the superconductivity in Th\(_3\)Ni\(_5\)Cs we found an electronic coefficient (Sommerfeld constant) of about 38.84 mJ mol\(^{-1}\) K\(^{-2}\). In our view these results are very unusual, but although the jump seen in our specific heat measurement is small, we can say that this compound is a bulk superconductor.

4. Conclusion

In this work we have shown that Th\(_2\)NiC\(_2\) is a superconductor with superconducting critical temperature close to 8.5 K. Our results also suggest that this phase is stable at high temperature and is extremely sensitive in air. The substitution of Th by Sc stabilizes the structure and decreases the instability in air. The substitution of Th by Sc also improves the superconducting properties and the superconducting critical temperature is optimized for the nominal composition Th\(_{1.8}\)Sc\(_0.2\)NiC\(_2\). The low value of the Sommerfeld coefficient is a surprising and unusual result since generally compounds with Th and Ni present values of the electronic coefficient which are relatively high. Our results shown unambiguously that Th\(_{1.8}\)Sc\(_0.2\)NiC\(_2\) is a new bulk superconductor material.

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