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Superconductivity at 7.3 K in Ti_2InN

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ABSTRACT

In this work the Ti_2InN phase is investigated by X-ray diffraction, magnetic and resistivity measurements. X-ray powder patterns suggest that all peaks can be indexed with the hexagonal phase of Cr_2AlC prototype. Electrical resistance as a function of temperature reveals superconductivity below 7.3 K. $M(H)$ hysteresis loops show typical type-II superconductivity. Using $R(H)$ versus T measurements we estimated $\mu_0 H_{c2}(0) \sim 10.8$ T and $\xi(0) \sim 55.2$ Å. The results show unambiguously that Ti_2InN is the first nitride superconductor belonging to the $M_{n+1}AX_n$ family.

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1. Introduction

The new family of nanolaminated phases called MAX phases has been discovered by Nowotny et al. [1]. These materials are ternary compounds consisting of an early transition metal M (elements from groups III–V A) and X = C and/or N. All the 60 known members of the family can be described by the formula $M_{n+1}AX_n$, where $n = 1, 2$ or 3 [2–4]. These phases have a layered structure in which the A element forms planes separated by MX slabs. This nanolaminated atomic arrangement gives rise to a unique set of properties, i.e. an unexpected combination of metallic and ceramic attributes. These combinations of properties place this class of materials as highly functional with the following aspects: (i) MAX phases can be easily machined like metals, (ii) they have good oxidation properties like ceramics, and (iii) they are excellent electrical and thermal conductors [1–8]. Among the ternary phases almost all the studies are concerned with carbide properties, but with few works on nitrides. In 1963 Jeitschko et al. discovered the Ti_2InN compound [9], which crystallizes in the same prototype structure as carbides (Cr_2AlC). In this structure the basic structural component is an octahedron of six Ti atoms with an N atom instead the carbon [10]. The electronic band structure shows that the interactions in the TiN octahedra are weaker

than those in the Ti_6N octahedra, in agreement with the general trend known for binary carbides and nitrides [10]. The electronic structure calculations show that Ti_2InC has 3.67 states/(eV cell) at the Fermi level (E_F), while the Ti_2InN has 4.02 states/(eV cell) at E_F [10]. It is clear that the nitrogen atoms change the electronic structure of these compounds and increase the state density at the Fermi level. The characteristic of band structure could probably affect the transport properties. Bortolozo et al. showed that the Ti_2InC superconducts at 3.1 K [11]. Motivated by this change in electronic structure, we decided to investigate the influence of the substitution of C for N on the M_2AX compound. This article reports the first superconductivity in a nitride of MAX-phase, with critical temperature close to 7.3 K.

2. Experimental procedure

The samples were prepared using mixtures of high purity TiN, Ti, and In powders in the Ti_2InN stoichiometry. The powders were compacted in square form of 10×10 mm² and 2 mm in thickness, sealed in quartz ampoules under Ar, and placed in a tubular furnace at 900 °C for 24 h. After this heat treatment, samples were ground and homogenized in agate mortar, compacted again in the same dimensions mentioned before, and heat treated at the same temperature for additional 96 h. After this procedure the samples were heat treated in a tubular furnace under 130 bar argon pressure at 900 °C for 10 h. The samples were characterized by X-ray diffraction using a XRD-6000 Shimadzu. The X-ray were simulated and refined using the PowderCell software and Rietveld method. Electrical transport properties' measurements were carried out by the

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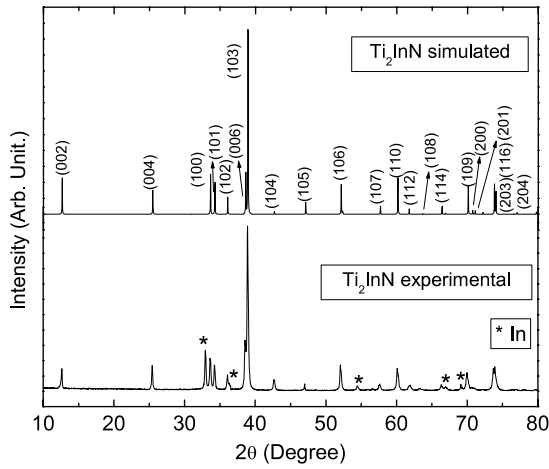


Fig. 1. Diffractogram of the Ti_2InN sample synthesized under 130 bar argon pressure (bottom). Simulated diffractogram (top) for the Ti_2InN compound which agree with the experimental results. The symbol (*) indicate the peaks due to impurities of In metal.

conventional four probe method between 2 and 300 K in an Oxford Instruments MagLab EXA-9 T. Magnetization measurements were performed in a Quantum Design 7T VSM-SQUID magnetometer.

3. Results and discussion

The experimental and simulated X-ray diffractogram for the Ti_2InN compounds, heat treated at 900 °C under high pressure are displayed in Fig. 1. The simulated diffractogram (top) agrees with the experimental result (bottom) which the peak positions are well indexed in the hexagonal structure with $P6_3/mmc$ space group. The calculated lattice parameters are $a = 3.074$ Å and $c = 13.975$ Å. The lattice parameters are in good agreement with those reported previously by Jeitschko et al. [9]. We can observe that there are few peaks that can be indexed with indium metal. For the $P6_3/mmc$ structure, Ti, In, and N atoms occupy the 4f, 2d, and 2a positions, respectively. The layered structure consists of three types of slabs, two Ti–In–Ti and one Ti–N–Ti, which obey the sequence N–Ti–In–Ti–N. Furthermore, it is important to emphasize that there are no Ti and In atoms placed below or above of the nitrogen atoms along the c -axis of the unit cell.

In order to study the transport properties of the Ti_2InN samples, the electrical resistivity as a function of temperature was measured. The $\rho(T)$ curve from 2 to 250 K is shown in Fig. 2. Between 8 and 250 K, the electrical resistivity shows metal like behavior. Furthermore, a clear superconducting critical temperature (T_c) can be observed close to 7.3 K (onset temperature). The upper of the Fig. 2 is shown details of the superconducting transition in which is possible to observe a $\Delta T_c \sim 1.3$ K. This width is related to In metal segregation in grain boundary. In lower inset of the Fig. 2 shows the $\rho(T, B)$ curves up to 7.0 T. From the $\rho(T, B)$ data pairs using the onset T_c criteria defined in the upper inset, we were able to define the upper critical field which is shown in Fig. 3 ($H_{c2}(T)$ vs T/T_c). The dot line represents the WHH fitting, which shows a clear deviates from WHH prediction [12]. Because the invalidity of using the WHH theory, we have estimated the upper critical field through of the Ginzburg–Landau (GL) theory [13–15] (solid line), where

$$H_{c2}(T) = \frac{\phi_0}{2\pi\xi^2(T)} = H_{c2}(0) \left(\frac{1-t^2}{1+t^2} \right). \quad (1)$$

In Eq. (1) $t = T/T_c$ is the reduced temperature. Using this equation we can determine $H_{c2}(0)$ as approximately 10.8 T. This upper critical field value yields a coherence length of $\xi \sim 55$ Å at zero temperature.

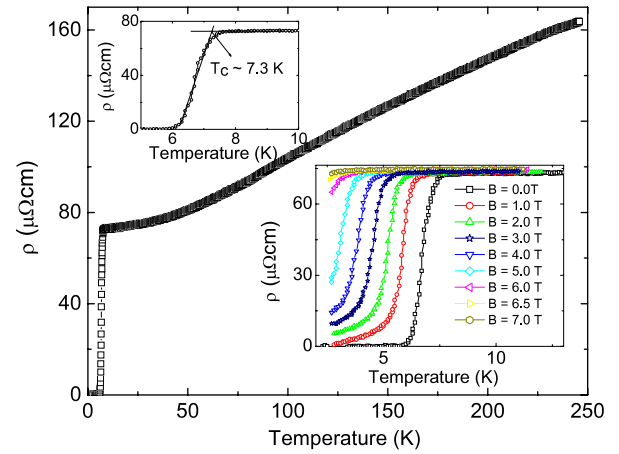


Fig. 2. Resistivity as a function of temperature showing a clear superconducting transition. Upper inset shows details of the superconducting transition and the T_c criteria definition. The lower inset displays the dependence of the $\rho(T, B)$ showing a systematic shift of T_c with increasing B .

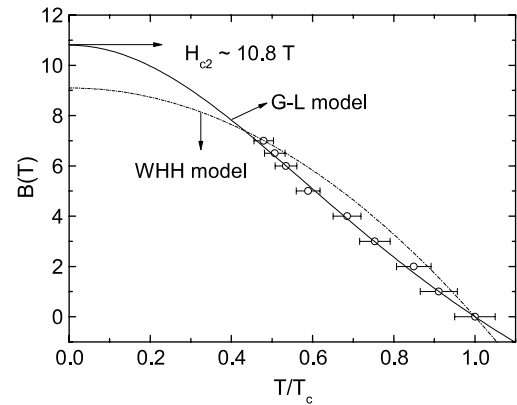


Fig. 3. Temperature dependence of the upper critical field H_{c2} for the Ti_2InN compound. The solid line represents the fitting results obtained using GL theory and the dot line is related to WHH prediction. Using that GL fitting, the zero temperature upper critical field $H_{c2}(0)$ is approximately 10.8 T.

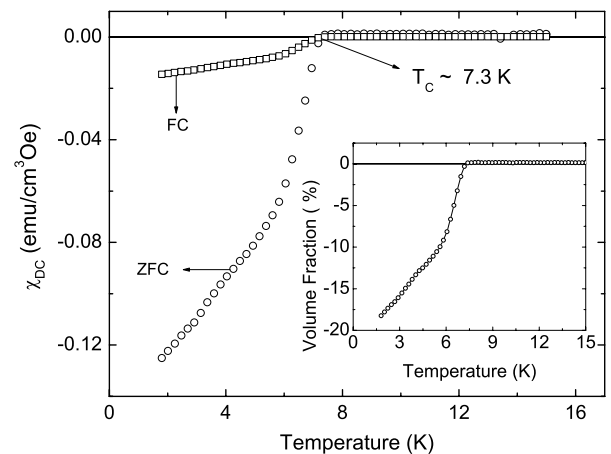


Fig. 4. Susceptibility measurement in the zero-field cooling (ZFC) and field cooling (FC) modes are shown. One can clearly see superconducting behavior below 7.3 K. In the inset, the temperature dependence of the ac susceptibility measurement is showing an estimation of the superconducting volume fraction of approximately 18% which suggests bulk superconductivity.

Fig. 4 displays a superconducting transition close to 7.3 K (onset temperature) in both zero-field cooling (ZFC) and field cooling (FC) magnetic susceptibility measurements. Superconducting

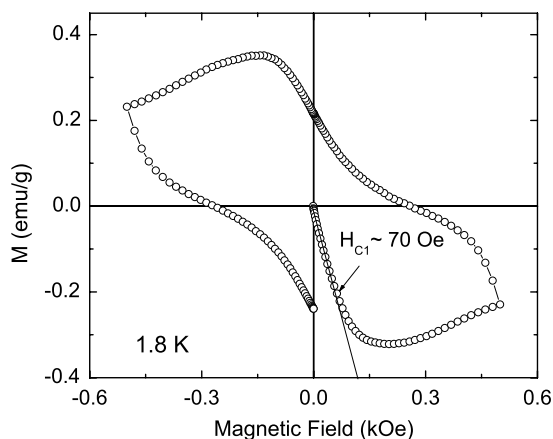


Fig. 5. Magnetization as a function of applied magnetic field measured at 1.8 K shows typical type-II superconductivity. The $M(H)$ measurements exhibit a typical butterfly loop of an irreversible type-II superconductor with large hysteresis due to strong flux pinning. The estimated lower critical field through this curve is about 70 Oe.

volume fraction of 18% (see inset of the Fig. 4) suggests bulk superconductivity. The $M(H)$ data also clearly show that Ti_2InN is a typical type-II superconductor (Fig. 5). An accurate determination of the lower critical magnetic field at this temperature is not possible due to the broadening of the $M(H)$ curves. This broadening also can be related to granular and screening effects. So, a very rough estimation of H_{c1} is related to the magnetic field where the initial slope intersects with the extrapolation curve of $(M_{up} + M_{down})/2$ yielding μH_{c1} of approximately 70 Oe at 1.8 K. With this lower critical field we can estimate the Ginzburg–Landau superconducting penetration depth λ_{GL} as $0.31 \mu\text{m}$ at 1.8 K.

The electronic band structure calculations for H-phases [10] suggest that the transition metal does not play role in the superconducting mechanism suggesting that the transport behavior of this material is two-dimensional. The nitrogen atom is more electronegative than carbon, and the chemical bond between Ti–N is more polarized than Ti–C. So, the basal plane may be responsible for the superconducting behavior in these compounds. Finally, with the N atoms substitution for C atoms in the Ti_2InX compound, the critical temperature increased more than twice (from 3.1 K for

Ti_2InC to 7.3 K for Ti_2InN). The results reported here unambiguously demonstrate the first nitride superconductor belonging to the $\text{M}_{n+1}\text{AX}_n$ family.

4. Conclusion

Resistivity and magnetic experiments performed on polycrystalline samples have been used to characterize Ti_2InN compounds. This work reveals that the Ti_2InN compound superconducts at 7.3 K. Magnetization as a function of temperature curves agree with the resistivity measurement and show diamagnetism behavior below 7.3 K. The $M(H)$ data displays typical type-II superconductivity with lower critical field of approximately 70 Oe at 1.8 K. An upper critical field $\mu_0 H_{c2}(0) \sim 10.8$ T. Finally, these results show the existence of the first superconductor nitride belonging to MAX phase which crystallize into Cr_2AlC prototype.

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