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THE HIGH TEMPERATURE PREPARATION AND PROPERTY MEASUREMENTS OF $CaTaN_2$: A TERNARY SUPERCONDUCTING NITRIDE

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Abstract—Highly crystalline $CaTaN_2$ was prepared by the reaction of $Ca(NH_2)_2$ and Ta_3N_5 in a specially designed reaction vessel at high temperatures (> 1300°C). Even when reaction conditions varied considerably, the samples were always contaminated by small amounts of Ca_2TaN_3, TaN, or $TaN_{0.1}$. SQUID measurements obtained on a sample contaminated by Ca_2TaN_3 and a sample contaminated by TaN and $TaN_{0.1}$ showed superconducting transitions at 9.6 K and 9.1 K, respectively. Resistivity measurements carried out on a sintered pellet of $CaTaN_2$ contaminated by $TaN_{0.1}$ showed a $\rho(300\,K) = 0.0147\,\omega cm$ and weakly rising resistivity with lower temperatures, likely due to the random alignment of the polycrystalline grains.

Keywords: A. superconductors, B. chemical synthesis, C. X-ray diffraction, D. electrical properties, superconductivity.

1. INTRODUCTION

Much of the interest in nitride chemistry has focused on the binary nitrides. These materials exhibit a wide variety of physical and chemical properties: mechanical hardness, chemical inertness, superconductivity and interesting electronic and magnetic properties. Nonetheless, the search for new ternary transition metal nitride phases, which may display a wider variety of useful properties, has begun only recently.

The unique chemistry of nitrogen presents a few challenges to the preparation of new ternary nitrides. The diffusion rate of nitrogen in many materials is very slow; consequently, high temperatures are often required for reasonable reaction rates. Furthermore, the greater strength of the nitrogen triple bond in N_2 in comparison to the strength of the oxygen double bond in O_2 (941 kJ mol^{-1} vs 499 kJ mol^{-1}) results in lower free energies of formation and lower thermodynamic stability of the nitrides at elevated temperatures [1]. Thus, optimal synthetic conditions are often bounded by the slow diffusion rate of nitrogen at lower temperatures and by the inherent instability of many nitride compounds at higher temperatures.

Many ternary nitride compounds have been prepared by teaming a transition metal with a more electropositive element, usually an alkali or alkaline earth metal [2, 3]. The electrons from the electropositive element help to stabilize the high oxidation state N^{3-} anion. However, the presence of large amounts of group 1 or 2 metals results in compounds in which the transition metal is bound to nitrogen in discrete nitridometallate anions surrounded by a sea of group 1 or 2 cations. These nitridometallate phases tend to be air and water sensitive and they exhibit insulating behavior due to the expectedly poor transition metal to transition metal orbital overlaps.

One of our principal interests then has been to explore nitride systems in which the ratio of alkaline earth to transition metal is low (≤ 1). As the amount of electropositive metal decreases, there is a tendency to greater connectivity of the transition metal–nitrogen polyhedra. [4] The enhanced metal overlaps should yield interesting properties and the greater degree of covalency should result in more stable and robust compounds.

The synthesis and structure of $CaTaN_2$ has been previously reported [5]. It was prepared through the reaction of $Ca(NH_2)_2$ and Ta_3N_5 in a 1 : 1 metal ratio at 1200°C under 1 atm of N_2 for 30 h. The black, polycrystalline powder was indexed on a hexagonal cell ($a = 3.164$ and $c = 16.649$ Å). The structure was refined by using $NaTaN_2$ as a model. The structure, isotypic with α-$NaFeO_2$, is an ordered rock salt structure comprised of close packed nitrogen layers with Ca and Ta in octahedral holes between alternating layers (Fig. 1).

Earlier magnetic data obtained on a Faraday balance indicated a superconducting transition around 9.7 K [6]. However, these results are ambig-

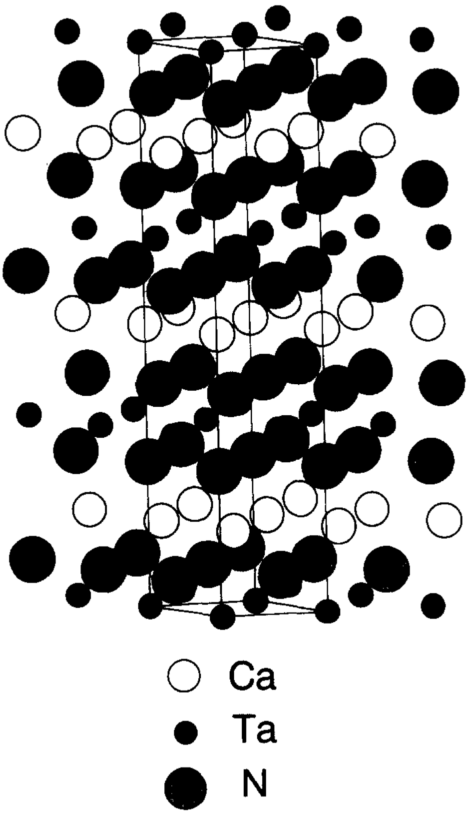

Fig. 1. Structure of $CaTaN_2$ showing the alternating layers of Ca, N and Ta perpendicular to the *c* axis.

uous because of the presence of a calcium deficient impurity in the sample, the possibility for contamination with the superconducting phase TaN and the difficulty in determining the superconducting fraction by that method. Our goal was to prepare pure phase $CaTaN_2$ for magnetic and electrical measurements. With respect to synthesis, $CaTaN_2$ is a traditional nitride: high temperatures (~ 1200°C) are required to achieve sufficient crystallinity; however, elevated or prolonged heating results in loss of Ca and the formation of $Ca_{0.74}TaN_2$ ($a = 3.129(1)$ and $c = 17.013(4)$ Å), whose powder diffraction peaks nearly overlap those of the parent phase, or possibly even the formation of TaN. Under such conditions, the choice of container as well as the exclusion of oxygen and water become important considerations.

Inductive heating is well suited to this task. It allows the attainment of high reaction temperatures without constraints on heating or quenching rates. Since heat is applied only to the metal susceptor and sample, reaction with container walls or air contamination by increased permeability of the furnace tube are significantly minimized. This technique has already been exploited in the preparation of VN [7] and more recently in the synthesis of ternary alkaline earth silicon nitrides [8, 9].

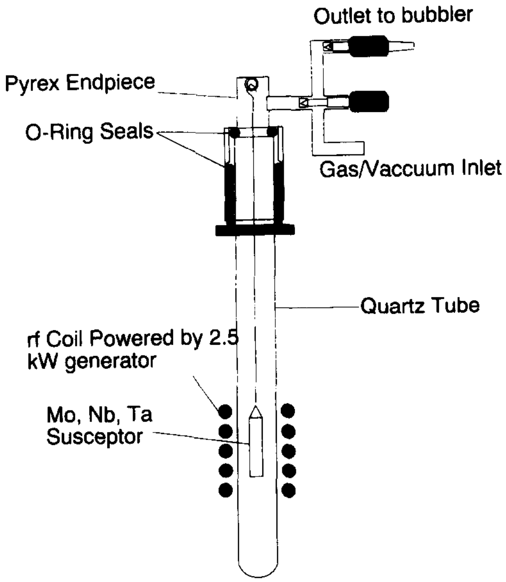

Fig. 2. Glass reaction vessel for preparation of samples by inductive heating.

2. EXPERIMENTAL

All manipulations were carried out in an argon filled glove box. The starting materials were calcium amide and tantalum (V) nitride. Calcium nitride was used to compensate for calcium loss in the final anneal. Calcium amide was prepared from Ca metal (Aldrich, 2N sublimed at 950°C, 10^{-6} torr) and liquid ammonia (distilled from a Na solution) in an autoclave at 120°C for 24 h. Tantalum (V) nitride was prepared from the ammonolysis of $TaCl_5$ (Alfa/Aesar, 4N) under flowing ammonia at 700°C for 12 h. Calcium nitride was prepared from the metal and nitrogen gas at 1000°C.

The preparation of the product samples was carried out in specially designed glass reaction vessels (Fig. 2), which were evacuated and filled with nitrogen gas that had passed through columns of copper catalyst and molecular sieves and finally through a Ti bed heated to 800°C to remove the last traces of oxygen and water. Before reaction, the vessel was evacuated and refilled with 1 atm of N_2, that was maintained throughout the run. The samples were heated inductively in a 2.54 cm diameter copper coil powered by a 2.5 kW radio frequency generator (Amerítherm Model SP-2.5). Temperature was monitored by optical pyrometry.

Calcium amide and tantalum (V) nitride in 1.15 : 1 metals ratio were ground and pressed into a single pellet (0.79 cm dia. and 670.8 mg) which was fired at 1100°C for 10 s in an open Nb susceptor (30 mm long × 9.5 mm OD × 0.6 mm wall). The temperature was then briefly lowered to 900°C and maintained at ~ 700°C for 10 min. The loose black pellet was reground and repelleted. The final anneal was carried

Table 1. Summary of preparation conditions for samples

Sample	Initial Ca : Ta	First anneal	Second anneal	Products
1	1.15 : 1	Open Nb susceptor 1100°C, 10 s 900°C, 10 s 700°C, 10 min	Open Nb susceptor 1450°C, 3 h	$CaTaN_2$ and Ca_2TaN_3
2	1.1 : 1	Open Mo susceptor 1200°C, 10 min	Sealed Mo susceptor 1350°C, 2 h	$CaTaN_2$ TaN and $TaN_{0.1}$
3	1.1 : 1	Open Mo susceptor 1200°C, 8 min	Sealed Mo susceptor 1200°C, 30 min	$CaTaN_2$ and $TaN_{0.1}$

out in an open Nb susceptor at 1450°C for 3 h. The product showed very crystalline $CaTaN_2$ as well as a small amount of Ca_2TaN_3 ($a = 4.747(1)$ Å), a previously reported green insulating compound [10].

For the second sample, calcium amide and tantalum (V) nitride in 1.1 : 1 metals ratio were ground and pressed into a single pellet (0.79 cm dia. and 808.8 mg). The sample was loaded into a Mo susceptor (50 mm long × 12.5 mm OD × 0.15 mm wall). It was heated in the RF coil to 1200°C for 10 min in order to decompose the starting material. It was weighed and a mass loss of 11.2% was recorded, which is consistent with

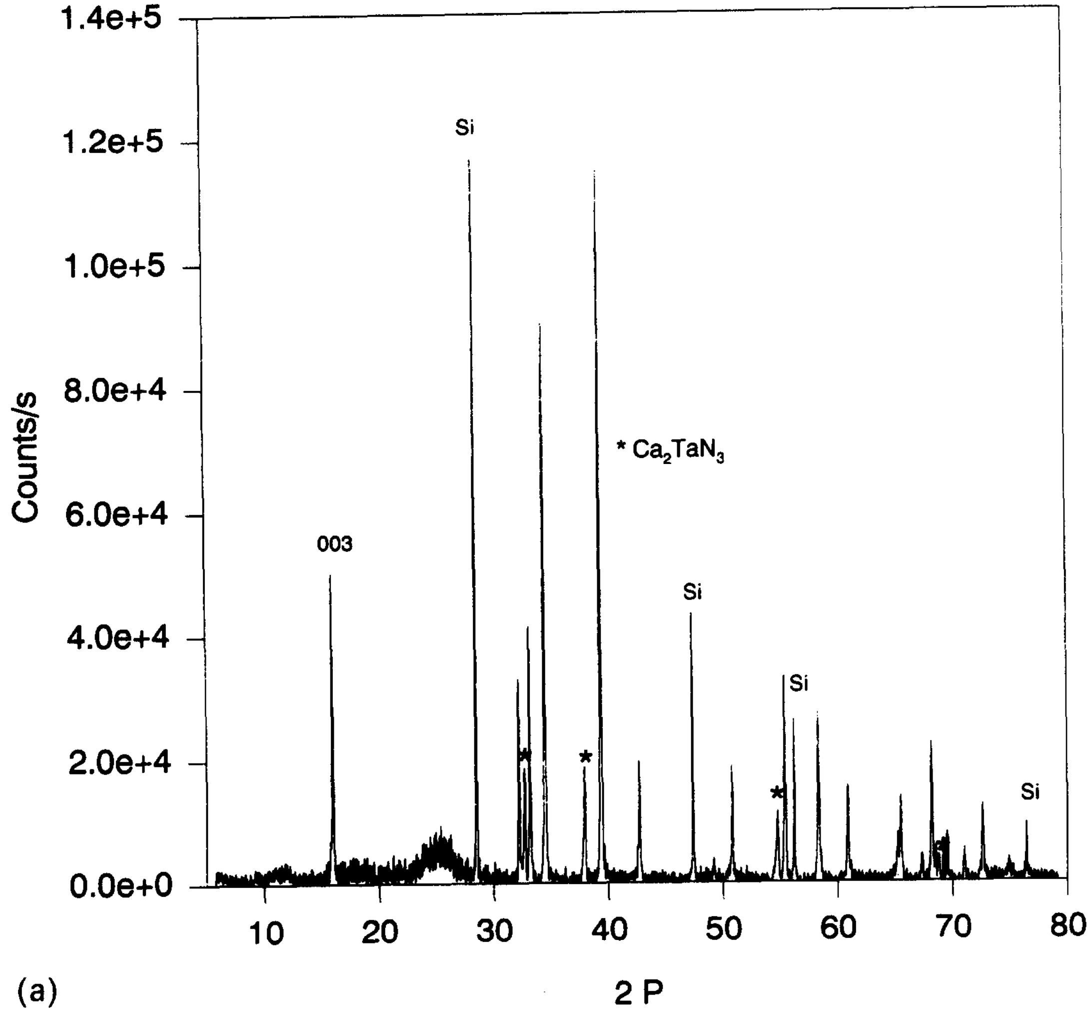

Fig. 3(a). X-ray powder diffraction pattern for Sample 1. $CaTaN_2$ sample is contaminated by Ca_2TaN_3, marked by *. (Si standard for the precise determination of lattice parameters is also present. (b) X-ray powder diffraction pattern for Sample 2. $CaTaN_2$ sample is contaminated by TaN and $TaN_{0.1}$, marked by + and *, respectively. (c) X-ray powder diffraction pattern for Sample 3. $CaTaN_2$ sample is contaminated by only $TaN_{0.1}$, marked by *.

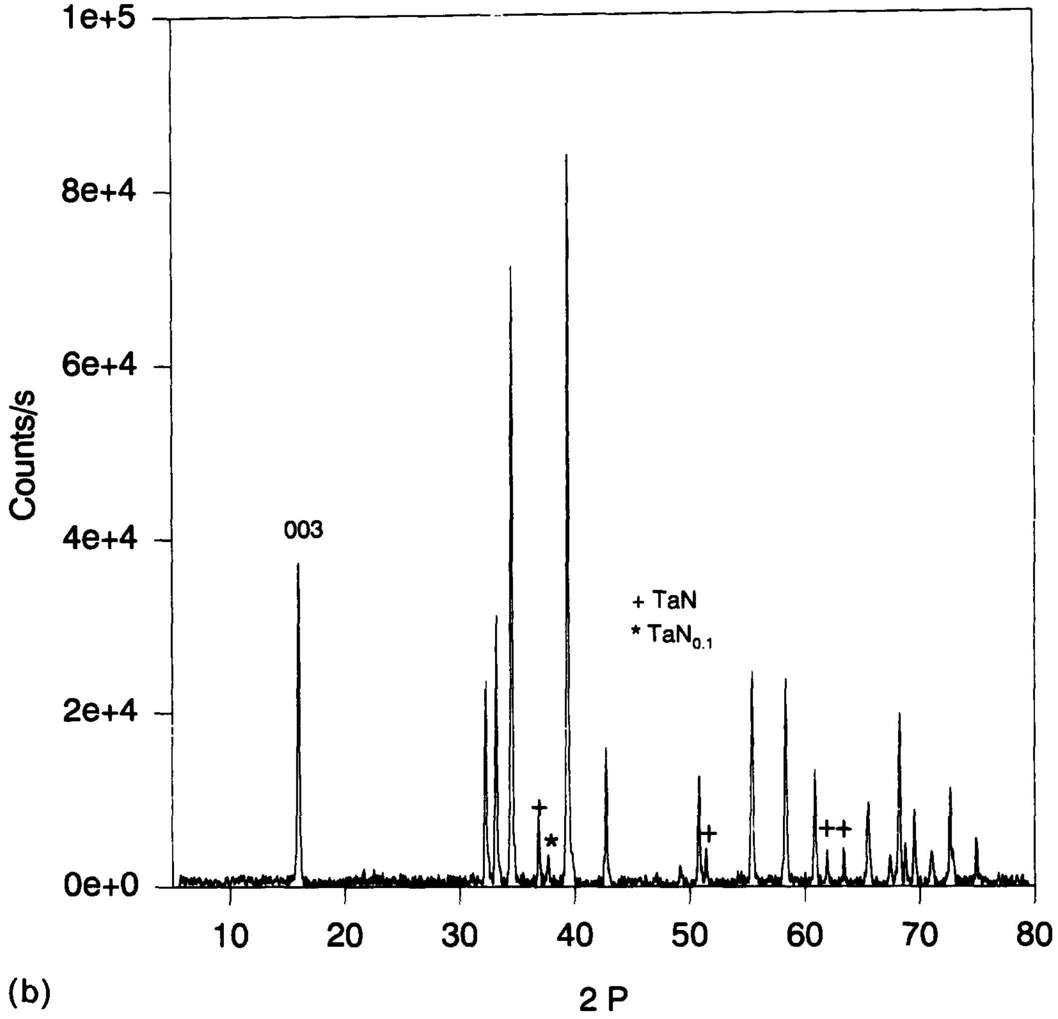

Fig. 3. (b)

the stoichiometric loss of N and H as well as excess Ca metal in the starting materials to form the product. The loose black pellet was reground with an additional 8.9 mg Ca_3N_2, which was calculated on the basis of typical Ca mass losses (~ 1% of sample) during the final anneals in prior preparations, and pressed into two pellets (each measuring 0.79 cm dia. and ~ 350 mg). The pellets were sealed in a Mo capsule (50 mm long × 12.5 mm OD × 0.15 mm wall). The capsule was heated at 1350°C for 2 h. A powder X-ray diffraction pattern of the black, sintered product showed highly crystalline $CaTaN_2$ and a small amount of TaN and $TaN_{0.1}$.

For comparison, magnetic data on both samples were collected on a Quantum Design SQUID Magnetometer (MPMS), at a d.c. field of 10 Oe. The superconducting magnet was degaussed before measuring each sample, using a careful procedure that has shown to leave a remanent stray field under 1 Oe throughout the 6 cm SQUID scanning range.

After the sample was cooled from 35 K to 2 K in zero field, a 10 Oe field was applied and the sample magnetization measured. Then the temperature was raised incrementally to 4.2 K, a magnetization measurement made at each step. Next, the sample temperature was raised to 35 K and recooled in zero field to 5 K. Again a 10 Oe field was applied and the magnetization measured at temperature steps up to 10 K. Finally, the temperature was then lowered to 5 K stepwise with 10 Oe field maintained and the magnetization measured at each step. Data between 4.2 and 5 K were not taken because the MPMS switches modes from pumped He to heated He gas and the temperature history cannot be assured.

A third sample was prepared by reacting calcium amide and tantalum (V) nitride in 1.1 : 1 metals ratio as a pressed pellet (0.79 cm dia. and 778.6 mg) at 1200°C for 8 min in an open Mo susceptor. The sample was weighed, again mass loss was consistent with the formation of the desired product. The sample was ground with 8.5 mg Ca_3N_2 and pressed into two pellets (0.79 cm dia. and each ~ 350 mg). They were

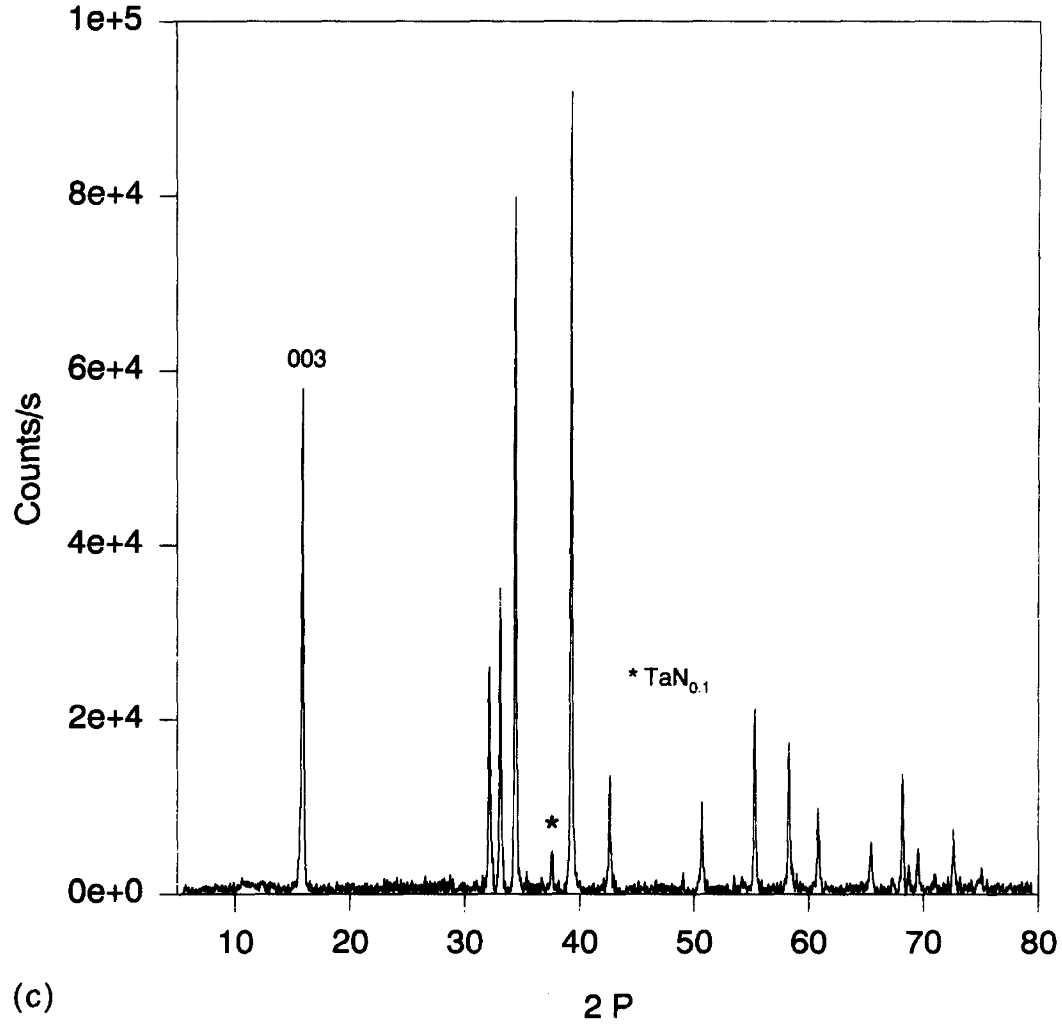

Fig. 3. (c)

fired in a sealed Mo capsule at 1200°C for 30 min. One pellet was used for X-ray powder diffraction; the other was reserved for resistivity measurements. In this case, nearly pure $CaTaN_2$ was obtained with only a very small impurity of $TaN_{0.1}$. Four point resistivity measurements were carried out down to liquid He temperature on the second sintered pellet (0.79 cm dia × 0.140 cm thick), which was sanded to expose fresh surface to the gold, spring-loaded contacts.

The identity of all products was confirmed by X-ray powder diffraction. Data was collected on a Scintag XDA 2000 diffractometer (flat plate configuration) using CuKα radiation.

3. RESULTS AND DISCUSSION

The preparation conditions, which are summarized in Table 1, greatly affect the products obtained. X-ray powder patterns for all three samples show very good crystallinity. The lack of peak broadening in the 003 reflection in the pattern for the first sample indicates the absence of the Ca poor phase $Ca_{0.74}TaN_2$ (Fig. 3(a)). The sample is contaminated by Ca_2TaN_3, a disordered rock salt phase. By visual inspection, this appears as a green phase upon grinding. The ratio of the peak heights of the most intense peaks of Ca_2TaN_3 and $CaTaN_2$ in the X-ray powder pattern is an estimate of the impurity content, which in this case is ~ 15% of the sample. Of course, this is only a semi-quantitative value as peak intensities in the powder diffraction pattern are determined by structure factors and peak multiplicities. A Rietveld refinement of the powder pattern using RIETAN [11] based on the reported model resulted in lattice parameters of $a = 3.164(1)$ and $c = 16.68(1)$ Å. These values are within several standard deviations of the reported parameters [3]. Our slightly better R factors ($R_p = 7.20$ and $R_{wp} = 9.10$ vs $R_p = 9.10$ and $R_{wp} = 11.37$) were due to the greater crystallinity of our sample. Attempts to produce the desired $CaTaN_2$ free of the Ca_2TaN_3 impurity under these conditions by incrementally reducing the excess of calcium were

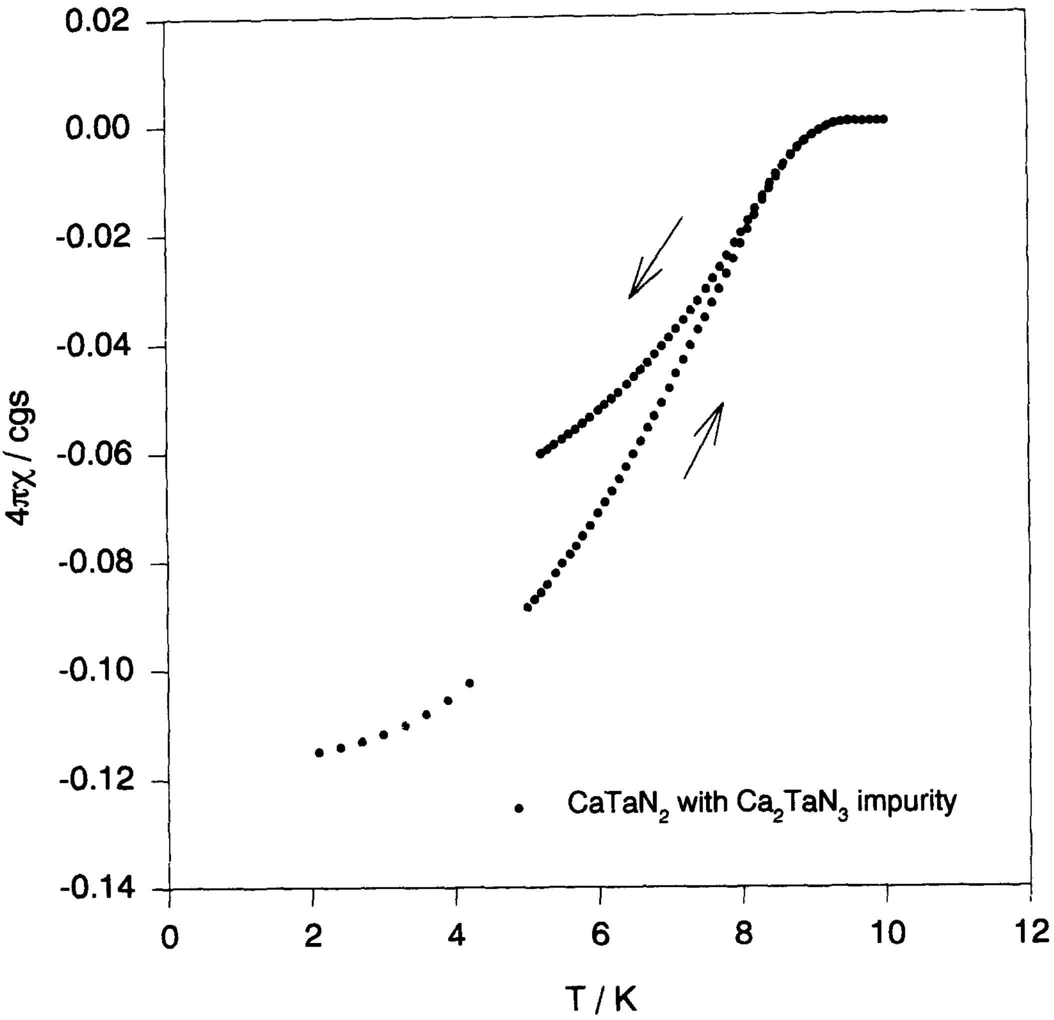

Fig. 4. SQUID magnetic susceptibility data for sample contaminated by Ca_2TaN_3 (Sample 1).

unsuccessful. Samples prepared with less than 15 mol % excess Ca resulted in samples contaminated by the calcium poor phase.

In the second sample, there are two peaks attributed to the presence of tantalum nitride impurities, the high temperature form of TaN and $TaN_{0.1}$ (Fig. 3(b)). The impurity levels are estimated at ~ 10% and 5%, respectively, by the approximation previously discussed. The identification of $TaN_{0.1}$ as an impurity phase should be taken with the caveat that only the most intense peak for $TaN_{0.1}$ is observed. This may be expected since the most intense peak of $TaN_{0.1}$ is more than three times the intensity of the next most intense peak. Furthermore, this peak nearly coincides with a peak for $CaTaN_2$, making it difficult to observe. Again, there is no broadening of the 003 reflection which would indicate the presence of the Ca deficient phase. A standardless least squares minimization of the lattice parameters of $CaTaN_2$ in this sample gave $a = 3.16$ and $c = 16.68$ Å. These values are consistent with the more accurate determination of the lattice parameters made for the first sample.

Given these considerations, it would seem possible to prepare a single phase sample of $CaTaN_2$ by the proper choice of conditions—viz., a longer initial firing in order to prevent the trapping of unreacted TaN, using a sealed container to inhibit Ca loss and shortening the second anneal in order to reduce further the likelihood of calcium loss. The sample used for resistivity was the closest to single phase that we could obtain. Here, only a small amount of $TaN_{0.1}$ is present, ~ 5%; again, the caveat concerning the identity of the second phase as $TaN_{0.1}$ applies. The brief second anneal, while preventing the formation of TaN, was sufficient to form $TaN_{0.1}$. This is perhaps surprising, since we would expect the formation of TaN before the formation of $TaN_{0.1}$. A standardless least squares minimization of the lattice parameters of $CaTaN_2$ in this sample gave $a = 3.16$ and $c = 16.68$ Å, again the same as the previous two samples.

The persistence of some form of tantalum nitride in reactions where the Ca : Ta ratio is less than 1.15 : 1 suggests that the TaN_x may not arise solely from the

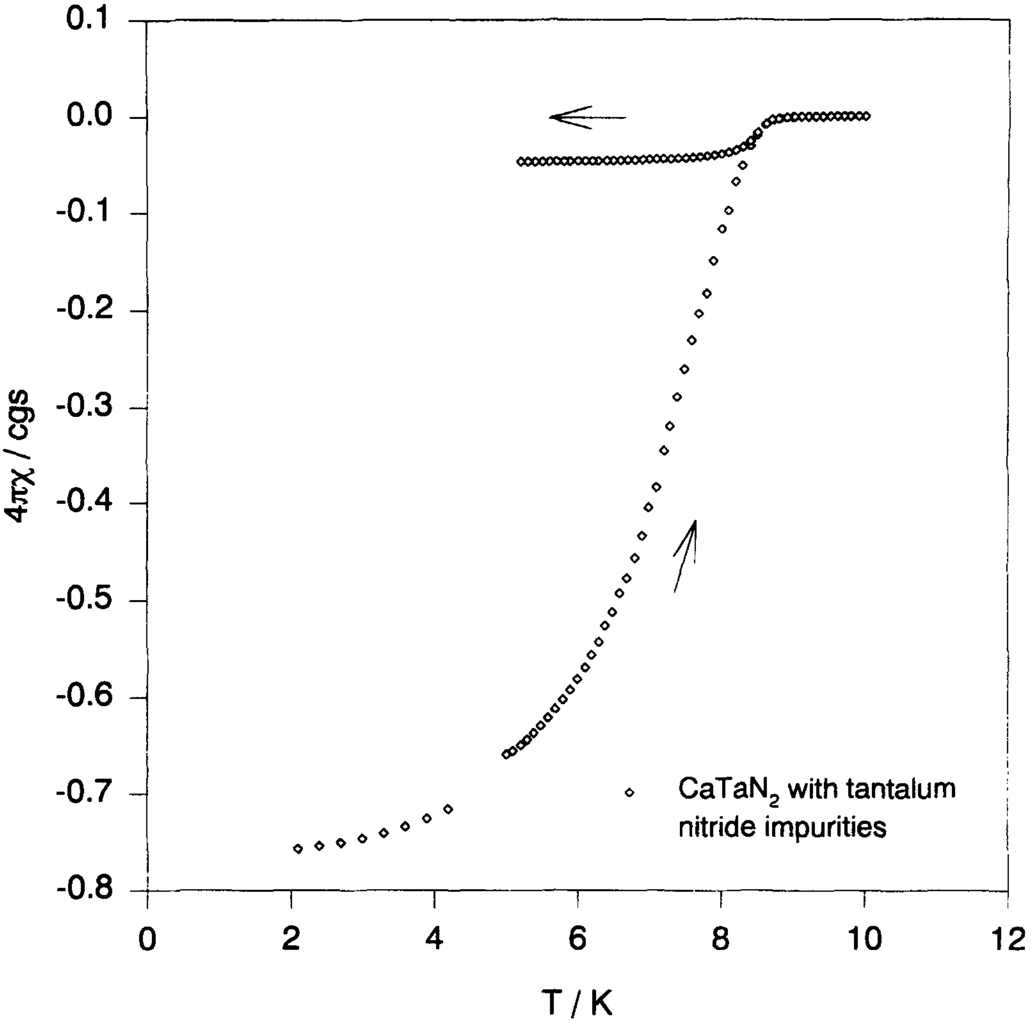

Fig. 5. SQUID magnetic susceptibility data for sample contaminated by tantalum nitrides (Sample 2).

decomposition of the desired $CaTaN_2$ phase. The tantalum nitride could be the result of either (1) the improper decomposition and reaction of the starting materials or (2) the ultimate decomposition product due to Ca loss. Insufficient mixing could result in pockets of inhomogeneity and formation of tantalum rich areas. The texture of the starting materials—$Ca(NH_2)_2$ is a flocculent powder while Ta_3N_5 is a very fine powder—makes thorough grinding and thorough mixing difficult. Since any extra Ca may react only with the closest Ca poor region before it evaporates, these tantalum rich areas may be kinetically trapped. The first explanation would seem to obtain in the third sample because the brief reaction times would make a significant loss of Ca unlikely. The second possibility, loss of Ca from $CaTaN_2$, certainly occurs at high temperatures. For instance, samples repeatedly heated to 1500°C show increasing Ca loss along with the formation of increasing amounts of TaN.

The results of the magnetic measurements are shown in Figs 4 and 5. Figure 4 contains the data for sample 1, the sample with the Ca_2TaN_3 impurity. Onset T_c is 9.6 K. The limiting value of $4\pi\chi$ (χ is the magnetic susceptibility) corrected for demagnetization is about -0.12 for the zero field cooled data, while the value of $4\pi\chi$ for the field cooled data is about -0.07. Figure 5 contains the data for sample 2, the sample with the TaN and $TaN_{0.1}$ impurities. Onset T_c is 9.1 K. The limiting value of $4\pi\chi$ without correction for demagnetization is about -0.8 for the zero field cooled data, while the value for the field cooled data is approximately -0.05. Such small values of $4\pi\chi$ for the field cooled data in both samples may indicate either (1) that the superconducting phase is a minor constituent or (2) that the sample porosity makes it difficult to expel the magnetic flux completely. The second interpretation is more likely since the zero field cooled value of $4\pi\chi$ for sample 2, is close to -1.

Both samples display a superconducting transition near 9 K. The Meissner effect probed by the field cooled experiment in these samples is limited by the high porosity of the samples but is consistent with

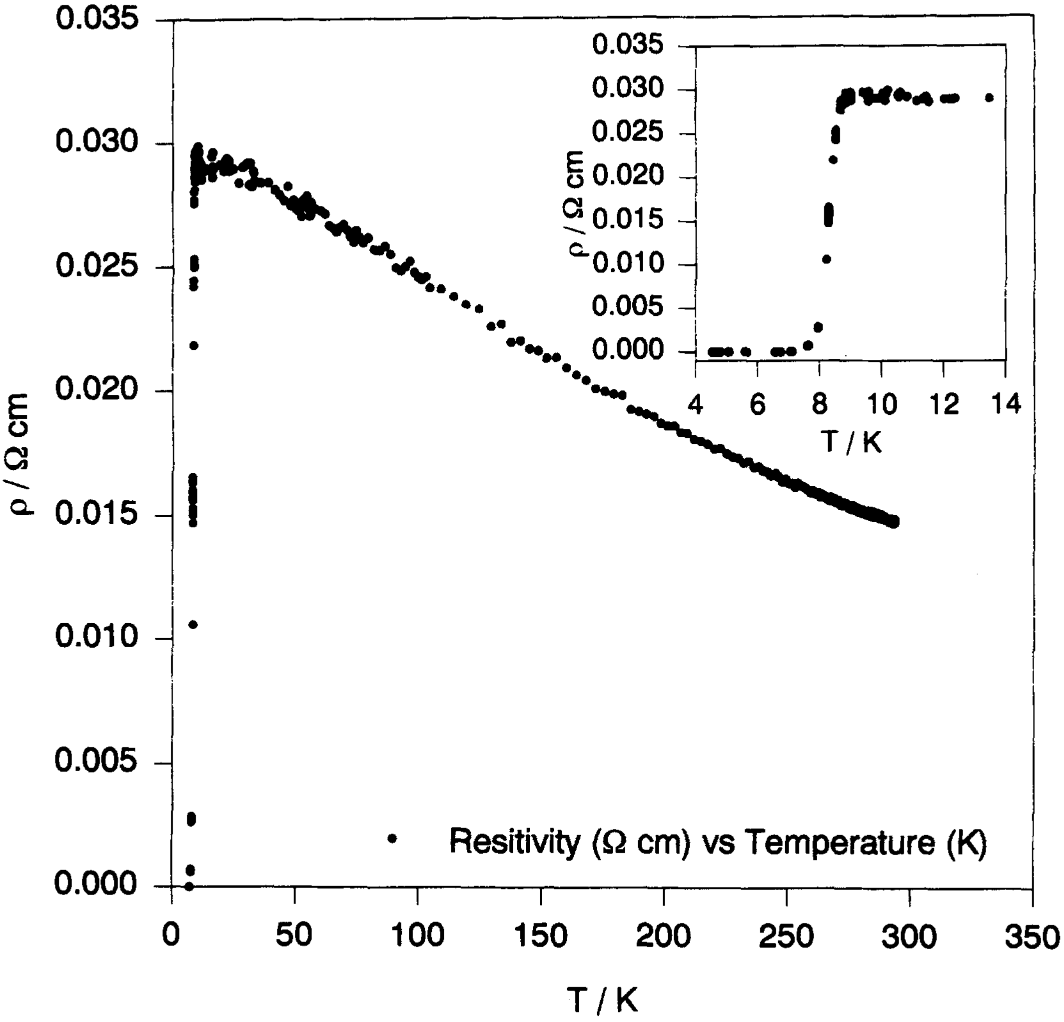

Fig. 6. Resistivity data for sample contaminated by a small amount of $TaN_{0.1}$ (Sample 3).

bulk superconductivity. The slight difference in onset temperature is likely to be due to the very different processing conditions undergone by the two samples, perhaps resulting in different defect concentrations. The Meissner signal is comparable in both samples. Since each sample contains different impurities, the superconductivity cannot be attributed to the impurity phases but must be due solely to $CaTaN_2$.

Resistivity data obtained for sample 3 is presented in Fig. 6. At high temperatures the magnitude of the resistivity is consistent with that expected for a poor metal. Upon being cooled to liquid He temperature, the resistivity increases slowly from a room temperature value of 0.0147 Ω cm until the superconducting transition at about 8.2 K (inset figure). The T_c obtained from the resistivity measurement differs from the result obtained from the magnetic measurements primarily due to an expected thermocouple offset (in our instrument, there is a separation of a few cm between the thermocouple and the sample) and perhaps to slightly different preparation conditions. The increasing resistivity with lower temperature contrasts with the decreasing resistivity expected for d^1 Ta in a metallic compound. It may, on the other hand, be consistent with the likely anisotropy in the resistivity due to the layered structure of $CaTaN_2$. The band structure of $CaTaN_2$ is expected to be rather two dimensional, since the Ca valence bands are expected to be empty. Consequently, the resistivity along the Ta layers, $\rho_{\parallel}$, is most likely typical of a metal; and the resistivity perpendicular to the layers, $\rho_{\perp}$, may be large and even activated. Since the resistivity of the sample, ρ_{pellet}, is the sum of $-\rho_{\parallel}$ and $-\rho_{\perp}$, assuming a random orientation of the polycrystalline grains, we can expect $\rho_{\perp}$ to dominate the measurement. Thus, the large value of ρ(300 K) and the weakly increasing ρ as T decreases is likely to be a consequence of the large anisotropy in ρ.

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