THE EFFECTS OF SOME 3d AND 4d SOLUTES ON THE SUPERCONDUCTIVITY OF TECHNETIUM*

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INTRODUCTION

Considerable effort¹ has been directed towards obtaining an understanding of the observed variation of the superconducting transition temperature of a metal on the addition of impurities in terms of the details of their magnetic character. Technetium would appear to be an interesting and experimentally convenient superconducting transition metal solvent for comparison with theory. It has both a high transition temperature (7.8 K), thus making unnecessary the very low temperature techniques needed to study such solvents as ruthenium and iridium, and apparently high mutual solubility with the "magnetic" 3d elements.² The 3d elements are not expected to possess well-defined local moments in solution in technetium due to technetium's position in group VII of the Periodic Table,^{3,4} but we are unable to anticipate how closely they will approach the non-magnetic limit.

This paper reports the results of an experimental study of the changes in the superconducting transition temperature, the magnetic susceptibility, and the electrical resistivity of technetium with concentrations of up to about 5 at. % Cr, Fe, Co, or Ni (3d "magnetic" solutes) as well as Ru (a 4d "non-magnetic" solute).

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EXPERIMENTAL

The pure technetium used in this work was obtained from the Isotopes Division of Oak Ridge National Laboratory, the preparation and chemical analysis having been described in detail before.⁵ Spectrographic analysis of the technetium used in this study indicated < 200 ppm total metallic impurities. The residual resistivity ratio (ρ^{298K}/ρ^{8K}) was 80. The other transition metals used were obtained from Johnson and Matthey Ltd., and described as "spectrographically pure" with < 10 ppm metallic impurities.

The alloys were prepared by arc-melting the constituents together in the conventional manner. The alloys with measurable weight losses, even though these were never excessive, were analyzed by the Analytical Sciences Section, Process Technology Division, AERE, Harwell. All alloys were given a homogenization anneal of 6 hr at 900°C in a dynamic vacuum of better than 10^{-7} torr.

Superconducting T_c measurements were made by a standard inductive technique. The transition temperature was defined at the midpoint of the inductance change between the superconducting and normal states. Typical transition widths for 90% of the total change in inductance were 0.2 to 0.3 K.

Magnetic susceptibility measurements from 4.2 to 298 K and in applied fields up to 42 kOe were made on samples weighing ~ 100 mg using the Faraday method. Measurements were made below T_c on several samples including pure technetium by first quenching the superconductivity with the applied field and then making magnetic measurements by switching on and off a superimposed gradient field.⁶

NOTICE

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Electrical resistance measurements were made by the usual four-point method from T_c up to 298 K.

RESULTS

The results of the T_c measurements for all the alloys are listed in Table 1 together with values of the magnetic susceptibility at 298 K. The initial rate of decrease of T_c with solute addition, i.e., $dT_c/dc \mid c \rightarrow 0$, was 0.18 K/at. % for Ru, ~ 0.47 K/at. % for Cr, Co, and Ni, and 0.85 K/at. % for Fe. However, a clearer picture of the alloying behavior is obtained if, instead of considering solute concentration, T_c is plotted versus average group number (AGN) in the Periodic Table. This has been done in Fig. 1 which also includes literature data on Tc-V,⁷ Tc-Mo,⁸ and Tc-Nb⁹ hcp solid solution alloys. It is then evident that for low concentrations Co and Ni are very similar to Ru in lowering the T_c of technetium whereas iron stands apart, exhibiting a much more drastic influence on T_c . The Tc-Cr alloys with their decreasing T_c values are in notable contrast with the other groups V and VI elements (V, Mo, and Nb), which markedly raise the transition temperature of technetium.

Results of magnetic susceptibility measurements as a function of temperature are presented for pure technetium and representative alloys in Fig. 2. With the exceptions of the low temperature anomalous behavior in Tc-Ni and Tc-Co, to be considered below, the magnetic susceptibilities are essentially temperature independent. It is concluded that no localized magnetic moments exist on the solute atoms in this series of Tc-base alloys. The value of χ at 298 K ($= 1.13 \times 10^{-6}$ emu/g) is lower than the value measured previously¹⁰ of 1.22×10^{-6} emu/g. This result may be due to the higher purity of the present sample of Tc. The χ 's at 298 K of all the alloys are plotted vs AGN in Fig. 3 along with data from the literature on Tc-V,¹¹ Tc-Mo,¹² Tc-Nb,¹⁰

and Tc-Ru¹³ normalized to our χ value for pure Tc. For the group VIII solutes, Ru lowers χ of Tc, Ni, and Co slightly lower and increase χ , respectively, and Fe dramatically increases χ . The group V and VI solutes in Tc also exhibit varied behavior. Chromium rapidly raises χ , Nb also increases χ but Mo and V both lower χ of Tc.

The band of χ values observed in the Tc-2.3% Ni and Tc-1.2% Co alloys at low temperatures (< 100 K) represent various sequences of measurements, but no clear pattern has yet been established for the apparent irreproducibility. It is possible this behavior may be caused by a martensitic-type phase transformation as e.g., hcp $\rightarrow$ fcc. It is consistent that the fcc phase is stable at the Ni- and Co-rich concentrations in these systems but not in the other alloys studied. Low temperature x-ray diffraction studies are being initiated to study this possibility.

Electrical resistivity was measured as a function of temperature from T_c to 298 K on selected alloys from each system. No resistivity minima with temperature were observed, nor any other obvious anomalies. It is therefore unlikely that any of these Tc-base alloys is a Kondo system.

DISCUSSION

If the concept of a band picture to describe the conduction electrons in a metallic lattice has any meaning in attempts to classify the physical properties of alloys, it should most nearly apply to neighboring elements in the same period, such as Tc-Ru and Tc-Mo. Therefore we shall assume that the decrease of both T_c (Fig. 1) and χ (Fig. 3) of technetium with concentration of "non-magnetic" Ru approximates the band picture for group VIII solutes. It then follows that the decrease of χ^{Pauli} , which is

proportional to the density of electronic states at the Fermi level, $N(0)$, would indicate that the decrease of T_c is mainly due to a lower $N(0)$. This is also consistent with measurements of the electronic coefficient of low temperature specific heat capacity, γ , in this part of the Periodic Table (e.g., Mo-Ru alloys¹⁴). If the band model can be extended to the 3d solutes, then both Co and Ni in Tc would also appear to be roughly obeying this concept at low concentrations.

Iron, however, decreases T_c and increases χ of technetium much more rapidly than the other group VIII solutes do. Thus the effect of iron impurities is not fully accounted for by valence changes in the band model, and there must be additional "pair-destroying" or "pair-weakening" interactions present.¹⁵⁻¹⁸ The initial rate of decrease of T_c due to Fe $\left| \frac{\partial T_c}{\partial c} \right|_{c \rightarrow 0} = 0.85$ K/at. % is comparable with the decreases observed in the similar systems Ru-Fe¹⁵ and Ir-Fe¹⁶ with $\left| \frac{\partial T_c}{\partial c} \right|_{c \rightarrow 0} = 0.21$ and 2.06 K/at. %, respectively. In these systems Fe is also depressing T_c more rapidly than other group VIII solutes, and spin fluctuations have been invoked to account for the difference. Unfortunately, it is not sufficient simply to compare these initial rates in order to distinguish the cause of the additional interaction. None of the theories describing the effects of impurities make quantitative predictions without some assumption about the magnitudes of the interaction. In addition it only seems to be possible to distinguish between them if the observations are extended close to concentrations at which superconductivity disappears. Since the attractive interaction is much greater in Tc than in Ru or Ir the concentration of Fe impurities needed will be much larger for an effective test. If the critical concentration is derived from the initial rates of decrease then it

corresponds to iron additions of 9, 2, and 0.06 at. % in Tc, Ru, and Ir, respectively. The present results only extend to an iron addition of 3.73% and further measurements on alloys containing larger concentrations of iron are in progress. However when comparing the observed behavior over such a large concentration range with spin fluctuation^{16,17} or non-magnetic resonant state¹⁸ theories care will be necessary since the theories are only applicable in the dilute limit.

Of the 3d and 4d solutes from groups V and VI, only Cr decreases the T_c of technetium as shown in Fig. 1. Since the magnetic susceptibility of Tc is also rapidly increased by Cr additions (Fig. 3), as in the Tc-Fe alloys, the decreases in the transition temperature due to Cr additions are also consistent with the need for one of the pair-weakening mechanisms mentioned above.

The literature data for the hcp alloys in the Tc-Nb, Tc-Mo, and Tc-V systems show no obvious or consistent correlation between T_c and χ . Further experimental work is therefore in progress to study these systems in more detail, as well as the Tc-group VIII element systems, in order to clarify the solute effects presented in this paper and to decide which pair-weakening mechanism is responsible for the "anomalous" behavior of Fe and Cr in technetium.

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Table 1. Superconducting Transition Temperature
and $\chi^{298\text{ K}}$ for Technetium Alloys

Alloy	AGN	T_c (K)	χ (298 K) $\times 10^{-6}$ emu/g
Tc	7.000	7.85	1.128
Tc-0.19 Cr	6.998	7.72	1.169
Tc-2.3 Cr	6.978	6.97	1.234
Tc-4.4 Cr	6.956	6.60	1.363
Tc-0.84 Fe	7.0084	7.15	1.212
Tc-2.01 Fe	7.0201	6.15	1.250
Tc-3.73 Fe	7.0373	4.90	1.398
Tc-0.22 Co	7.0044	7.77	1.150
Tc-1.2 Co	7.024	7.35	1.132
Tc-3.0 Co	7.060	6.65	1.151
Tc-5.9 Co	7.118	5.98	1.180
Tc-0.12 Ni	7.0036	7.75	1.124
Tc-0.64 Ni	7.0192	7.50	1.116
Tc-1.64 Ni	7.0492	7.28	--
Tc-2.33 Ni	7.0699	7.25	1.119
Tc-1.9 Ru	7.0190	7.50	1.133
Tc-4.3 Ru	7.0430	7.07	1.080

Transition Temp. vs. Average Group Number
for Tc with 3d and 4d solutes.

Transition Temp. vs. Average Group Number for Tc with 3d and 4d solutes.

Tc-Nb
Tc-Mo

W. J. #

CR#

76630

72-9038

2

Fig. 2
Magnetic Susceptibility vs. Temperature

1.4-270

Fig. 3

Magnetic Susceptibility at 298 K vs. Atomic
Group Number for Tc with 3d and 4d solates

6.74 6.96 6.98 7.00 7.01 7.07 7.06 7.09

Fig. 3

Magnetic Susceptibility at 298 K vs. Average Group Number for Tc with 3d and 4d solutes.