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Superconductivity of α-Phase U–Mo Alloys at Zero and High Pressures

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Heat-capacity measurements and determinations of the superconducting transition temperature as a function of applied pressure up to 10 kbar have been made on a number of α-phase uranium-molybdenum alloys. Small additions of molybdenum rapidly change the superconducting properties of the α phase. The strong initial pressure dependence of T_c for pure α-U is destroyed, and bulk superconducting behavior at zero pressure develops.

INTRODUCTION

INVESTIGATIONS[1–9] of the anomalous superconducting properties of α-U have recently led to a number of comparisons of the superconducting properties of the α, β, and γ phases of uranium. It has been shown[1,7] that (i) the β and γ phases are bulk superconductors at zero pressure, whereas α-U is only a bulk superconductor under pressure[8]; (ii) the T_c of α-U is initially very sensitive to pressure,[3,9] whereas T_c for β- and γ-U is only slightly pressure-dependent[3]; (iii) α-U exhibits[4] a *positive* isotope effect (i.e., T_c increases with increasing isotopic mass), whereas the normal dependence, with a mass exponent of −0.5, is observed[5] for γ-U. Now it is important to realize that only the α phase of pure uranium is stable at low temperature and that it is necessary to alloy in order to retain the β and γ phases with quite a considerable addition (∼11 at.%) being required to stabilize the latter phase. Thus before considering possible causes for the different behavior of the three phases it is first necessary to determine the effects of alloying on the superconducting properties of the α phase. We have made measurements of the heat capacity at zero pressure and also the pressure dependence of the superconducting transition temperature for a number of isoelectronic α-phase U–Mo alloys to determine to what extent the anomalous behavior of pure α-U is exhibited by the alloys.

EXPERIMENTAL DETAILS

Alloys containing 0.3, 0.6, 3, 4, 5, and 7 at.% Mo were arc cast[10] in an argon atmosphere, given a homogenizing anneal at 900–950°C, and then fast quenched into mercury (Harwell) or into iced water (Argonne). The metallurgy of the U–Mo system is complex and involves six, or possibly seven different phases produced by quenching from the γ phase, depending upon the composition. We may summarize the final products of a quench from 950°C in the composition range relevant to the present investigation as follows[11]:

0 to ∼0.7 at.%. The transition sequence is $\gamma \rightarrow \beta \rightarrow \alpha$, and the final product is known as α′, where the prime indicates a contraction of the b lattice parameter relative to that of pure α-U.

0.7 to ∼1.9 at.%. In this composition range the

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TABLE I. Data obtained for the uranium-molybdenum alloys at zero pressure from heat-capacity and magnetic measurements.

Alloy (at.% Mo)	γ (mJ mole^{-1} deg^{-2})	b (mJ mole^{-1} deg^{-4})	Θ_D (°K)	T_c[a] (°K) Magnetic	Heat capacity
7	12.60±0.05	0.320±0.018	182±4	0.827±0.003	0.79±0.06
5	12.23±0.0	0.382±0.010	172±2	0.828±0.01	0.79±0.06
3[b]	11.80±0.04	0.373±0.012	173±2	1.02_5±0.02	c
3[d]	11.74±0.04	0.350±0.013	177±4	1.00_7±0.01	c
3[d,e]	11.99±0.09	0.316±0.035	183±7		
0.6	11.56±0.02	0.498±0.006	157±2	1.20[f]±0.1	1.06±0.4
0.3	11.33±0.03	0.435±0.008	165±2	1.20[i]±0.1	1.18±0.5
0.3[e]	11.40±0.03	0.453±0.011	163±4		
0[g]	10.03±0.01	0.219±0.002	207±1	1.21±0.05	h
0[i]	12.2	0.323	182	2.15±0.06	2.0±0.2

[a] Limits quoted indicate the width of the transition.
[b] Sample prepared at the Argonne National Laboratory.
[c] Transition starts at ~1.05°K, but no maximum in the heat capacity was observed down to 0.61°K.
[d] Sample prepared at the Atomic Energy Research Establishment, Harwell.
[e] Measured in a magnetic field of 8 kG.
[f] As determined on the small sample.
[g] Data from Ref. 6.
[h] No heat-capacity anomaly.
[i] Measurements made at 10 kbar, Ref. 8.

$\beta \rightarrow \alpha$ transition is suppressed to below room temperature, though at the low Mo end of the range the β phase is very unstable and transforms quite rapidly to α at room temperature.

1.9 to 4.3 at.%. Here there is a direct $\gamma \rightarrow \alpha$ martensitic transformation with the final product denoted as α_a', where the subscript refers to the acicular (needle-like) grain structure.

4.3 to ~11 at.%. The kinetics here are more complex and involve transformations in the γ phase with a final transition to the α_b'' phase, where the double prime refers to a slight distortion from the orthorhombic to monoclinic symmetry and the subscript indicates a banded grain structure.

For convenience the alloys used in the present investigation may be considered to be in the α phase since the lattice of the metastable phases obtained is very close to the orthorhombic lattice of pure α-U.

Heat-capacity measurements were made between 0.55 and 2.2°K in a conventional He^3 cryostat, which has a double-acting mechanical switch. When operated in one mode, the switch thermally connected both sample and He^3 bath to the He^4 bath. In the second mode, the switch connected the sample to the He^3 bath. When the switch was open the sample was thermally isolated. Sample temperatures were measured with a 470-Ω Speer resistor. Temperatures below 1.4°K were obtained from the equation $T=[A \ln R/(\ln R-B)^2]$, where the constants A and B were determined by calibrating the resistor against He^4 vapor pressures between 1.4 and 2.1°K. The resistor was calibrated after each specific-heat run, and separate calibrations were made for the specific-heat measurements in a magnetic field.

The high-pressure studies above 1.2°K were made in the He^4 cryostat used in previous investigations.[3,9] Below 1.2°K the measurements were made in a miniature "clamp" arrangement suspended from a He^3 refrigerator. In both cases the transition to the superconducting state was observed magnetically with a compensated coil system and an ac signal. Pressures were measured relative to the superconducting transitions of tin and zinc above and below 1.2°K, respectively.[12]

With the exception of the 4 at.% alloy the sample used for the pressure measurements was cut from the ingot used in the heat-capacity determination.

RESULTS

Magnetic Superconducting Transition

(i) *Zero Pressure*

Values for the superconducting transition temperature determined magnetically at zero pressure are listed in Table I. The transitions for the 7- and 5-at.% samples were sharp (10–20 mdeg wide) and a value for T_c can be readily defined. However, the transitions observed for the lower molybdenum concentrations were very much broader and it became increasingly more difficult to assign a value to T_c. Limits for T_c defined by the intersection of the linear central portion of the transition curve with the extrapolation of the background signal on either side of the transition are therefore also indicated in Table I. Zero-pressure T_c values were also determined from the heat-capacity measurements and they are given in Table I. In this case the limits given on T_c were determined from the width of the heat-capacity anomaly between its onset and maximum. In general the transitions observed in the heat-capacity measurements were considerably broader than those determined magnetically.

It was observed for the 0.3- and 0.6-at.% samples that the transition temperature was sensitive to the sample size. Transitions determined for the large

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