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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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[9] T. F. Smith and W. E. Gardner, Phys. Rev. **140**, A1620 (1965). A positive isotope effect was predicted at this time from an empirical relationship due to Olsen and co-workers [J. L. Olsen, E. Bucher, M. Levy, J. Müller, E. Corenzwit, and T. H. Geballe, Rev. Mod. Phys. **36**, 168 (1964)] relating the pressure dependence of T_c and the mass coefficient α. Although this predicted value for α is in good agreement with the experimental value (Ref. 4) we must regard this as coincidental as it has been subsequently shown that the empirical relationship upon which the prediction was based is not as general as was first believed [E. Bucher, J. Müller, J. L. Olsen, and C. Palmy, Cryogenics **5**, 283 (1965)].
[10] We are indebted to Dr. B. W. Howlett of the Atomic Energy Research Establishment, Harwell, England for preparing the 0.3-, 0.6-, 4-at.% alloys and a 3-at.% alloy and to Dr. N. Peterson of the Argonne National Laboratory for the preparation of a second 3-at.% alloy and the 5- and 7-at.% alloys.
[11] B. W. Howlett, J. Nucl. Mater. (to be published); K. Tangri and G. I. Williams, *ibid.* **4**, 226 (1961).

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

[12] T. F. Smith, C. W. Chu, and B. M. Maple (to be published).

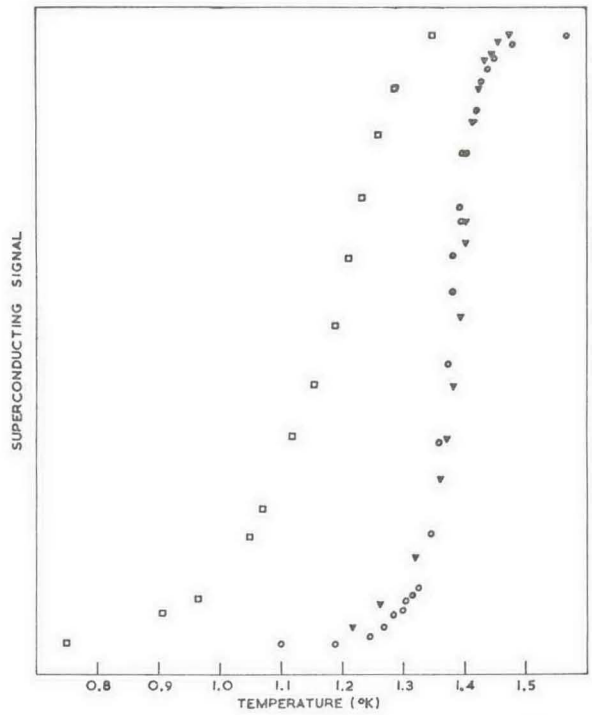

FIG. 1. Superconducting transitions for a U 0.6-at.% Mo alloy: large sample, ○ ($P=0$); small sample, □ ($P=0$), ▽ ($P=0.75$ kbar).

heat-capacity sample (a roughly cylindrical ingot 0.8 cm in diameter, 2.5 cm long) were sharper and at a higher temperature than those for the small sample (a half disk, 0.3 cm thick, 0.5 cm in diameter) cut from it for the pressure measurements. This is illustrated in Fig. 1 which shows zero-pressure transitions for the 0.6-at.% sample.

The present T_c values for the α-phase U–Mo alloys are in marked disagreement with the earlier values of Chandrasekhar and Hulm[13] who found that T_c first increased rapidly with the addition of Mo and then passed through a maximum at the composition corresponding to the $\alpha \rightarrow \gamma$ transition. We find that the T_c values from 0.3-at.% Mo fall with the addition of further Mo up to 4 at.% and then are almost independent of composition up to 7 at.%. This behavior is illustrated in Fig. 2.

(ii) *High Pressure*

Measurements of T_c were made up to a maximum pressure of 10 kbar, and the results are presented in Fig. 3. In addition, data for the variation of T_c over the same pressure range are shown for pure α-U. It is clearly seen that the addition of Mo rapidly destroys the initial sensitivity of T_c to pressure and with more than 3-at.% Mo the transition temperature is almost independent of pressure. For further comparison with the zero-pressure transitions, the 10-kbar values of T_c are also shown in Fig. 2.

[13] B. S. Chandresekhar and J. K. Hulm, J. Phys. Chem. Solids **7**, 259 (1958).

Heat-Capacity Measurements

(i) *Normal State*

Normal-state heat-capacity measurements[14] were made above T_c in zero magnetic field. In addition measurements for the 0.3- and 3-at.% alloys were taken in 8 kG. The data taken between 1.4 and 2.1°K have been least-squares fitted to the usual $\gamma T+bT^3$ relationship, and values for γ, b, and the related Θ_D are given in Table I. The uncertainties listed correspond to the standard deviations in the constants and do not reflect any possible systematic errors.

The heat capacity of the addenda was determined separately and can be represented as $0.1273T+0.0167T^3$ mJ mole^{-1} deg^{-1}. The addenda contribution to the linear term in the heat capacity was constant from run to run. Thus, even including systematic errors arising from the addenda correction, the uncertainty in the γ values is not likely to be much greater than ± 0.1 mJ mole^{-1} deg^{-2}. However, the T^3 contribution of the addenda to the heat capacity varied somewhat from run to run because of the slightly varying amounts of grease used to provide thermal contact between the sample and a pair of copper plates which provided the thermal link to the mechanical switch. Thus, the actual uncertainties in the Θ_D are probably considerably larger than the statistical values listed in Table I. Nevertheless, the internal consistency of most of these data plus data obtained on other alloy systems with this apparatus lead us to believe that the surprisingly low Θ_D values for the 0.3- and 0.6-at.% U-Mo alloys cannot be explained by inappropriate addenda corrections.

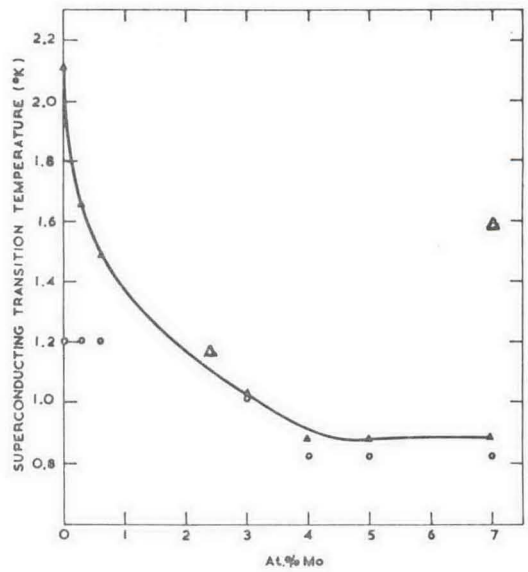

FIG. 2. Magnetically determined transition temperature at $P=0$ and 10 kbar as a function of Mo content: ○ ($P=0$), ▲ ($P=10$) kbar. △ data of Chandrasekhar and Hulm (Ref. 13).

[14] A preliminary report on these measurements was given by J. E. Gordon and T. Soller at the 22nd Annual Calorimetry Conference, Thousand Oaks, Calif., 1967 (unpublished).

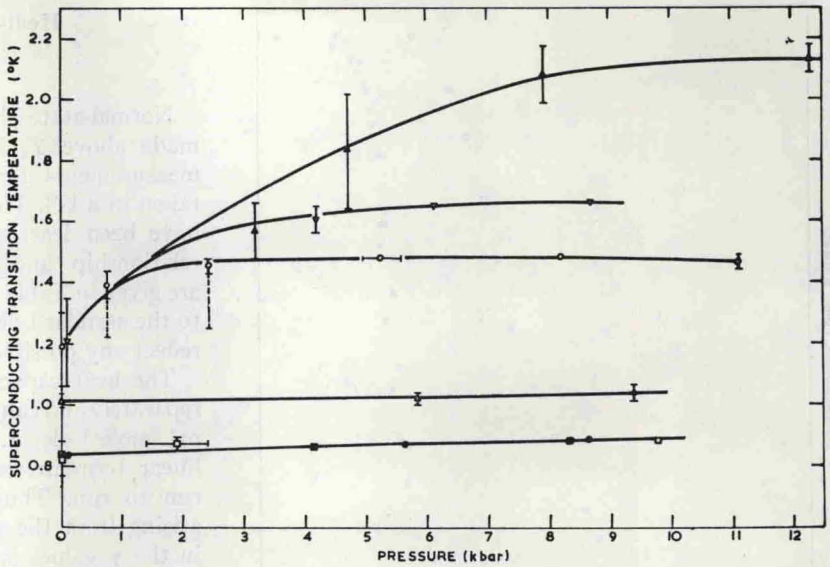

FIG. 3. Magnetically determined transition temperature as a function of pressure: Mo content in at.%, ▲0, ▽0.3, ○0.6, △3, □4, ●5, ■7.

A plot of the dependence of γ on Mo concentration is presented in Fig. 4. Initially, γ increases rapidly with the addition of Mo, but there is a rapid change in slope at $\sim$0.5 at.%, followed by an approximately linear variation described by $d\gamma/dc=0.17$ mJ mole^{-1} deg^{-2} at.%$^{-1}$. The measurements made in a magnetic field for the 0.3- and 3-at.% samples indicate that the normal-state heat capacity is slightly field-dependent. This field dependence, while small, appears to be real, but its significance is not clear. Plots of the zero-field and 8-kG data for the 0.3-at.% samples are given in Fig. 5.

(*ii*) *Superconducting State*

Well-defined heat-capacity jumps typical of the type observed at the transition to the superconducting state were observed for the 7- and 5-at.% samples (Fig. 6). Jumps observed for the lower-concentration alloys were much broader and more ill-defined, and in the case of both 3-at.% samples the temperature limitations of the cryostat prevented measurements at sufficiently low temperatures for observation of a maximum. In order to determine whether these broader transitions (particularly that of the 3-at.% alloy) were associated with a transition to the superconducting state, measurements were made on the 0.3- and 3-at.% samples in a field of 8 kG. For both alloys this field was sufficient to destroy the transition down to the lowest temperature available (see Fig. 5).

Estimates of the fraction of the sample which has become superconducting at various temperatures below

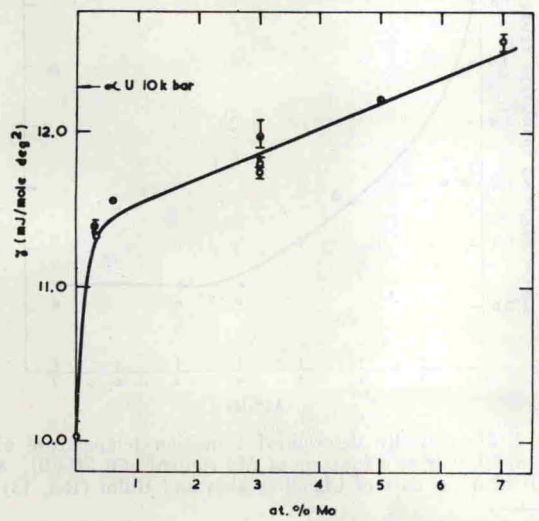

FIG. 4. Coefficient of electronic specific heat γ as a function of Mo content.

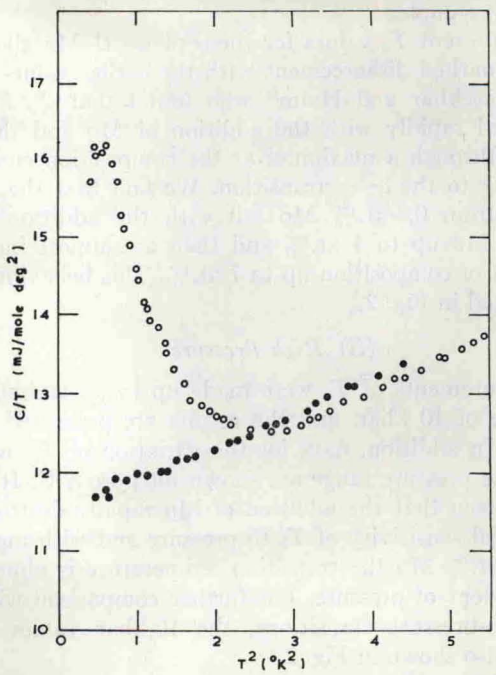

FIG. 5. Heat-capacity data for the 0.3-at.% Mo alloy taken in zero field and 8 kG: ○ ($H=0$), ● ($H=8$) kG.

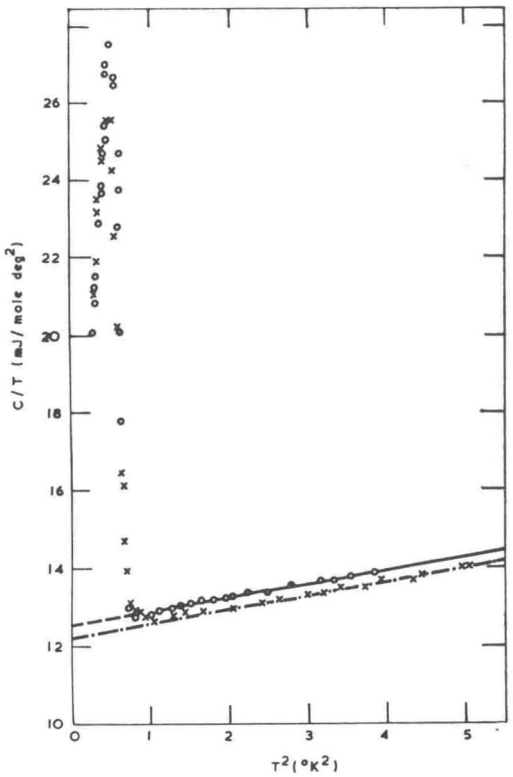

FIG. 6. Heat-capacity data for the 5- and 7-at.% Mo alloys in zero field showing the superconducting transition: ○ 5 at.%, × 7 at.%.

the onset of the heat-capacity jump were made using the method outlined by Bucher *et al.*[15] The results of this analysis are presented in Fig. 7, where it is seen that only the 7- and 5-at.% samples become fully superconducting in the available temperature range. Although the 3-, 0.6-, and 0.3-at.% samples are each more than 50% superconducting by 0.7°K, we cannot say whether they will become fully superconducting by 0°K. In view of this the assignment of a transition temperature at zero pressure to these alloys is of very limited meaning.

DISCUSSION

It is evident that small additions of Mo rapidly change the superconducting properties of α-U. Thus, the addition of as little as 0.3-at.% Mo is sufficient to produce an alloy of which at least 50% is superconducting at 0.6°K. The strong initial pressure dependence of T_c is retained up to this concentration, but is reduced by further addition of Mo until at 5-at.% Mo T_c has become essentially independent of pressure. Moreover, this further addition of Mo also renders a greater fraction of the sample superconducting at 0.6°K, and it can be seen in Fig. 7 that almost the entire volume of the 5-at.% sample has become superconducting by this temperature. Associated with this behavior is the marked decrease, as a function of Mo concentration, of the maximum value of T_c obtained under pressure. T_c(max) falls from 2.2°K for pure α-U to the pressure- and concentration-independent value of 0.8°K for the alloys above 4-at.% Mo.

A further strong dependence on concentration is found for the density of states, as characterized by the coefficient γ of the electronic specific heat. The addition of up to 0.6-at.% Mo causes a rapid increase of γ, which is followed by a much slower increase with the further addition of Mo (Fig. 4).

From a knowledge of the density of states, T_c, and the isotopic mass dependence of T_c for α-U under pressure, it is possible to calculate a value for the attractive interaction V_{ph} responsible for the formation of the superconductive state.[16] Taking $T_c=2.1$°K, $\alpha=-2$, where $T_c \propto M^{-\alpha}$ and $\gamma=12.2$ mJ mole^{-1} deg^{-2} we calculate $V_{ph}\sim 0.73$ eV. A similar calculation with data[7] for γ-phase U alloys, which have a normal isotope effect,[5] leads to a much smaller value for the attractive

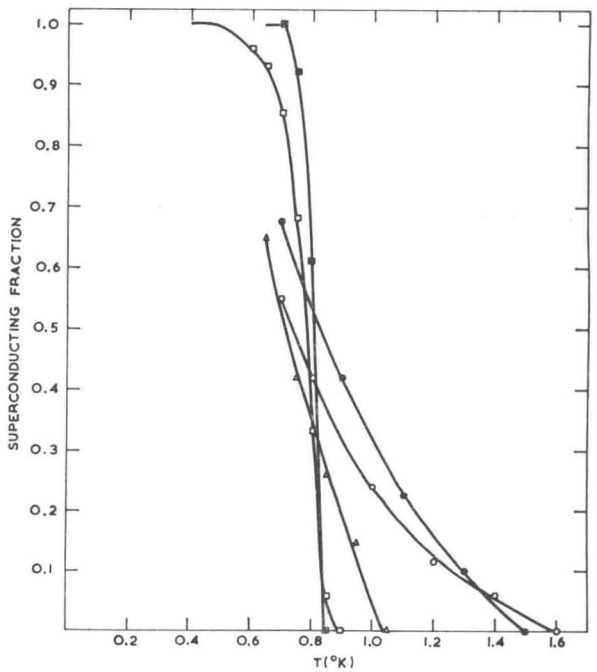

FIG. 7. The superconducting fraction as a function of temperature as determined from the heat-capacity data. Mo content in at.%, ○ 0.3, ● 0.6, △ 3, □ 5, ■ 7.

[15] E. Bucher, F. Heiniger, and J. Müller, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio*, edited by J. A. Daunt *et al.* (Plenum Press, Inc., New York, 1965), p. 482.

[16] See, for example, P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962); W. L. McMillan, *ibid.* **167**, 331 (1968). The relevant relationships are

$$T_c=0.85\Theta_D \exp(-1/g),$$
$$g=(V_{ph}-U_c)N_0/(1+N_0V_{ph}),$$
$$N_\gamma=N_0(1+N_0V_{ph}),$$
$$\alpha=0.5[1-(N_0U_c/g)^2],$$

where, V_{ph}=phonon interaction, U_c=screened Coulomb interaction, N_0="bare" density of states, N_γ=density of states calculated from the electronic heat capacity.

interaction, namely, $V_{ph} \sim 0.14$ eV. Thus, if one ignores the possibility of effects from the structure change, it would appear that the addition of ~15-at.% Mo has lowered appreciably the strength of the attractive interaction. It follows, therefore, that an investigation of the isotopic mass dependence of T_c within the α phase itself would be of considerable interest, since if, for example, a 5-at.% alloy were to have a normal isotope effect this would require a precipitous drop in the attractive interaction.

It has been previously proposed[2,3] that an association exists between the anomalous superconductivity of α-U and the transformation which occurs at 43°K. Furthermore, it was considered that the inhibition of the $\alpha \rightarrow \alpha_0$ transformation, where α and α_0 denote the phase at temperatures above and below the transformation, respectively, was a necessary condition for the occurrence of the bulk superconductivity which was achieved[8] under pressure. The filamentary superconductivity of α_0-U at zero pressure was then explained[3] by the presence of strain-produced filaments of the α phase distributed in the α_0 matrix.

Fisher and Dever[17] have recently adopted this model to account for the anomalous behavior that they observe in the elastic constants of α-U below 43°K, but they further propose that the transformation involves a sluggish structural change over the temperature range 35 to 43°K. However, the absence of extra lines, line splitting, or even line broadening in x-ray patterns taken[18] on samples slowly cooled through this temperature range provides no support for the coexistence of appreciable proportions of two different phases, and, in fact, only a smooth and continuous change in the lattice parameters is observed.

Recent thermal expansion measurements[19] on α-U have demonstrated the possibility of suppressing the $\alpha \rightarrow \alpha_0$ transition in polycrystalline material by rapid cooling (~5°K/sec from 50 to 4°K). A comparison of resistance measurements for quenched and slow cooled material has not revealed any evidence for a change in the superconducting behavior; in both cases the resistance began to fall at just above 1°K. Thus we may certainly conclude from the absence of a transition at 2°K that T_c for the α phase is initially strongly pressure-dependent.

Now whereas heat-capacity measurements have established the absence of bulk superconductivity in the α_0 phase above 0.1°K at zero pressure, the question still remains open for the quenched-in α phase. Unfortunately, such an investigation for the α phase at zero pressure is made difficult by the rapid rate of cooling required to retain this phase.

The importance of strain in respect to the superconducting behavior of the 0.3- and 0.6-at.% alloys may be inferred from the dependence of their values of T_c on the size of the sample, where we would associate the higher value of T_c for the larger sample with a greater strain experienced on cooling (see Fig. 1). Support for this contention is found in a comparison of the transition curve taken at zero pressure for the larger 0.6-at.% sample with that taken at 0.75 kbar for the smaller sample. These transitions are shown in Fig. 1 and can be seen to be very similar, implying that cooling the larger sample introduced an average strain which is equivalent to a pressure of about 0.75 kbar. In this connection it should also be noted that the onset temperature for the heat-capacity jump in the low-concentration alloys corresponds closely to the maximum value of T_c obtained under pressure, thus indicating that some portion of the sample is subjected to an appreciably greater stress than the over-all average value. This sensitivity of the superconductivity of the 0.3- and 0.6-at.% alloys to strain makes it difficult, if not impossible, to determine the zero-pressure transition temperature, and indeed even whether the strain-free alloy would actually be superconducting. In the case of the pure α_0-U the absence of any detectable heat-capacity jump indicates that the fraction of the sample responsible for the magnetically observed transition is small. However, if the volume of strained material is related to the degree of alloying we might expect a considerable proportion of the alloy sample would exhibit strain-induced bulk superconductivity.

The actual physical nature of the "43°K transformation" in α-U has been the subject of some speculation.[2,3,20,21] Fisher and McSkimin[20] first suggested that it was an electronic transition in the absence of any evidence of a crystallographic change. More recently[2,3] it was suggested that the transformation is magnetic in origin, and specifically,[3] by analogy with the physical properties of chromium, due to the formation of a spin density wave (SDW).

The first direct evidence for the possibility of magnetic behavior associated with the transformation is found in the magnetic susceptibility data of Ross and Lam[21] for a single crystal, which exhibited anomalies in the principal crystal directions of some 2% of the total susceptibility below 50°K. However, as these authors point out the behavior may equally well be explained in terms of a nonmagnetic Fermi surface effect. Thus, at the present time this remains an open question, and an effort is being directed towards obtaining a definitive answer.

ACKNOWLEDGMENTS

We are indebted to B. W. Howlett for discussions on the metallurgical properties of U-Mo alloys and for alloy preparation. We would also like to thank T. Soller, R. Tobón, and C. W. Dempsey for help in the construction of some of the heat-capacity equipment.

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