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Superconductivity of α-Uranium and Uranium Compounds at High Pressure

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The pressure dependence of the superconducting transition temperature T_c of α-uranium has been measured to a maximum pressure of 22 kbar and constitutes an important extension of the pressure range of previous measurements. It has been observed that T_c increases rapidly as a function of pressure up to ~9 kbar, passes through a broad maximum, and then decreases. A possible explanation of this behavior is offered on the basis of a pressure-induced transformation in the electronic properties of uranium. Data are also reported for observations of the T_c under pressure of the compounds U_6Fe and U_6Mn and the solid solution alloy $U_{0.85}Mo_{0.15}$.

INTRODUCTION

MEASUREMENTS of the pressure dependence of the superconducting transition temperature of α-uranium, reported earlier,[1] identified uranium with the small group (Tl,[2,3] La,[4] Ti,[5] Zr,[6] V,[7] and U [1]) of superconducting elements for which T_c increases with a decrease of volume. Since the report of these measurements, the superconductivity of α-uranium has been the subject of extensive investigation and speculation.[8–13] Possibly the most important fact to emerge from this work is that all previously reported[1,14] superconducting transition temperatures at zero pressure, ranging from 0.5 to above 1°K, which were magnetically or resistively determined were not associated with bulk superconductivity, but instead resulted from a connected network of superconducting filaments. The first evidence for this conclusion can be found in the specific-heat data of Dempesy, Gordon, and Romer[15] for U^{238} down to 0.15°K, which failed to show the characteristic anomaly associated with the transition to the superconducting state. Unfortunately, they made no attempt to detect a magnetic transition in this sample and so very reasonably concluded that the lack of superconductivity above 0.15°K was associated specifically with their particular sample rather than a property of α-uranium. However, recent,[10,11] more extensive specific-heat measurements on samples exhibiting magnetic transitions have also failed to show any evidence of bulk superconductivity, not only at the magnetic transition, but from the measurements of Phillips and Ho[11] even down to 0.1°K. Thus on the basis of these latter measurements, even the most recently reported[9] transition between 0.21 and 0.25°K

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[3] J. Hatton, Phys. Rev. **100**, 1784 (1955).
[4] W. E. Gardner and T. F. Smith, Phys. Rev. **138**, A484 (1965); T. F. Smith and W. E. Gardner, *ibid.* **146**, 291 (1966).
[5] N. B. Brandt and N. I. Ginzburg, Usp. Fiz. Nauk **85**, 485 (1965) [English transl.: Soviet Phys.—Usp. **8**, 202 (1965)].
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[11] N. E. Phillips and J. C. Ho (to be published).
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[14] G. Ascherman and E. Justi, Physik. Z. **43**, 207 (1942); N. Alekseywsky and L. Migunov, J. Phys. U.S.S.R. **11**, 95 (1947); B. B. Goodman and D. Shoenberg, Nature **165**, 442 (1950); J. E. Kilpatrick, E. F. Hammel, and D. Mapother, Phys. Rev. **97**, 1634 (1955); R. A. Hein, W. E. Henry, and N. M. Wolcott, *ibid.* **107**, 1517 (1957).
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for a good single crystal of α-uranium is not associated with bulk superconductivity.

Two suggestions have been made[8,9] concerning the nature of the filaments responsible for the observed magnetic transitions of α-U. Firstly, from work[8] on stabilized β-U (formed by the addition of 2 at.% of either Pt, Rh, or Cr) and from a consideration of earlier work[16,17] on stabilized γ U-Mo alloys, Matthias *et al.* postulated that the filaments consisted of impurity-stabilized networks of β and γ phases. However, this suggestion has been criticized by Howlett[13] on the basis that there is no metallurgical evidence for the presence of such stabilized phases in high purity α-U. In our opinion, the pressure dependence of the transition temperatures of the uranium compounds and the stabilized β and γ phases, which we have measured and report here, is inconsistent with the possibility of filaments of these alloys being responsible for the observed pressure dependence of T_c for α-U. Secondly,[9] the observed transitions were associated with filaments from two distinct origins, depending on the temperature range of the observed transition. Thus the first postulate of stabilized β- or γ-phase filaments was retained for transitions above 0.8°K, whilst transitions below 0.8°K were considered to arise from strain filaments produced by the highly anisotropic thermal expansion[18] of uranium at low temperatures. The presence of a network type of structure in uranium has been observed[13,19] in recent transmission electron microscopy investigations. However, it has not been possible to identify the nature of the material comprising the network and hence distinguish impurity-stabilized phases from regions of strain or dislocation.

Whilst the nature of the observed magnetic transitions at zero pressure suggests, and the zero-pressure specific-heat data confirms, filamentary rather than bulk superconductivity, it is difficult to believe that filamentary superconductivity, due to strain, is maintained up to 10 kbar since, by this pressure, the strain within the grains must be larger than that initially present at the grain boundaries. Recent specific-heat[12] measurements made on uranium at 10 kbar have, in fact, demonstrated that the superconducting transitions measured at high pressure are representative of bulk superconducting properties.

In view of the importance of pressure measurements in helping to understand the properties of uranium there was considerable incentive to extend the pressure range of the T_c measurements beyond the previous[1] limit of 10 kbar. Thus T_c has now been studied, as a function of pressure, to a maximum pressure of 22 kbar revealing a dramatic change in its pressure dependence.

EXPERIMENTAL METHOD

The two samples of α-U, U9 and U10, used in the present investigation, were cut from separate lots of high purity Los Alamos uranium, kindly made available by Dr. C. E. Olsen. Both of these samples were taken from material used in the extensive heat-capacity measurements of Phillips and Ho,[11] the sample U10 coming from the same lot as the sample for which specific-heat measurements[12] at 10 kbar were made. The alloy samples were prepared by melting the required amounts of the constituents in an argon arc furnace.

The transition temperatures of the alloy samples were determined in the same high pressure apparatus as was used for the original measurements[1] on α-uranium. A redesigned piston and cylinder assembly was used to extend the pressure range of the previous measurements on α-uranium. The cylinder was fabricated from a hardened Be–Cu (Berylco 25) alloy and the $\frac{1}{4}$-in.-diam piston was unsupported tungsten carbide, tipped with high-density alumina. The alumina tip was supported by the cylinder walls and served to transmit the force from the carbide pistons to the sample assembly. Such an arrangement was necessary in order to reduce pickup in the detection coils from the superconductivity and weak ferromagnetism of the tungsten carbide. A small piece of tin was included in the sample assembly to serve as a direct low-temperature manometer. The pressure was calculated from the superconducting transition temperature of the tin using the absolute pressure-dependence data of Jennings and Swenson.[2] As these data only extend to 10 kbar, we were obliged to extrapolate their empirical relationship, which can be written (P expressed in kbar) as,

$$\Delta T_c = -4.89\times10^{-2}P + 3.8\times10^{-4}P^2$$

in order to determine the higher pressures involved in the present study of α-U. Powdered Teflon was used as the quasihydrostatic pressure-transmitting medium.

RESULTS AND DISCUSSION

(i) Compounds and Alloys

From the limited number of superconducting compounds of uranium we chose U_6Fe and U_6Mn[16] in order to study and compare the effect of pressure upon the superconducting transition temperature of uranium compounds. No significant change in T_c could be observed up to 10 kbar for either compound, though it is possible that a small effect was masked by the width of the transitions. The results are presented graphically in Fig. 1, where T_c is plotted as a function of applied pressure. The solid vertical line indicates the width of a transition, which was determined from an extrapolation of the central linear portion of the transition curve.

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

[17] B. B. Goodman, J. Hillairet, J. J. Veyssié, and L. Weil, in *Proceedings of the Seventh International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, Canada, 1961), p. 350.

[18] C. S. Barrett, M. H. Mueller, and R. L. Hitterman, Phys. Rev. **129**, 625 (1963).

[19] G. O. S. Arrhenius (private communication).

Both compounds exhibited transition curves with "tails," which in the case of U_6Fe comprised up to approximately 50% of the transition. The extent of these "tails" is indicated by the broken-line extensions below the vertical solid lines. In addition, U_6Mn showed high-temperature structure, which had the appearence of a smaller transition preceding the main transition, as well as a low-temperature tail in its transition. The low-temperature "tail," on the other hand, looked more like rounding-off of the transition as in the case of the U_6Fe. However, the width of the transition curve prevented any significant resolution of the two contributions. The minor high-temperature transition was probably due to sample inhomogeneity, or possibly the inclusion of a small quantity of a second superconducting uranium-manganese phase.

The main reason for examining stablized β and γ phase alloys of uranium was in order to make a simple test of the postulate[8] that filamentary networks of β- and γ-U could account for the superconducting behavior of α-U, both at zero and high pressure. In order to investigate the behavior under pressure of γ phase alloys we chose to examine $U_{0.85}Mo_{0.15}$, which has a zero-pressure transition of about 2.1°K,[16] which is well within the range of temperatures accessible to the cryostat in which the pressure measurements were made. As the transition curve for this alloy was sharp and well defined it was possible to resolve a small positive pressure dependence of its transition temperature ($\partial T_c/\partial P = 0.9\times10^{-5}$°K bar^{-1}). These data are also presented in Fig. 1. Thus the presence of a γ-U phase could account for the high values of T_c (~2°K) observed in α-U under pressure, but could not account for the observed pressure dependence of T_c. However, it is unlikely that such a phase would be produced by pressure since such phases are associated with a larger atomic volume.

The superconducting transition temperatures (~0.8°K) of reported[8] stabilized β-U alloys fall below the lowest temperature that can be achieved in the high-pressure cryostat. However, if the presence of such a phase were responsible for the apparent superconductivity of α-U at zero pressure, then we would anticipate that the application of pressure to a stabilized β alloy should raise its T_c to well within the accessible temperature range. Two stabilized β phase samples[20] containing 2 at.% Rh and 2 at.% Pt were investigated. At zero pressure, the U-Rh and U-Pt samples showed sharp magnetic transitions at 0.96 and 0.87°K, respectively, in a standard cryostat.[20] On being transferred to the high-pressure cryostat measurements were made on both samples at ~9.5 kbar, but no superconducting transition for either sample was observed above 1.15°K. These observations place an upper limit on $\partial T_c/\partial P$ for β-U of $2\text{–}3\times10^{-5}$°K bar^{-1}. Also, it is now evident that even a combination of β- and γ-U alloy phases in a filamentary network cannot explain the observed pressure dependence of T_c for α-U.

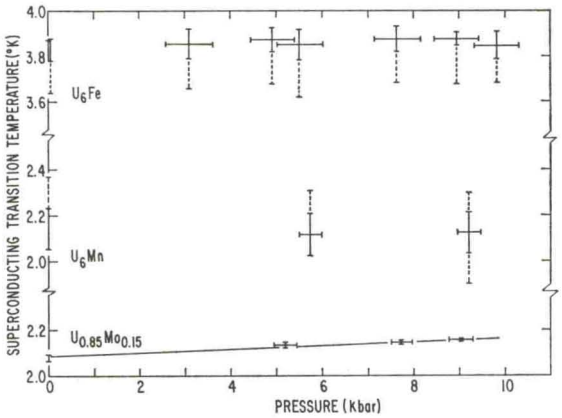

FIG. 1. Superconducting transition temperature as a function of pressure for U_6Fe, U_6Mn, and $U_{0.85}Mo_{0.15}$. Note the broken vertical scale.

The absence of any marked pressure dependence of T_c for the β and γ phase alloys prompted us to investigate an α-phase alloy. We chose the alloy $U_{0.97}Mo_{0.03}$ as the measurements of Chandrasekhar and Hulm[16] indicated a transition temperature of ~1.2°K for this alloy, placing it just within our available temperature range for high pressure measurements. The sample[21] was homogenized for 5 days at 950°C, following casting in the arc furnace, water quenched, and then given a further 1-h anneal at 900°C, terminated by a mercury quench. Photomicrographs of the sample following this treatment showed structure which is typical of the α_a' phase resulting from the martensitic transformation $\gamma \rightarrow \alpha$. For convenience we will merely refer to this as the α-phase.

Measurements at zero pressure and a number of pressures up to ~8 kbar failed to detect superconductivity above 1.15°K for this sample. A subsequent, zero-pressure measurement in a He^3 cryostat on a portion of the sample material which had not been subjected to pressure (thus ruling out the possibility of a pressure induced change of phase affecting T_c) detected a sharp transition centered at 1.0°K. At first sight the close similarity of this T_c with those observed for the β phase samples would suggest that the sample was in this phase rather than the required α phase. However, the metallographic examination ruled out this possibility.

Thus not only do the β and γ phases of uranium show different pressure dependence of T_c from that of pure α-U, but the addition of solute atoms to the α phase also changes the pressure dependence. This would suggest that the strong pressure dependence is peculiar to pure α-U.

Finally, it is also of interest to contrast the pressure dependence of these uranium rich alloys with the be-

[20] We are indebted to T. H. Geballe, Bell Telephone Laboratories, Murray Hill, New Jersey for these samples and for measurements made below 1°K.

[21] We are indebted to B. W. Howlett, Atomic Energy Research Establishment, Harwell for the preparation and examination of this alloy.

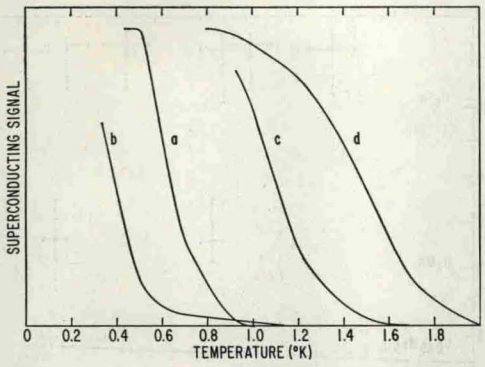

FIG. 2. Magnetically determined transition curves for α-uranium at zero pressure, following various heat treatments. (a) "as received" condition, measured at 95 cps, (b) annealed 8 h 500°C, slowly cooled to room temperature, measured at 95 cps, (c) and (d) $\frac{1}{2}$ h at 900°C, quenched into iced brine; curve (c) measured at 22 cps, curve (d) at 16 kcps.

havior observed for lanthanum rich alloys.[22] Whereas it has been found that lanthanum-rich solid solutions[23] and superconducting compounds[22] in which lanthanum is the major constituent preserve the strong positive pressure dependence of the superconducting transition temperature observed[4] for lanthanum, this is not the case for the uranium alloys examined.

(ii) α-Uranium

We consider that a strain-filament model provides the most reasonable explanation for all of the various magnetic transitions observed in α-U at zero pressure. A representative selection of zero-pressure transition curves, determined magnetically, for the α-uranium samples examined in the earlier investigation[1] are reproduced in Fig. 2, where (a) is for a sample of the "as received" material and has an unknown thermal history, (b) is for a sample annealed, *in vacuo*, for 8 h at 500°C, in the α phase and slowly cooled to room temperature, and (c) and (d) are for a sample held at 900°C, in vacuo, in the γ phase for $\frac{1}{2}$ h and then quenched into iced brine. Transitions (a), (b), and (c) were measured at low frequency (<100 cps), whereas (d) was measured at 16 Kc/sec by the Schawlow-Devlin technique.[24] Such frequency dependence of T_c is a positive indication of filamentary superconductivity, the high-frequency Schawlow-Devlin technique being particularly sensitive to the presence of filaments. Comparing the transition (c) for the sample quenched from the γ phase with that (b) for the sample annealed in the α phase clearly demonstrates the sensitivity of the zero pressure T_c of α-U to thermal history. The high T_c associated with the quenched sample is consistent with the large residual strains which this thermal treatment will produce. Careful annealing in the α phase will reduce the strain and consequently result in a lower T_c, as observed for transition (b). However, due to the highly anisostropic thermal expansion[18,25] of α-U below 500°C, no polycrystalline sample can be expected to remain strain free upon cooling to liquid-helium temperatures. Even for a good single crystal, which should be strain free on cooling, a magnetic transition is observed[9] between 0.21 and 0.25°K which is not associated with bulk superconductivity,[10,11] indicating the presence of slight residual strain.

It is also important to consider the implications of the results of Fig. 2 from a second point of view. Namely, the sample for which the curves (c) and (d) were measured received a heat treatment which should ensure the solubility of any impurity atoms in the α phase, whereas for the sample associated with curve (b) the impurity atoms should have diffused to the grain boundaries and precipitated. Thus on the basis of an impurity filament explanation, one would have expected curves (b) and (c) to be interchanged.

The superconducting behavior of the U9 and U10 samples was initially examined at atmospheric pressure in a cryostat measuring down to 0.3°K. Both samples showed very broad high temperature structure in their magnetic transitions which extended from ~1.5°K, for sample U9, and ~1.25°K, for U10 and which preceded the major magnetic transition in the vicinity of 0.6°K. These transitions, as in all previous cases, are *not* associated with bulk superconductivity.

The samples were next examined magnetically in the high-pressure cryostat at pressures ranging from approximately 3–23 kbar, which represents a considerable extension of the pressure range of the previous[1] measurements, namely 3–10 kbar. The variation of these transitions as a function of volume change is shown in Fig. 3. The volume changes were calculated from the pressure measured at the low temperature using the room temperature compressibility data of Bridgman.[26] A number of equivalent pressures are also indicated. The vertical bars indicate the width of the transition as determined from an extrapolation of the central linear portion of the transition curve, neglecting rounding at the ends of the transition. The data for the two samples are in good agreement, the only difference being that the transitions for the sample U10 tend to occur at a slightly higher temperature than those for sample U9. Furthermore, the transitions determined below 10 kbar are in good agreement with the earlier work[1] on samples of similar high purity, but from a different source.

The specific-heat measurements of Phillips, Ho, and Smith[12] for α-U at 10 kbar clearly show that the mag-

[22] T. F. Smith and H. L. Luo (to be published).
[23] T. F. Smith, Phys. Rev. Letters **17**, 386 (1966) and unpublished data.
[24] A. L. Schawlow and G. E. Devlin, Phys. Rev. **113**, 120 (1959).
[25] H. H. Chiswick, A. E. Dwight, L. T. Lloyd, M. V. Nevitt, and S. T. Zegler, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958* (United Nations, Geneva, 1958).
[26] P. W. Bridgman, Daedalus **76**, 71 (1948). The corrected *P-V* relationship obtained from Bridgman's data was taken from K. A. Gschneidner, Jr., Solid State Phys. **16**, 275 (1964).

netically determined transition at ~2.1°K for this pressure is associated with bulk superconductivity. We believe, on the basis of our model (see below), that all the magnetically observed transitions at pressures above about 3 kbar are associated with bulk superconductivity and await specific-heat measurements at these pressures to test whether this is correct or not. The upper limit of 0.1°K imposed upon the T_c of α-U at zero pressure by the specific-heat measurements,[11] coupled with the specific-heat measurements at 10 kbar,[12] clearly indicates the sensitivity of the T_c of α-U to pressure below 10 kbar.

An examination of Fig. 3 shows a marked change in the pressure dependence of T_c above 10 kbar. Thus, following the initial rapid increase (by more than an order of magnitude) T_c levels off at about 2.1°K above 9 kbar. These results confirm the decrease in $\partial T_c/\partial P$ with increasing pressure suspected from the trend of the earlier measurements.[1] T_c then remains essentially pressure independent between 9 and 13 kbar, and then decreases slowly as the pressure is increased further. The rate at which T_c decreases is obscured by a gradual, but considerable broadening of the transition at pressures above 15 kbar. This may be an indication of increasing pressure inhomogeneity within the sample, possibly due to the deformation of the cylinder walls. However, there was no evidence for such behavior in the transition of the tin manometer since its width remained essentially constant over the entire pressure range. Furthermore, the transition width decreased upon reducing the pressure so that the cause of the broadening appeared to be quite reversible.

In view of the upper limit of 0.1°K on any possible transition to the bulk superconducting state we shall consider α-U to be nonsuperconducting at zero pressure. The following considerations, however, will not be appreciably affected in the event that α-U is found to be a bulk superconductor at a temperature lower than 0.1°K. Now any discussion of the superconducting properties of α-U has to explain the three main features of the T_c-pressure curve: (i) the pressure-induced superconductivity, (ii) the initial, abnormally rapid, increase of T_c with pressure—namely a rise from 0 to 2°K for an applied pressure of ~9 kbar, which corresponds to a volume decrease of less than 1%, (iii) the broad maximum in T_c, centered about 11 kbar, followed by a relatively slow decrease of T_c with further application of pressure.

Other known systems showing pressure-induced superconductivity are the semimetal bismuth,[27] the semiconducting elements Te,[28] Sb,[29] Si,[30] Se,[31] and Ge,[30] and

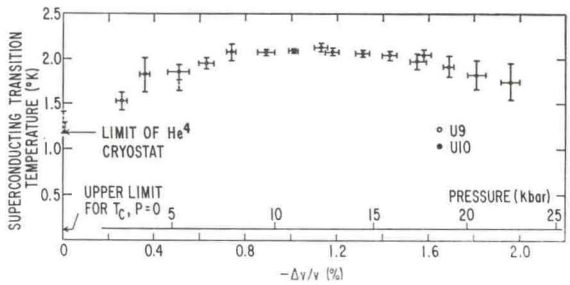

FIG. 3. Superconducting transition temperature of α-uranium as a function of % change of volume.

a number of semiconducting compounds[32] all of which become superconductors following a pressure-induced transformation, with an associated decrease in volume, to a metallic phase. However, neither resistivity nor compressibility measurements on α-U as a function of pressure at room temperature indicate the occurrence of a phase change. It is possible that such a phase change takes place below room temperature, but we think this is unlikely. Thus the possibility arises that α-U may be the first pressure-induced superconductor which does not undergo a first-order crystallographic transition to the superconducting phase.

The second feature of the T_c–P curve, the initial rapid increase of T_c with pressure, is peculiar to pure α-U since it has not been observed in α-, β-, and γ-uranium alloys. This change on alloying contrasts strongly with the behavior of lanthanum-rich solid solutions[23] with Y, Th, Yb, Pr and Gd (but not Ce) which retain the rapid increase of T_c with pressure observed in pure La. This suggests that the cause of the initial rapid increase of T_c with pressure in α-U is due to a weak electronic transformation. Such a transformation has been postulated by Fisher and McSkimin[33] to account for an anomaly at 43°K in their elastic-constant data and anomalies which have been observed by a number of workers in several other properties of α-U, such as Hall constant,[34] resistivity[34] and thermal conductivity[35] at this temperature. However, there does not appear to be any anomaly in the magnetic susceptibility in the region of 43°K[36] (Fig. 4). X-ray and neutron diffraction measurements[18] subsequently showed that although there is no crystallographic phase transformation at 43°K there is, however, a change in the temperature dependence of the atomic position parameter and that there is also an increase in volume amounting to some 0.2% between 50 and 4.2°K. In addition extra reflections were observed in the neutron pattern

[27] P. F. Chester and G. O. Jones, Phil. Mag. **44**, 1281 (1953); N. B. Brandt and N. I. Ginzburg, Fiz. Tverd. Tela **3**, 3461 (1961) [English transl.: Soviet Phys.—Solid State **3**, 2510 (1962)].

[28] B. T. Matthias and J. L. Olsen, Phys. Letters **13**, 202 (1964).

[29] T. R. R. McDonald, E. Gregory, G. S. Barberichi, D. B. McWhan, T. H. Geballe, and G. W. Hull, Jr., Phys. Letters **14**, 16 (1965).

[30] W. Buckel and J. Wittig, Phys. Letters **18**, 187 (1965).

[31] J. Wittig, Phys. Rev. Letters **15**, 159 (1965).

[32] H. E. Bömel, A. J. Darnell, W. F. Libby, and B. R. Tiltman, Science **139**, 1301 (1963); **141**, 714 (1963); D. B. McWhan, G. W. Hull Jr., T. R. R. McDonald, and E. Gregory, *ibid.* **147**, 1441 (1965).

[33] E. S. Fisher and H. J. McSkimin, Phys. Rev. **124**, 67 (1961).

[34] T. G. Berlincourt, Phys. Rev. **114**, 969 (1959).

[35] H. M. Rosenberg, Phil. Trans. Royal Soc. (London) **A247**, 55 (1955).

[36] We would like to thank J. Penfold, Atomic Energy Research Establishment, Harwell for magnetic susceptibility measurements.

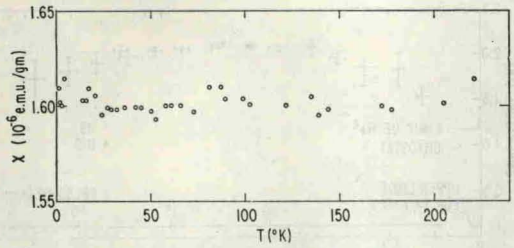

FIG. 4. The magnetic susceptibility of α-U from 1–200°K. The value observed at 297°K was $1.645\pm0.030\times10^{-6}$ emu/gm.

which were tentatively ascribed to a magnetic contribution. However, these extra reflections were also present at room temperature and therefore cannot be associated immediately with the "43°K transformation."

We propose, for convenience, to label the phase of α-U below 43°K at atmospheric pressure as α_0. Since there is an increase in volume with decrease of temperature below the $\alpha \rightarrow \alpha_0$ transformation it is not unreasonable to suppose that the effect of pressure would be to inhibit the formation of the α_0 phase. We propose therefore to associate superconductivity with the α-U phase, but not with the α_0-U phase. We can now describe the superconducting behavior of uranium at zero pressure since the grains are in the nonsuperconducting α_0 phase, whereas the grain boundaries, because of the associated strains introduced upon cooling, behave like the α phase and are responsible for the filamentary superconductivity. This description calls for an $\alpha - \alpha_0$ phase boundary which is strongly depressed in temperature by the application of a few kbar pressure. A study of the effect of pressure upon any of the anomalies observed in the physical properties of α-U at 43°K would be of considerable interest and would provide a positive test of this explanation. Though Geballe *et al.*[9] have also suggested this explanation for transitions observed below 0.8°K we differ from them in believing that the entire superconducting behavior of uranium may be accounted for by this model, rather than a combination of two explanations such as they adopted.

We should first like to consider one possible picture for this "43°K transformation" as suggested by Geballe *et al.*,[9] but which we shall express slightly differently. Namely, that an electron transfer takes place at 43°K from a $5f6d7s$ conduction band to a virtual bound (vb) state[37] constructed from the $5f$ conduction-electron wave functions. We shall assume that such a vb state just overlaps the Fermi level and we associate an increase in its population with an upward movement of the Fermi level, relative to the bottom of the vb state, as the volume increases below 43°K. Such a vb state could be either magnetic (m) or nonmagnetic (nm).

In order to estimate the effect of populating vb states we shall consider some examples of known behavior. Unfortunately, it is impossible to consider a nmvb state involving $4f$ electrons since vb states involving such electrons are usually well localized and carry a magnetic moment,[38] so we are obliged to compare the relative behaviors of magnetic and nonmagnetic $3d$ vb states. The addition of 1 at% Fe to V to form a nmvb state[39] lowers T_c by $\sim$1°K.[40] However, this decrease in T_c is consistent with the "valence effect"[41] (the systematic variation of T_c with electron concentration across the transition series) and does not require that the actual presence of the nmvb state contributes to the lowering of T_c. In fact, since scattering from a nmvb state does not destroy the time-reversal invariance of the electron wave functions, there is no reason to expect that such scattering would decrease T_c.[42] Thus unless the formation of a nmvb state in α_0-U can be considered to alter the effective valence we would not expect such a state to change T_c markedly.

Magnetic vb states, on the other hand, play an active role in reducing the value of T_c. For example Fe dissolved in Mo[43] reduced T_c at a rate of 60–80°K per at%.[44] However, should a mvb state with a moment as small as 10^{-2} μ_B form in U below 43°K and produce paramagnetic behavior there would be a temperature dependence of the susceptibility which would result in an increase of about 5% between 40 and 1°K. As no such temperature dependence of the susceptibility is observed (Fig. 4), this model is only appropriate if the extra postulate is made that the mvb states order antiferromagnetically as they form.

We should like to offer an alternative explanation for the behavior of α-U in terms of the formation of a spin-density wave (SDW)[45] at 43°K which opposes the superconductivity of α_0-U. The creation of a SDW scarcely affects the magnetic susceptibility,[46] but does reveal itself in anomalies in other physical properties such as Young's modulus,[47] resistivity,[47,48] Hall coefficient,[48] and thermal expansion[47,49]—anomalies which are also observed in α-U at 43°K. We then suggest that the application of pressure destroys the SDW, as is

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observed for the SDW of Cr,[50] and thus results in the anomalously high-pressure dependence of T_c in α-U. It would appear that at pressures $\sim$10 kbar any remaining SDW has a negligible effect of T_c and therefore T_c achieves its maximum value. The subsequent decrease of T_c with further application of pressure is then typical of the behavior observed in the majority of superconductors.[51]

It is of interest to compare this reported pressure dependence of the T_c for uranium with that of thallium[2,3] since there is a superficial similarity. However, the maximum increase of T_c for Tl is two orders of magnitude smaller than that observed for U. Measurements[52] of the change of length along the principal crystal directions upon quenching the superconductivity of a Tl single crystal in a magnetic field indicate that the maximum in T_c arises from a strong anisotropy in the pressure dependence of T_c. An explanation of this anisotropy has been offered on the basis of the shape of the Fermi surface for Tl.[53]

A comparison may also be made with the maxima in T_c as a function of pressure, which have recently been reported by Köhnlein[54] for vanadium, niobium, and tantalum. However, this should only be done with caution since the maxima are not observed directly, but are produced by the method in which the data were represented. In addition, his direct observations are somewhat questionable since there is a serious discrepancy between his Ta data and those previously reported.[2,55] In the opinion of the authors the most reliable absolute determinations of the pressure dependence of the T_c for tantalum are those of Jennings and Swenson[2] and Hinrichs and Swenson[55] which were made to a maximum pressure of 10 kbar and which employed solid hydrogen as the pressure-transmitting medium. We therefore consider it advisable that further measurements of T_c, as a function of pressure, be made for these elements at pressures above 10 kbar before any serious attempt is made to compare these maxima in T_c with that observed in uranium. It is worth noting, however, that the maximum reported increase of T_c for V and Nb, whilst larger than that for Tl, is still considerably smaller than that observed for uranium.

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