Isotope Effect in Superconducting γ -Uranium Alloys*

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We have measured the isotope effect in stablized γ -uranium alloys and found $T_{e} \propto M^{\alpha}$, $\alpha = -0.53 \pm 0.02$. We find $T_c \approx 2.1^{\circ}$ K to be a more representative value for the extrapolated superconducting transition temperature of a hypothetical pure γ -uranium than the previously reported estimate of 1.8°K.

I. INTRODUCTION

THE superconducting isotope effect has been deter- \mathbf{I} mined by us in room-temperature stabilized γ -phase uranium alloys. The high-temperature body-centered cubic (bcc) (γ) phase of uranium is stable only over the range 775 to 1132°C,¹ the melting point of uranium. A γ phase can be retained at room temperature, however, by rapid cooling if sufficient molybdenum or niobium is added as a stabilizer.² This metastable alloy becomes a superconductor at $T_c \sim 2.1^{\circ} \text{K.}^3$

Attention was first drawn to the possible particular significance of the isotope effect in uranium by Hamilton and Jensen,⁴ who suggested that superconductivity in uranium was due to an attractive force between the conduction electrons (as a result of their interaction with the lattice) which arose from the magnetic polarization of neighboring uranium ions in the lattice rather than from the normal lattice deformation potential responsible for superconductivity in the BCS theory.⁵ In the latter case, the transition temperature T_c is proportional to the energy of the lattice vibrations (phonons) created. This leads to the prediction of a "normal" (negative) isotope effect, namely, $T_c \propto M^{\alpha}$, $\alpha = -0.5$, where M is the mass of a lattice ion. Since the interaction of Hamilton and Jensen is not mediated by phonons, T_c would be independent of M ($\alpha = 0$).⁶

Smith and Gardner⁷ rejected the Hamilton-Jensen proposal on the basis of their measurements of the dependence of T_c on pressure in uranium but were led to the prediction of an even more anomalous isotope

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effect: $\alpha = +2$. They obtained this result by treating uranium as a transition metal and by using a previously established empirical relationship between the isotope effect and the pressure dependence of T_{c} in transition metals.8,9

Both Hamilton and Jensen⁴ and Smith and Gardner⁷ theorized that the superconductivity of (α) uranium arose from the 5*f*-like nature of its conduction electrons. This was suggested by the similarity of the superconducting properties of uranium to those of lanthanum,¹⁰ which is thought to have an incipient 4f character due to its proximity to Ce in the periodic table, and in view of the absence of superconductivity in the otherwise similar elements Sc, Y, and Lu.¹¹ Hamilton and Jensen postulated that, in uranium, conduction electrons were scattered into a localized 5f state just above the Fermi surface, while Smith and Gardner believed that a 5f band existed at the Fermi level¹² and the (pressure-enhanced) admixture of 5f wave functions into the otherwise 6d7s wave functions of the conduction electrons was responsible for the superconducting properties of α -U, primarily the dramatic increase in T_c from <0.1 to 2.2°K with the application of only 10 kbar pressure.13

Smith and Gardner have more recently suggested¹⁴ that the formation of a spin-density wave among the conduction electrons when α -U goes through its presumed electronic phase change¹⁵ and volume minimum¹⁶ at \sim 43°K inhibits the formation of the superconducting state. Application of pressure replaces the spin-density wave¹⁷ with the 5*f*-enhanced superconductivity and its

 ¹⁴ W. E. Gardner and T. F. Smith, Phys. Rev. 154, 309 (1967).
 ¹⁵ E. S. Fisher and H. J. McSkimin, Phys. Rev. 124, 67 (1961).
 ¹⁶ A. F. Schuch and H. L. Laquer, Phys. Rev. 86, 803 (1952);
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¹⁷ For pressures greater than 10 kbar, T_c is relatively insensitive to pressure. The authors now believe that the strong dependence of T_{σ} on pressure at the lower pressures is not characteristic of the pure superconducting state, hence not appropriate for a prediction of the isotope effect. Also, the empirical relationship relating the isotope effect to the pressure dependence of T_c may itself be doubtful. [T. F. Smith, (private communication). Also, see Ref. 9.] 356

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 ¹⁴ W. E. Cordner and T. F. Smith, Phys. Rev. **154**, 200 (1967).

high transition temperature (relative to uranium's position in the periodic system¹⁸). Geballe et al.,¹⁹ on the other hand, suggest that superconductivity in α -U is destroyed by the population, below $\sim 43^{\circ}$ K, of a 5f level just below the Fermi surface and that the application of pressure moves the 5f level above the Fermi surface and depopulates it. They go on to suggest that the superconducting behavior of β -U^{20,21} and γ -U indicate that these phases of uranium possess no 5fcharacter at all.

It was our hope in measuring the isotope effect in gamma uranium to determine whether or not γ -U appeared to have the f character so often discussed for α -U, or possibly the *d* character of a transition metal, or neither. One would expect transition metal (d) character to be evidenced by an exponent α intermediate between 0.0 and -0.5^{22} (e.g., Mo, Os, Ru, Zr, and Re).²³ If the transition temperature and its dependence on pressure¹⁴ of γ -uranium are substituted into the previously mentioned empirical relationship relating $\partial T_c/\partial P$ and α for transition metals,⁸ one obtains a prediction of $\alpha \sim -0.2$. This is only approximate since one assumes identical values of Θ_D , γ_G , and κ for α -U and γ -U (where Θ_D is the Debye temperature, γ_G is the Grüneisen constant, and κ is the compressibility), but such a value does fall within the intermediate range expected for transition metals.

Presumably, if γ -U possessed some of the f character postulated by Hamilton and Jensen for α -U, one might once again expect an exponent intermediate between 0.0 and -0.5, α being closer to 0.0 the more completely the superconductivity is determined by f-like conduction electrons and closer to -0.5 the less this is the case. Since the presence of the superconductivity-inhibiting localized f electrons postulated by Geballe et al.¹⁹ would presumably not alter the isotope effect, a determination of α alone does not argue directly for or against their existence.

Only Morel and Anderson,²⁴ among those theoretical workers^{25,26} who have modified the BCS theory within the framework of the electron-phonon interaction to account for deviations of the isotope effect from $\alpha =$ -0.5, have concerned themselves with (α -) uranium. If we assume again that α -U and γ -U have the same Debye temperature, Morel and Anderson's semiempirical relation yields $\alpha = -0.40$ for γ -U. It is noteworthy, in this context, that similar predictions are made for Sn and Tl, whose experimental α -s lie much closer to -0.5, and that their one prediction of α for a transition metal which has been checked experimentally $(Zr)^{27}$ is seriously in error $(\alpha_{\text{theor}} = -0.30,$ $\alpha_{\text{expt}} = -0.0$).

II. SAMPLES AND EXPERIMENTAL METHOD

Our samples were prepared by arc-melting together the appropriate amounts of molybdenum or niobium and uranium on a water-cooled copper hearth in a Zr-gettered helium-argon atmosphere. The rate of cooling from the molten state and subsequently from the γ -phase equilibrium temperature region provided by the arc-melter was sufficient to stabilize the γ phase at room temperature. The buttons were quite small ($\sim 250 \text{ mg}$ total mass) and were remelted several times in preparation, so were very likely quite homogeneous. Especially in the case of the Mo-stabilized alloys, this assumption of sample homogeneity was borne out by the sharpness of the superconducting transition curves. The uranium used consisted of the seven purest batches of uranium metal available to us (three batches of ²³⁸U, four batches of ²³⁵U). These lots of uranium and the amounts of the more significant impurities contained in them are listed in Table I. The molybdenum and niobium used were metallurgical grade sheet, 0.005 in. thick, nominally 99.9% pure. The main impurities in the Mo were W:90 ppm and Fe:40 ppm. In the Nb, the principal impurities were Ta:550 ppm and O₂:115 ppm.

Alloys were prepared using 15, 16, 18, and 20% Mo and 18, 20, and 22% Nb as stabilizers. (All compositions are indicated in at.%.) These concentrations were suggested by the earlier work of Chandrasekhar and Hulm.³ The superconductivity of the alloys was detected by placing the samples in one coil of a balanced resonant low-frequency (~ 200 cps) ac bridge circuit²⁸ and observing the (amplified) imbalance signal, produced by the occurrence of superconductivity, on the graduated scale of an oscilloscope. Both the sample coil and the balancing coil were immersed in the liquid-helium bath of a cryostat of conventional design. A four-terminal germanium resistor placed at the sample level in the bath and calibrated against the vapor pressure of the bath was used as the sample temperature indicator. Several layers of Co-netic type AA magnetic shielding material were placed around the cryostat to shield the sample and detection coils from stray external magnetic fields.

Figure 1 shows typical superconducting transition curves obtained, running samples both individually

 ¹⁸ B. T. Matthias, in *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1957) Vol. II, Chap. V, p. 138.
 ¹⁹ T. H. Geballe, B. T. Matthias, K. Andres, E. S. Fisher, T. F. Smith, and W. H. Zachariasen, Science 152, 755 (1966).
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²¹ Charles W. Tucker, Jr., Peter Senio, J. Senio, J. Thewlis, and H. Steeple, Acta Cryst. 9, 472 (1956). See also Ref. 1. ²² John J. Engelhardt, George W. Webb, and Bernd T. Matthias,

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 ²⁶ James C. Swihart, Phys. Rev. 116, 45 (1959); IBM J. Res. Develop. 6, 14 (1962).

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^{6, 213 (1966).}

Lot number	Isotope	Si	Fe	v	С	Mo	$\mathbf{M}\mathbf{g}$	w	Ni	
5765	U^{235}	30	35	200	100	<25	25	•••	4	
5795	U^{235}	20	30	<20	100	<25	25	•••	30	
11345	U^{235}	10	15	<20	250	<25	2	<30	20	
17391	U^{235}	20	150	<30	•••	<25	12	•••	25	
242	U^{238}	15	20	<20	70	<25	40	•••	7	
15707	U^{238}	30	40	<20	60	8	<2	•••	4	
17406	U^{238}	30	20	<30	•••	<25	20	•••	5	

TABLE I. Significant impurity contents (in ppm) of the uranium batches used. The oxygen content of all batches is unknown.

and, when curve sharpness allowed, simultaneously. Figure 2 shows the dependence of the superconducting transition temperature on alloy concentration as well as on the uranium isotope used. We have chosen to use the "onset" of superconductivity as our transition temperature. This temperature is determined by the intersection of a line drawn through the linear portion of the transition curve and a horizontal line representing zero superconductivity. Table II is a compilation of the transition temperatures for all of the samples measured, along with the widths of the curves. The widths were determined by extending the line through the linear portion of the curve to a horizontal line representing complete superconductivity. Since, within our accuracy, the isotopic shift in transition temperature is independent of the particular stabilizer used or the amount of a given stabilizer used, we have computed the exponent α in the isotope effect by considering the variation only in the mass of the uranium used in the alloy rather than any average mass. This yields an exponent $\alpha =$ -0.53 ± 0.02 for γ -U.

The uncertainty in our result arises almost exclusively from the scatter in transition temperatures produced by our use of different batches of uranium. Inaccuracies in the weighing out of samples and losses in melting were never serious enough to cause variations



FIG. 1. Typical superconducting transition curves obtained. The U-18% Mo curves were measured simultaneously. The U-22% Nb curves were determined individually. For purposes of comparison, the imbalance signal for the U(235)-22% Nb sample has been scaled-up by a factor of 1.5 to compensate for its smaller size.

in transition temperatures as much as 1 mdeg, our thermometric limit of resolution; whereas different lots of uranium yielded, at times, transition temperatures differing by several millidegrees. Our previous experience with uranium (including α -U, β -U, and U₆Fe) had indicated that this would be the case, inasmuch as all uranium metal seems to contain several impurities to which the superconducting properties of the uranium are extremely sensitive. It was thus our belief that an isotope effect could be measured only if it could be resolved over and above the inevitable scatter due to differing amounts of impurities. With this in mind we deliberately chose to work with several batches of uranium, all relatively pure, but possessing differing amounts of the impurities found to affect its superconductivity.

The transition temperatures of our Mo-stabilized alloys ($\sim 2.12^{\circ}$ K) agree quite well with those of Chandrasekhar and Hulm³ ($\sim 2.10^{\circ}$ K), especially if the midpoints rather than the onsets of our curves are used for comparison. This is of more than passing interest, since Chandrasekhar and Hulm quenched their samples from the γ -phase equilibrium temperature



FIG. 2. Dependence of superconducting transition temperature upon alloy concentration for the two systems studied.

U-Mo series:	16 at. % Mo			18	18 at. % Mo			20 at. % Mo		
	Lot	Tc	δ	Lot	T_{c}	δ	Lot	Tc	δ	
U235	11345 17391	2.132 2.133	16 11	5765 5795 11345 17391	2.130 2.131 2.130 2.131	5 6 9 3	11345 17391	2.124 2.127	6 7	
U ²³⁸	15707	2.121	10	15707	2.119 2.118 2.118 2.120	6 6 7 7	15707	2.113	6	
	17406	2.121	10	17406	$\begin{array}{c} 2.118\\ 2.116\end{array}$	8 6	17406	2.113	6	
U-Nb series:	18	at. % Nb		20 at. % Nb			22 at. % Nb			
	Lot	T _c	δ	Lot	Tc	δ	Lot	Tc	δ	
U235	11345	2.023	56	5765 11345	$\begin{array}{c} 2.023\\ 2.023\end{array}$	28 27	11345	2.024	20	
	17391	2.022	41	17391	2.021	30	17391	2.023 2.023 2.025	19 20	
U ²³⁸	15707	2.011	45	15707	2.009	32	15707	2.010 2.012	25 24	
	17406	2.009	54	17406	2.013	24	17406	2.011 2.012	23 24	
U-18 at. % Mo:		U^{235}			U^{238}					
(simultaneous runs)	Batch	T_{c}	δ	Batch	T_{c}	δ		ΔT_{c} (°K)		
	5765 5765 5765	$2.130 \\ 2.130 \\ 2.131$	3 3 5	242 15707 17406	$2.119 \\ 2.118 \\ 2.116$	3 3 5		$\begin{array}{c} 0.011 \\ 0.012 \\ 0.015 \end{array}$		
	5795 5795 5795	$2.133 \\ 2.133 \\ 2.133 \\ 2.133$	4 4 4	242 15707 17406	$2.121 \\ 2.120 \\ 2.119$	3 3 7		$\begin{array}{c} 0.012 \\ 0.013 \\ 0.014 \end{array}$		
	11345 11345 11345	$2.130 \\ 2.131 \\ 2.131$	4 4 4	242 15707 17406	$2.119 \\ 2.118 \\ 2.116$	3 4 5		0.011 0.013 0.015		
	17391 17391 17391	2.131 2.133 2.133	3 4 4	242 15707 17406	2.119 2.118 2.116	4 3 5		0.012 0.015 0.017		

TABLE II. Superconducting transition temperatures $T_{e}({}^{\circ}K)$ and curve widths $\delta({}^{\circ}K \times 10^{-3})$ for all γ -uranium samples measured. (The samples prepared with 15% Mo indicated in Fig. 2 are not characteristic of good γ -U.) The method used in determining the transition temperatures and measuring the curve widths is explained in the text.

region directly into water, after annealing for 24 h in the γ region. The transition temperatures of the Nbstabilized alloys do not agree with the earlier work, however. Whereas Chandrasekhar and Hulm show U-22% Nb to be superconducting at $\sim 1.8^{\circ}$ K, our onset temperature for this alloy is $\sim 2.01^{\circ}$ K, and the corresponding midpoint is $\sim 2.00^{\circ}$ K. It was our experience that niobium did not stabilize the γ phase so well as molybdenum, especially at the lower concentrations, so that the difference in results in the case of Nb may follow from a greater sensitivity to type of heat treatment and quenching when a poorer stabilizer is used. It is of interest in this connection that, while the midpoints of our U-Nb transition curves increased with increasing Nb content (as indicated in the work of Chandrasekhar and Hulm), the onset temperatures were almost independent of concentration. We observed a related behavior in our U-15% Mo samples when we reran their transition curves after they had aged several months. The curves had broadened considerably but possessed the same onset-temperature values. It is known that 15% Mo is not sufficient to give good γ phase stabilization,² thus we believe that the greater broadness of our U-Nb curves for less than 22% Nb is evidence of poorer stabilization and that the onset transition temperatures are more representative of the actual transition temperature of γ -U.

On the basis of their results with the U-Nb alloys, Chandrasekhar and Hulm proposed that 1.8° K represented the hypothetical superconducting transition temperature of pure γ -U. This was done by extrapolating their curve showing the dependence of T_e on Nb concentration to zero niobium content. Since the curve was flat at the minimum amount of Nb required

to stabilize the γ phase (~16% Nb), their T_c at this point (1.8°K) reasonably represented the extrapolated value. This was done, however, at the expense of their U-Mo curve, which was also flat at $\sim 2.1^{\circ}$ K. It is our belief that molybdenum represents the better γ -U stabilizer (as indicated by the greater sharpness of the U-Mo curves) and that it should certainly receive at least equal consideration in an estimation of the T_c of pure γ -U. (Although we show below that it is probably not a major consideration, the fact that Mo and not Nb has the same number of valence electrons as uranium also emphasizes the relative importance of Mo in this consideration.) While we cannot readily offer an explanation at this point for the lower transition temperatures obtained by Chandrasekhar and Hulm with their niobium alloys, we prefer to use our values $(\sim 2.0^{\circ} \text{K})$ because of their constancy with concentration and their proximity to the values obtained with the molybdenum alloys. We believe, therefore, that a

transition temperature of pure γ -U. In order to eliminate any effects due to possible changes in the characteristics of our germanium resistor with time, our most crucial determination of the isotope effect was made by running all of our U-22% Nb samples on the same day and by running all of our ²³⁵U-18% Mo and our ²³⁸U-18% Mo pairs simultaneously in the cryostat. The U-22% Nb curves were too broad to make simultaneous runs meaningful. The average isotopic ΔT_o among the four U-22% Nb samples (2²³⁵U and 2^{238} U) was $0.013 \pm 0.003^{\circ}$ K. The average ΔT_{c} among the 12 U-18% Mo samples was $0.0133\pm$ 0.0025°K. These averages lead to values of the mass exponent α in the isotope effect of -0.54 ± 0.02 and -0.53 ± 0.02 for the cases of Nb and Mo, respectively. Because of the scarcity of certain of our batches of uranium and because the U-Nb results were considered only to be backup results to those of the U-Mo series, as indicated previously, not as many U-Nb samples were prepared as were U-Mo samples. Thus $\alpha =$ -0.53 ± 0.02 is our best value. It is of interest in the case of the U-18% Mo series that one arrives at the same average exponent if our six very purest pairs are given a double weighting in the determination of α .

value of $\sim 2.1^{\circ}$ K represents a better estimate of the

In order to calculate α , we used atomic masses of 238.05 and 235.19 for the ²³⁸U and ²³⁵U isotopes, respectively. While one of our ²³⁸U batches was normal uranium (99.3% ²³⁸U) and the other two were depleted of ²⁸⁵U (~99.8% ²³⁸U), any error caused by using the atomic mass of pure ²³⁸U is negligible for our purposes. Our ²³⁵U samples were typically 93.2% ²³⁵U and 5.3% ²³⁸U, the rest being ²³⁴U and ²³⁶U. The atomic mass used represents an appropriate weighted average of the constituent isotopes.

If we use the midpoints of our U-18% Mo curves to calculate α , the result is unchanged. This is not the case for our U-22% Nb curves, because of a slight difference in width of the ²³⁸U curves compared to the ²³⁵U curves. A plot of midpoints versus Nb concentration shows, however, that this difference is becoming smaller the higher the Nb concentration and would be expected to vanish as the curves become sharper on the high side of 22% Nb.

The sudden drop in transition temperatures at 15% Mo in Fig. 2 is due to the formation of a slightly modified form of γ -U (called γ^0 -U).² A minimum of 16% Mo seems to be required to stablize γ -U in an undistorted cubic form. Slight tetragonality sets in at lower concentrations.² As a check on the character of our higherconcentration alloys, 16% Mo and 20% Mo samples were given x-ray examinations utilizing both glancingincidence photographs and diffractometer scans. In both samples only γ -U was detected. Because of the small size of the samples, the detection limit of other phases was 10%.

III. DISCUSSION

This is the first determination of an isotope effect in an alloy system and, as such, warrants more than the usual scrutiny in the evaluation of its significance in relation to the pure substance under consideration, γ -U. As mentioned previously, we have chosen to calculate the isotope effect as if the superconductivity of the samples were determined almost exclusively by the uranium atoms in the lattice. This cannot really be the case, since $\frac{1}{5}$ of the atoms are either Mo or Nb. It does seem, however, to be the best approximation to the actual situation in view of the relative insensitivity of the transition temperature and the isotope effect to the amount of stabilizer used or the particular stabilizer used. Certainly, if the electronic properties of the Mo or Nb were important, one would expect¹⁸ a considerable difference in transition temperatures between the two systems, since Mo and Nb (both of which have a bcc structure) are so different electronically that the addition of Mo to Nb reduces the superconducting transition temperature of Nb by more than two orders of magnitude.²⁹ One is left with the problem of how the phonon spectrum of the lattice is altered by the presence of the stabilizing atoms. One might wish to use a simple average alloy mass to calculate the isotope effect. If this is done for 18% Mo and 22% Nb, the result is $\alpha = -0.58 \pm 0.02$ in both cases. However, using this approach, one would expect a concentration-dependent shift in the transition temperature for a given isotope as large as the measured *isotopic* shift if the alloy concentration were changed, say, from only 16% Mo to 18% Mo. Such a strong dependence of T_c upon concentration is obviously not observed. It is conceivable, but highly unlikely, that this shift is just compensated for by changes in the electronic nature of the alloys. In view of this pronounced dependence of T_{c} only on *isotopic* changes in the mass, we prefer simply to use

²⁹ R. A. Hein, J. W. Gibson, and R. D. Blaugher, Phys. Rev. Letters 11, 6 (1963).

the uranium masses alone in calculating the isotope effect. This yields $\alpha = -0.53 \pm 0.02$.

We find thus that γ -U has a "normal" isotope effect. Although there is inevitably some 6d character in the conduction electrons of the metal, the s-d scattering which influences superconductivity in the transition metals is not evidenced in γ -U. Since γ -U is not a transition-metal superconductor, it is understandable that the prediction for α using the formulas of Morel and Anderson²⁴ gives the same incorrect value as for Sn and The support to the validity of the approach used in that theory. Similarly, a prediction of α based on the pressure dependence of the superconducting transition temperature of γ -U, treating it as a transition metal, is inapplicable.

Our result of $\alpha = -0.5$ also obviates the necessity of introducing any notions of the 5f-level-type superconductivity of Hamilton and Jensen^{4,6} into that of γ -U. Furthermore, in this light, the suggestion by Geballe et al.19 that the localized 5f electrons which they postulate for α -U are in fact not present in γ -U seems all the more reasonable. More recently, it was also found to be the case that there is no evidence of felectrons in the superconductivity of thorium.³⁰ It seems likely, by analogy, that protactinium³¹ will be found to possess a similar superconducting high-temperature phase.

It would seem likely that the d and f character that is bound to be present to some extent in uranium must arise from admixed d and f bands. The admixture of 5f wave functions at the Fermi level has been discussed for α -U by Smith and Gardner,⁷ as previously noted. The determination of specific 6d and 5f character in uranium (and possibly especially in γ -U, as we shall see) is made less unequivocal than in the cases of the transition metals or the rare earths because of the relative instability of³² and hybridization among¹² the 6d

and 5f levels in the actinides as compared to the better characterized d levels of the transition metals and the 4f levels of the rare earths. Friedel¹² has suggested, in this context, that in γ -U the only non-s-like states at the Fermi surface are those in a band made up from a mixture of 5f orbitals and the two most unstable of the 10 available 6d orbitals. The eight stable 6d orbitals are involved in bonding and constitute a separate, completely filled band. (This reduction in s-d interaction due to the involvement of d electrons in bonding to promote lattice stability is very likely related to a similar situation in tungsten,²² which is a transition metal occupying the same column in the periodic table as uranium and for which the isotope effect was recently determined to be $\alpha \sim -0.41$,²² a value which, for a transition metal, is unusually close to $\alpha = -0.5$.)

Friedel's paper¹² also indicates that d and f electrons would be expected to play a more dominant role in the superconducting properties of the other two phases of uranium. This is supported by the recent suggestion³³ that the peculiar crystal structures of α - and β -uranium are, in fact, due to the considerable amount of 5fcharacter in the hybridized wave functions of their valence bands. Hopefully, a determination of the isotope effect in the α and β phases of uranium will provide additional insight into the characteristics of the "finfluenced" superconductors in the periodic system: lanthanum.⁴ protactinium,³¹ and uranium. Experiments are underway in this laboratory to make these measurements, although, as mentioned, the problems of sample purity are considerable.

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