

Pressure Dependence of the Superconducting Transition Temperature of Uranium*

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The superconducting transition temperature T_c of uranium has been observed to increase from 1.0 to 2.3°K on the application of a pressure of 10 kbar. From this result the possibility that T_c will increase with isotopic mass has been suggested.

THE pressure dependence of the superconducting transition of uranium has been measured to a maximum pressure of ~10 kbar. The results provide the first indication of the possibility of a superconductor being able to have a transition temperature which increases with isotopic mass, i.e., that a positive isotope effect exists in superconductivity.

Two samples of high-purity (~99.98 wt%) polycrystalline uranium have been investigated. One sample was obtained from the Argonne National Laboratory (A.N.L.), the other sample from Minereux et Métal, France (M.M.). The analyses of the two samples are given in Table I.

As the low-temperature limit of the He⁴ cryostat in which the superconducting transition temperatures under pressure are determined is 1.25°K, the transition temperature of the uranium samples at atmospheric pressure was initially determined in a He³ cryostat.¹ The transition of both samples was found to extend from 1.0° to 0.5°K.

In view of the high purity of these samples the width of the transition is rather excessive. Furthermore an anneal at 500°C *in vacuo* for 8 h followed by an etch of

the surface of a sample did not decrease its transition width. Hein, Henry, and Wolcott² have also reported measurements at atmospheric pressure on uranium of comparable purity. Their transition extended from 0.68° to 0.23°K. Thus, although the widths are similar, the actual temperature range differs. This difference may be associated with their use of a magnetic salt as coolant. Hein *et al.*² made some further measurements on a large-grained uranium sample of comparable purity and obtained similar results. This seems to suggest that the width is not due to strain induced in the specimen upon cooling due to the large anisotropy of the thermal expansion of uranium.³ This conclusion may be in error since impurities, in particular silicon, may well be much greater than stated in the large-grained sample and be mainly responsible for the width observed in this specimen.

The samples, embedded in AgCl, were next investigated in the pressure capsule⁴ in which the superconducting transitions were detected using a standard ac technique, and the maximum pressure available (~10 kbar) applied. The temperature range of the superconducting transition was observed to increase for the A.N.L. sample to between 2.05° and 2.37°K and for the M.M. sample to between 2.04° and 2.32°K. The transition temperature was then determined for a number of intermediate pressures. The variation of transition temperature with pressure for both samples is shown in Fig. 1. The vertical bars indicate the width of the superconducting transition and not the uncertainty in the measured temperature, which was less than 10 mdeg. The numbers indicate the sequence in which the measurements were taken. Cn runs 2, 5, 6, 7, and 9 the superconducting transitions were not complete at the lowest temperature available in the He⁴ cryostat. By comparison with higher pressure transitions the following estimates of the percentage of the total transition were made; run 2, 5%; run 5, ~100%; run 6, 60%; run 7, <20%; run 9, ~100%. The increase in temperature of the atmospheric-pressure super-

TABLE I. Analyses of uranium samples. C and O were determined by fusion analyses, N by chemical analysis, and all other elements were determined by spectrographic analyses.

Element	ppm	wt	Element	ppm	wt
	ANL	MM		ANL	MM
C	15	11	K	<50	<20
N	<10		Li	<1	<2
O	16	25	Mg	<2	<10
Ag	<1	<0.5	Mn	1	<1
Al	<5	<20	Mo	<20	
As	<10		Na	<10	<5
B	<0.1	0.15	Ni	<5	<3
Be	<0.5		P	<50	≤50
Bi	<1		Pb	<1	≤3
Ca	<20		Sb	<1	
Cd		<0.5	Si	15	≤20
Co	<5		Sn	<5	
Cr	<1	<4	Ti	<50	
Cu	<1	<5	Zn	<50	
Fe	<2	11			

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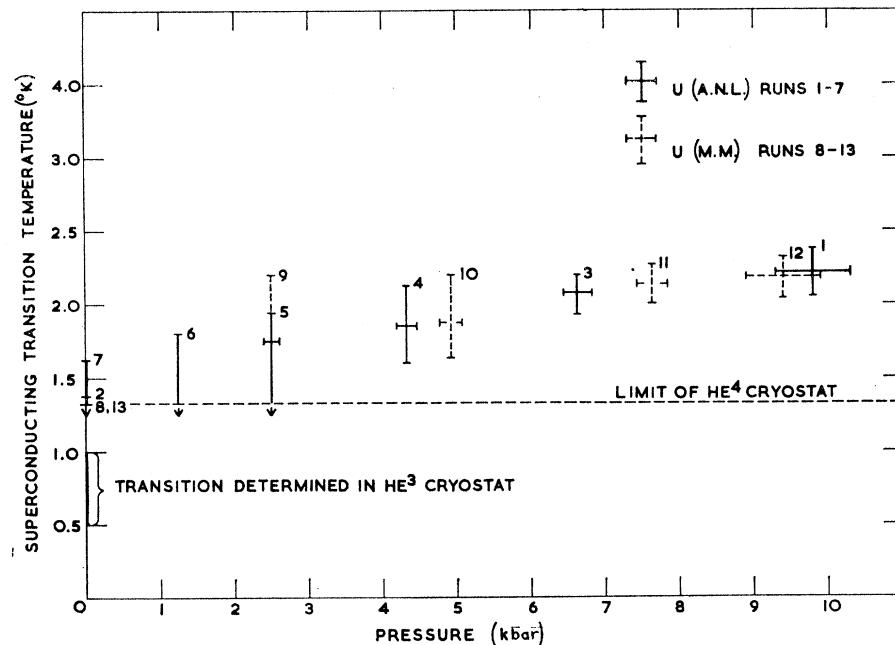
¹ D. C. Hamilton, thesis, University of California, San Diego (unpublished).

² R. A. Hein, W. E. Henry, and B. M. Wolcott, Phys. Rev. **107**, 1517 (1957).

³ L. T. Lloyd, U. S. Atomic Energy Commission Report No. ANL 5972, 1959 (unpublished).

⁴ W. E. Gardner and T. F. Smith, Phys. Rev. **138**, A484 (1965).

FIG. 1. Variation of the superconducting transition temperature with pressure for uranium. Vertical bars indicate the width of the transition.



conducting transition of the A.N.L. sample after releasing the pressure (particularly run 7) is probably due to straining of the sample, which was found to be distorted upon removal from the pressure capsule. The superconducting transition temperature of the M.M. sample, both before and after the application of pressure, was below the temperature limit of the He⁴ cryostat. The transition temperature increases monotonically with applied pressure and there seems to be a decrease in dT_c/dP with increasing pressure. In addition, the width of the transition is reduced by the application of pressure. This may be due to the reduction of anisotropy effects upon the application of pressure. We expect pressure to have only a small effect on any impurities present.

It has recently been reported⁴ that the superconducting transition temperature of lanthanum exhibits a marked increase upon the application of pressure. It was suggested that the occurrence of superconductivity in lanthanum was a consequence of the admixture of 4*f* wave functions at the Fermi surface and that the increase in T_c with pressure was due to an increase in the admixture of the 4*f* wave functions.

Although the free-atom configuration of uranium contains three 5*f* electrons,⁵ uranium does not appear to have localized 5*f* electrons in the metallic state.⁶ This may be due to the suggested overlap of the 5*f* wave functions between nearest neighbors,⁷ resulting in a 5*f* band. There will then be considerable admixture of 5*f*

wave functions at the Fermi surface⁸ which has to be without any associated localized electron behavior. We should like to suggest that it is 5*f* character at the Fermi surface which is responsible for the superconductivity of uranium.

While the effect of pressure upon the superconducting transition temperature is analogous to that in lanthanum, the results for uranium are considerably more dramatic. Adopting a BCS⁹ approach we find the observed increase in T_c at 10 kbar would require an increase of approximately 20% in the value of $N(0)V$, $N(0)$ is the density of electron states at the Fermi surface, and V the electron-phonon interaction parameter. This is more than twice the change required in lanthanum for the application of the same pressure. We do not think this is surprising in view of the greater inherent instability of the 5*f* levels in uranium, compared with the 4*f* levels in lanthanum.⁷ We would expect, therefore, that a given pressure would result in a proportionally greater increase in the admixture of 5*f* wave functions at the Fermi surface in uranium, than of 4*f* wave functions at the Fermi surface in lanthanum. It does not seem unreasonable that such an increase in the *f* character of the electrons at the Fermi surface would be associated with an increase in the density of states at the Fermi surface.

On the other hand it might be suggested that such a dramatic increase of the superconducting transition temperature upon the application of pressure was due to a pressure-induced phase change. However, there is no sign of a transition in this pressure range in the

⁵ J. J. Katz and E. Rabinovitch, *Chemistry of Uranium* (Dover Publications, Inc., New York, 1951), Part 1.

⁶ L. F. Bates and D. Hughes, *Proc. Phys. Soc. (London)* **B67**, 28 (1954).

⁷ Y.-A. Rocher, *Advan. Phys.* **11**, 233 (1962).

⁸ J. Friedel, *J. Phys. Chem. Solids* **1**, 175 (1956).

⁹ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

TABLE II. Volume effect in uranium.

$\frac{\partial T_c}{\partial p}$ (°K bar ⁻¹)	K (bar ⁻¹)	T_c (°K)	Θ_D (°K)	γ_G^a
10.5×10^{-5}	-8.97×10^{-7}	1.0	200	2.2

^a Estimated.

room-temperature compressibility¹⁰ and resistance¹¹ measurements made by Bridgman.¹² A brief consideration of the elastic-constant data¹³ and the crystal structure of α uranium^{14,15} shows that the effect of increasing pressure is to oppose the formation of an hcp lattice, which might have been thought a possible pressure induced phase change. However, it is conceivable that this increase in T_c is associated with the transition responsible for the anomalous temperature dependence of a number of physical properties of uranium in the region of 40°K.¹⁶⁻¹⁹ At present there is no conclusive evidence to support a crystallographic phase change,¹⁵ but it has been suggested¹⁹ that the anomalous behavior of the physical properties is due to changes in the electronic band structure. As there is a marked increase¹⁵ of the atomic volume below 40°K it might be anticipated that the application of pressure would oppose the transition. However, in the absence of any data relating to the effect of pressure upon this low-temperature transition, a direct correlation between the change of T_c under pressure and this transition is not possible.

This result for uranium is also considered to be further evidence⁴ against the proposed model of Kuper, Jensen, and Hamilton²⁰ for the occurrence of superconductivity in lanthanum and uranium. Though their model of a sharp f level lying just above the Fermi surface may just be feasible for the $4f$ level in lanthanum, it would be extremely unlikely that a similar situation could exist for the $5f$ levels in uranium.⁸

The volume dependence of the BCS expression for the superconducting transition temperature T_c

$$T_c = 0.85\Theta_D \exp[-1/N(0)V],$$

¹⁰ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 55 (1948).

¹¹ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **58**, 158 (1923).

¹² Recent resistance-pressure measurements of C. C. Bradley (private communication) on the A.N.L. uranium are in good agreement with those of Bridgman.

¹³ E. L. Francis, United Kingdom Atomic Energy Establishment Document IGR-R/R-287 (unpublished).

¹⁴ A. N. Holden, *Physical Metallurgy of Uranium* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958).

¹⁵ C. S. Barrett, M. H. Mueller, and R. L. Hitterman, Phys. Rev. **129**, 625 (1963).

¹⁶ W. W. Tyler, A. C. Wilson, and C. J. Wolga, Trans. AIME **197**, 1238 (1953).

¹⁷ T. G. Berlincourt, Phys. Rev. **114**, 969 (1959).

¹⁸ H. M. Rosenberg, Phil. Trans. Roy. Soc. (London) **A247**, 55 (1955).

¹⁹ E. S. Fisher and H. J. McSkimin, Phys. Rev. **124**, 67 (1961).

²⁰ C. G. Kuper, M. A. Jensen, and D. C. Hamilton, Phys. Rev. **134**, A15 (1964).

where Θ_D is the Debye temperature, may be written

$$\begin{aligned} \varphi &= \frac{\partial \ln[N(0)V]}{\partial \ln v} = \left(\frac{\partial \ln T_c}{\partial \ln v} - \frac{\partial \ln \Theta_D}{\partial \ln v} \right) \left[\ln \left(\frac{0.85\Theta_D}{T_c} \right) \right]^{-1} \\ &= \left(\frac{1}{KT_c} \frac{\partial T_c}{\partial p} + \gamma_G \right) \left[\ln \left(\frac{0.85\Theta_D}{T_c} \right) \right]^{-1}, \end{aligned}$$

where K is the compressibility and γ_G is the Gruneisen constant. Using the values given in Table II we have calculated a value of $\varphi \sim -23$. If we now assume that the pressure dependence of T_c arises from the electronic behavior of uranium and is not due to a phase or structural transformation, it is interesting to consider the implication of this value of φ in an empirical relationship which has been suggested by Olsen, Bucher, Levy, Muller, Corenzwit, and Geballe.²¹ This may be written as²²

$$\varphi \sim 10(\alpha - 0.25),$$

where α is a measure of the isotope effect, namely,

$$T_c \propto M^{-\alpha}.$$

Using our calculated value of φ we have obtained a value of $\alpha \sim -2$. However, this calculated value of α requires a considerable extrapolation of the empirical relationship, which has not been determined beyond the value of $\varphi \sim -3$ by Olsen *et al.* and, therefore, little significance should be placed upon the actual numerical value obtained for α . In addition, a further uncertainty in determining the value of α arises in the particular choice of T_c . However, these uncertainties do not affect the sign of α which is the prime outcome; and from the empirical relationship of Olsen *et al.* and the present measurement of the pressure dependence of the superconducting transition temperature we are led to conclude that uranium will exhibit a *positive* isotope effect. However, it must be remembered that such a conclusion depends on the pressure dependence of T_c arising from purely electronic considerations and not a pressure induced phase, or structural change. Unfortunately, in view of the inherent difficulties involved in a direct determination of the isotope effect in uranium²³ there is, at present, little hope of testing this conclusion by direct measurement.

In the BCS theory, α can only have a value of 0.5 since the attractive interaction between electrons originates predominantly from an electron-phonon interaction. Swihart,²⁴ Morel and Anderson,²⁵ and Garland²⁶ have given other treatments which involve modifications (basically in the method of including the

²¹ J. L. Olsen, E. Bucher, M. Levy, J. Muller, E. Corenzwit, and T. Geballe, Rev. Mod. Phys. **36**, 168 (1964).

²² E. Bucher, J. Muller, J. L. Olsen, and C. Palmy, Phys. Letters **15**, 303 (1965).

²³ H. H. Hill (private communication).

²⁴ J. C. Swihart, Phys. Rev. **116**, 45 (1959).

²⁵ P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

²⁶ J. W. Garland, Jr., Phys. Rev. Letters **11**, 111 (1963); **11**, 114 (1963).

screened Coulomb interaction) to the original attractive interaction and obtained values of α from 0.5 to 0. These theories have thus been capable of accounting for the isotope effect in transition metals. It is also possible, by having a screened Coulomb interaction almost as large as the electron-phonon interaction, to obtain a negative value of α , and account for the suggested behavior of uranium.

Finally, neptunium and plutonium have been found to be nonsuperconducting down to 0.41° and 0.5°K, respectively, at atmospheric pressure.²⁷ Susceptibility data show^{28,29} that the 5f electrons are not localized in

²⁷ G. T. Meaden and T. Shigi, *Cryogenics* 4, 90 (1964).

²⁸ L. Weil, G. Quézel, J. Cohen, and R. Pascard, in *Plutonium 1960*, edited by W. B. Lord (John Wiley & Sons, Inc., New York, 1961), p. 104.

²⁹ W. E. Gardner and J. Penfold (unpublished data).

these elements so that their failure to become superconducting may be due to the presence of impurities. Should very pure samples of Pu and Np fail to become superconducting it would be interesting, in view of the instability of the 5f levels, to investigate the effect of applying pressure since one might expect pressure to make them become superconducting at a temperature comparable with that of uranium.

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Longitudinal Spin Relaxation Time of Cr³⁺ in Fe-Doped MgO*

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In this paper we study the longitudinal spin relaxation time T_1 of a paramagnetic ion placed in a crystal doped with paramagnetic ions of a different species which couple strongly to the lattice. As an example, we consider a Cr³⁺ ion placed in MgO doped with Fe²⁺. The presence of the Fe²⁺ ions can significantly affect the longitudinal relaxation time of the Cr³⁺ spin if their concentration is sufficiently high. The magnetic dipole interaction between the Cr³⁺ and Fe²⁺ spins gives a contribution to $1/T_1$ which is comparable in magnitude to the contribution from the Cr³⁺ spin-lattice coupling if there are 10¹⁹ Fe²⁺ spins/cm³. This contribution varies with temperature more slowly than the relaxation time of a Cr³⁺ ion from the one-phonon process in an undoped crystal. The contribution from the Cr³⁺ spin-lattice coupling is also modified by the Fe²⁺ spins, although this effect is small for the concentrations considered here.

I. GENERAL DISCUSSION

RECENTLY a number of studies of the longitudinal spin relaxation time T_1 of the Cr³⁺ ion in ruby have been performed.¹⁻⁷ Many of the measurements have been carried out at liquid-helium temperatures. Microwave fields with a frequency of approximately 10 kMc/sec were employed to excite the spins.

In a pure sample, the spin-lattice relaxation time of Cr³⁺ in ruby is found to be¹ approximately 1 sec at 1°K.

In some of the measurements,¹⁻⁷ T_1 has been found to be a function of the Cr³⁺ concentration. Standley and

Vaughan¹ have suggested that the presence of impurities other than chromium which are strongly coupled to the lattice may allow cross relaxation to occur, because the strong coupling to the lattice may broaden the resonance line sufficiently so that overlap with the Cr³⁺ line may occur. It has also been suggested^{3,8} that the single Cr³⁺ ions may relax by interacting via the magnetic dipole interaction with exchange-coupled Cr pairs.

In this note, we discuss the longitudinal spin relaxation of an ion weakly coupled to the lattice (such as Cr³⁺) which has been placed in a crystal containing a number of ions which couple strongly to the lattice. To be specific, we consider a Cr³⁺ ion placed in an MgO crystal which also contains $\approx 10^{19}$ Fe²⁺ ions/cm³. The spin-phonon coupling constants and g factors are known for both of these ions in MgO.⁹⁻¹¹

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† National Science Foundation Graduate Fellow.

¹ K. J. Standley and R. A. Vaughan (to be published).

² J. C. Gill, *Quantum Electronics* (Columbia University Press, New York, 1960), p. 333.

³ J. C. Gill, *Proc. Phys. Soc. (London)* 79, 58 (1962).

⁴ S. Y. Feng and N. Bloembergen, *Phys. Rev.* 130, 531 (1963).

⁵ J. H. Pace, D. F. Sampson, and J. S. Thorp, *Proc. Phys. Soc. (London)* 76, 697 (1960).

⁶ A. Manenkov and A. Prokhorov, *Zh. Eksperim. i Teor. Fiz.* 42, 75 (1962) [English transl.: *Soviet Phys.—JETP* 15, 54 (1962)].

⁷ A. Atsarkin and V. I. Popov, *Zh. Eksperim. i Teor. Fiz.* 47, 864 (1964) [English transl.: *Soviet Phys.—JETP* 20, 578 (1965)].

⁸ J. H. Van Vleck, *Quantum Electronics* (Columbia University Press, New York, 1960), p. 392.

⁹ A table of spin-phonon coupling constants for transition-metal ions in MgO and references to the original literature may be found in C. D. Jeffries, *Dynamic Nuclear Polarization* (Interscience Publishers, Inc., New York, 1963), p. 68.

¹⁰ W. Low, *Phys. Rev.* 105, 80 (1957).

¹¹ W. Low, *Phys. Rev.* 101, 1827 (1956).