

Low-Temperature Phase Transition in Alpha Uranium

E. S. FISHER

Argonne National Laboratory, Argonne, Illinois

AND

H. J. MCSKIMIN

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received June 2, 1961)

A phase transition in alpha uranium at $42^\circ\text{K} \pm 1^\circ\text{K}$ is indicated by measurements of the single-crystal elastic moduli using ultrasonic pulse techniques. The indicated transition coincides closely to anomalies noted in the thermal expansion, Hall coefficient, electrical resistivity, and thermoelectric power. An examination of the literature specific heat data shows that the transition is associated with an inflection point in the entropy vs temperature curve. On the basis of the elasticity and available lattice parameter data it is postulated that the temperature dependence of the γ positional parameter becomes relatively large in this range and the phase instability is a result of a change in the nature of certain interatomic bonds.

IN an earlier paper we reported on the temperature dependence of the elastic moduli in single-crystal alpha uranium between 78° and 573°K .¹ It was then noted that the stiffness modulus c_{11} changes anomalously in this temperature range, having a maximum value at 256°K , and decreases with increasing temperature coefficient on cooling. These earlier measurements were carried out in an open Dewar flask using the ultrasonic pulse, phase comparison technique.² We have since been carrying out measurements in a liquid helium cryostat in attempting to obtain all nine elastic

moduli for alpha uranium to the range of 1°K . This has turned out to be a much more demanding task than anticipated, primarily because of the high attenuation of the ultrasonic waves in the small specimens in the temperature range below 45°K . The modifications in the technique will be presented at a later date; the results we have obtained to date are, however, most interesting in that the existence of a phase transition at some distinct temperature between 41° and 43°K is definitely shown.

Figures 1, 2, and 3 show the temperature dependence of the 9 elastic moduli as computed from the measured

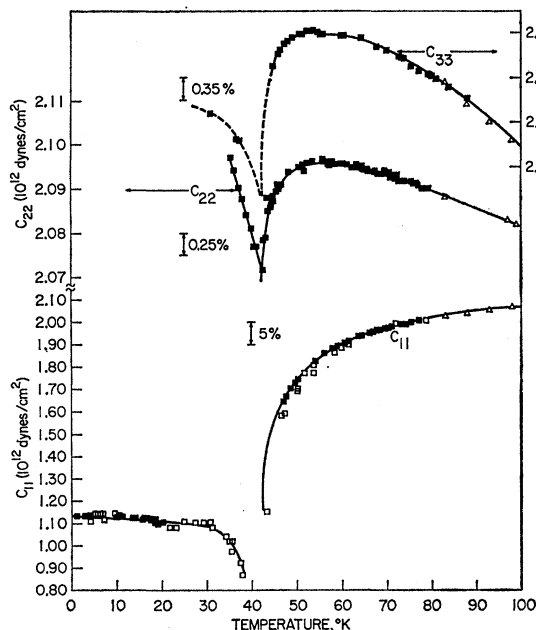


FIG. 1. Temperature variation of c_{11} , c_{22} , and c_{33} . Filled squares are new phase comparison data, open squares are from new time delay data, and Δ 's are from reference 1.

¹ H. J. McSkimin and E. S. Fisher, J. Appl. Phys. **31**, 1627 (1960).

² H. J. McSkimin, IRE Trans. on Ultrasonics Eng. **AE-5**, 25 (1957).

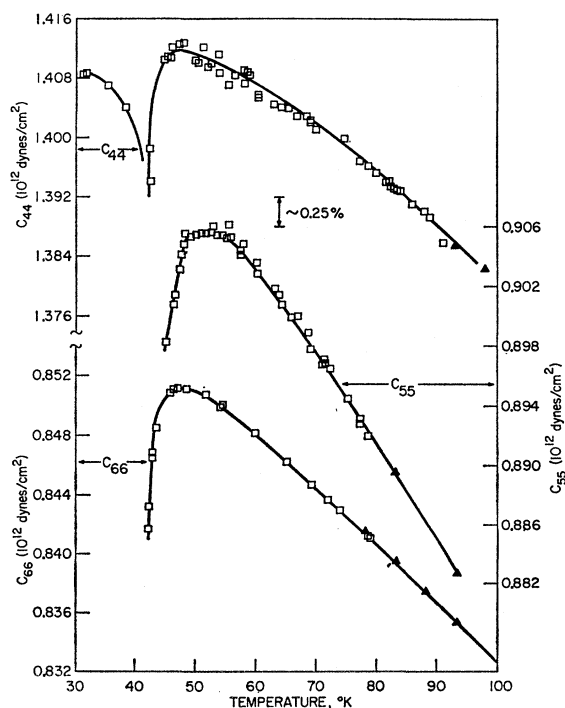


FIG. 2. Temperature variation of shear moduli, c_{44} , c_{55} , and c_{66} . Δ 's are from data given in reference 1.

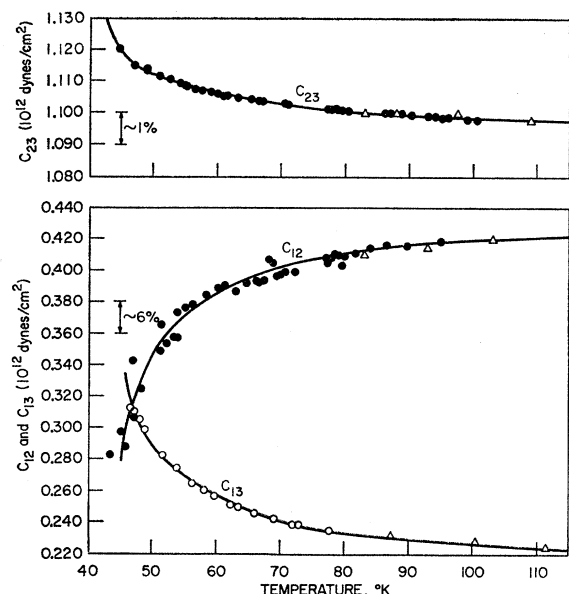


Fig. 3. Temperature variation of cross coupling moduli c_{12} (●), c_{13} (○), and c_{23} (●). Δ 's are from reference 1.

frequency data as follows:

$$(M)_T = \left(\frac{f_T}{f_0}\right)^2 \left(\frac{t_T}{t_0}\right)^2 \frac{d_T}{d_0} (M)_0, \quad (1)$$

where M is the stiffness modulus, f_0 is the measured frequency (between 35–60 Mc/sec) for $n + \frac{1}{2}$ wavelengths in a specimen (n being an integer) at the reference temperature of 77.8°K, f_T is the frequency for the same value of n at the temperature of measurement, t_0 and t_T are the specimen thicknesses, d_0 and d_T are the densities, and $(M)_0$ is the value of M at 77.8°K. Derivation of Eq. (1) is given in reference (1). Based on the reproducibility and the cross-checks afforded, the f_T measurements used for evaluating the data here presented are probably not more than 0.05% in error. In the temperature region where the energy losses in the specimens became unusually large and phasing effects between specimen waves were difficult to observe, the measurements were discontinued. For certain wave modes this region was relatively narrow and the pulses reappeared on passing through the 40°–43°K range. For shear waves, however, the loss mechanism generally persisted on cooling through the range to 30°K.

Because of the very large effect of the transition on c_{11} , the longitudinal wave in the [100] crystal direction was of special interest and measurements were attempted as low as 1.5°K. In this case the phase comparison measurements could not be made in the range 20°–47°K, as noted in the lower curve of Fig. 1. To fill in the gap, direct time-delay measurements were made for a wave traveling a round trip in the specimen. Because of the short times involved (approximately 2 μ sec), these measurements could be more than 1% in error, as indicated by a check in the region where the

2 sets of data overlap. This accuracy is, however, more than adequate to indicate the form of the curve in the region of 50°–20°K, since the modulus decreases to a minimum which is less than 50% of its value at 50°K.

The thickness ratios t_T/t_0 and the density ratios d_T/d_0 in the temperature range between 63°–20°K and 20°–1°K were of necessity estimated by interpolation from the lattice parameter measurements of Bridge *et al.*,³ assuming a continuous curve and zero thermal expansion for the [100] direction and for the volume at 42.5°K. The latter estimate seems reasonable on the basis of the earlier dilatation measurements reported by Laquer.⁴

The c_{11} vs T data clearly indicate a deep trough with possibly a sharp discontinuity in dc_{11}/dT at some temperature between 38° and 43°K. Although the remaining data are not sufficient to determine whether the modulus-temperature slopes are indeed discontinuous, they all show at least quasi-cusps with minimum modulus values between 41° and 43°K. In addition, the dM/dT increase very sharply approaching infinity on cooling to the singular temperature, whereas the recovery of the modulus on the low-temperature side seems to be less spectacular.

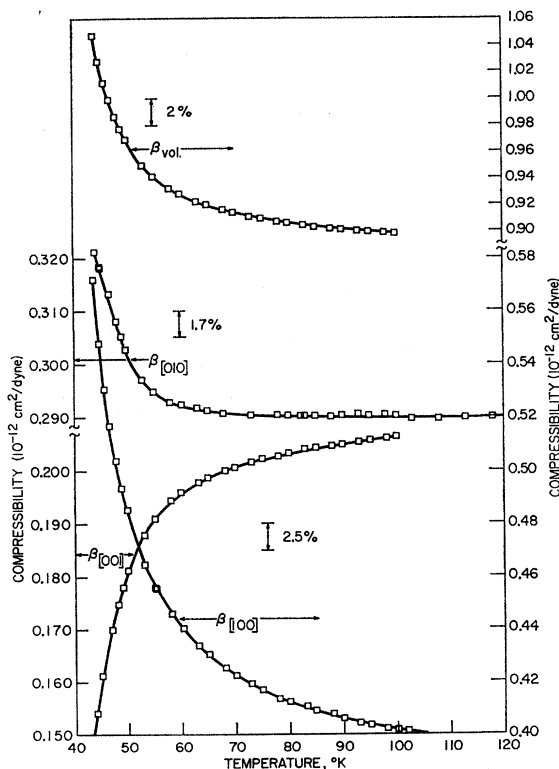


Fig. 4. Temperature variation of linear compressibilities in the principal crystallographic direction and volume compressibility as computed from stiffness moduli.

³ J. P. Bridge, C. M. Schwartz, and D. A. Vaughan, Trans. AIME 206, 1282 (1956).

⁴ H. L. Laquer, Atomic Energy Commission Report AECD 3706, 1952 (unpublished).

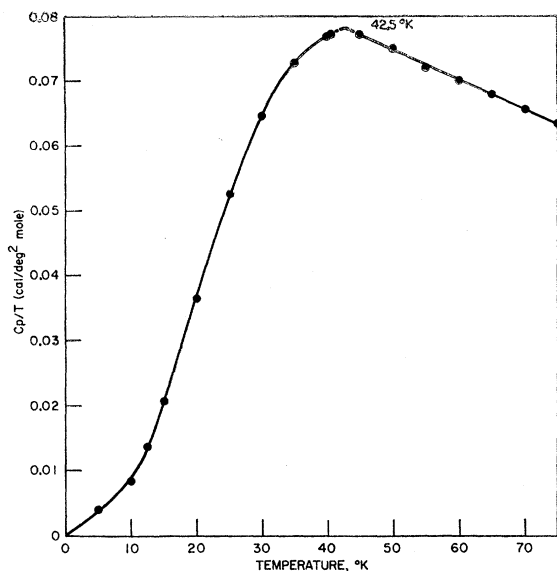


FIG. 5. Specific heat/temperature ratio variation computed from data of Flotow and Lohr.⁸

The anisotropic effects of the transition are probably best shown through a comparison of the temperature dependence of the linear compressibilities in the three principal crystallographic directions, shown in Fig. 4. Between 100° and 44°K, the [100] compressibility increases by greater than 40%, that for [010] increases by 10%, whereas that for [001] decreases by 25%. The net result is about a 15% increase in volume compressibility between 100° and 44°K.

These data are not the first to show that anomalies in the properties of alpha uranium occur in the range of 40° to 60°K. Laquer and collaborators reported in 1952 on the change in sign of the linear thermal expansion coefficients of various polycrystalline samples at 47°K.⁴ Since the initial discovery, anomalies in the temperature dependence of the thermoelectric power between 40° and 45°K,⁵ the Hall coefficient between 18° and 43°K,⁶ and the thermal conductivity at 60°K⁷ have been reported. The specific heat data, however, have shown neither discontinuities nor λ points associated with C_p below the phase transformation at 933°K.⁸ Consequently, there has been no attempt nor, in fact, any justification, to associate these anomalies with a low-temperature transition in the thermodynamic sense. In view of our results, however, we have given a closer look at the specific heat data by plotting C_p/T versus T . The results, given in Fig. 5, show quite clearly that there is a singularity in C_p between 42° and 44°K which causes either a point of inflection or a sharp change in slope in the entropy-temperature curve. In

addition, Berlincourt has reexamined his previously reported electrical resistivity data⁶ and has found a significant evidence of a break in the variation of the slope with temperature, as shown in Fig. 6. Above 200°K the resistivity curve is quite linear and extrapolates to $\rho=0$ at $T=0$. The ρ/T plot is then a gage of the change in the slope of the ρ vs T curve.

It appears, then, that all of the anomalies mentioned above are, together with the elastic moduli anomaly, associated with a transition in the atom arrangement and/or electron band structure occurring at 42° to 44°K. It appears quite conclusive that we are not dealing with a classical first-order transformation and highly probable that second-order transformations involving magnetic changes are not involved. In fact it is not clear, as yet, that there is a thermodynamic instability occurring at the transition which would fit in with the basic requirements proposed by Tisza⁹:

$$\begin{vmatrix} -(\partial P/\partial V)_s & (\partial T/\partial V)_s \\ (\partial T/\partial V)_s & T/C_V \end{vmatrix} = 0,$$

where P , V , T , and s are pressure, volume, temperature, and entropy, respectively. If we assume the volume expansion coefficient to be zero at the transition temperature (as is indicated in reference 4), the instability determinant reduces to

$$\begin{vmatrix} 1/\beta_{vol} & 0 \\ 0 & T/C_P \end{vmatrix} = 0,$$

which is not satisfied unless C_p or the volume compressibility go to infinity. The slopes of the C_p/T curve given in Fig. 5 do not indicate an infinite C_p , and reason does not permit us to deduce an infinite compressibility, although the curve in Fig. 4 rises with almost infinite slope. Consequently, we can only state that on cooling

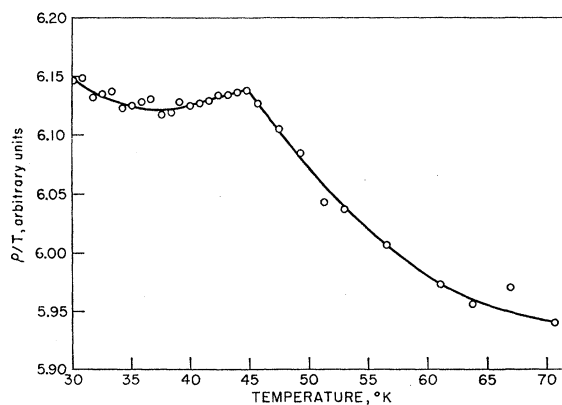


FIG. 6. Ratio of electrical resistance ρ to temperature as plotted against temperature. (Courtesy of T. G. Berlincourt, Atomics International, Inc.).

⁵ W. W. Tyler, A. C. Wilson, and C. J. Wolga, *Trans. AIME* **197**, 1238 (1953).

⁶ T. G. Berlincourt, *Phys. Rev.* **114**, 969 (1959).

⁷ H. M. Rosenberg, *Phil. Trans. Royal Soc. (London)* **A247**, 55 (1955).

⁸ H. E. Flotow and H. R. Lohr, *J. Phys. Chem.* **64**, 904 (1960).

⁹ *Symposium on Phase Transformations in Solids* (John Wiley & Sons, Inc., New York, 1951).

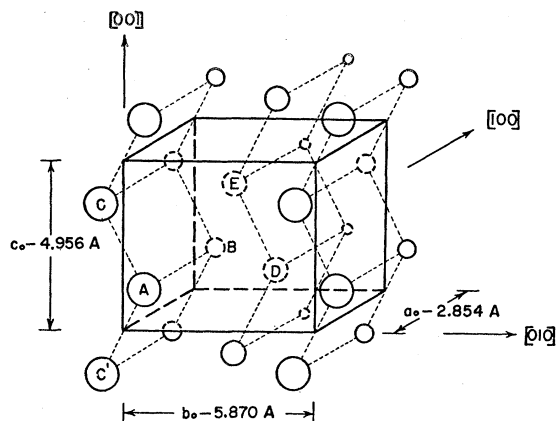


FIG. 7. Atomic arrangement in alpha uranium structure. Lattice parameter values apply to 300°K. Unit cell boundaries are outlined.

or heating to the transition temperature, the structure approaches thermodynamic instability.

In regard to the mechanism of the transition, the primary difference between the two phases is apparently the character of the second-nearest-neighbor bond (atoms *A-B* of Fig. 7 spaced in the $[100]$ direction). At 0°K the modulus c_{11} is about $\frac{1}{2}$ the value which one would obtain by extrapolating from the high-temperature curve assuming a normal temperature dependence. The problem then lies in finding a mechanism by which the number of bonding electrons for this bond changes rapidly with temperature above the transition or a mechanism by which the available bonding electrons are localized to the *AB* bond. We wish here to point out a mechanism which could result in such changes occurring due to somewhat extraordinary changes in the symmetry of the electron distribution. In Fig. 7 is a schematic picture of the alpha-uranium structure in which the basic units are the crooked chains formed by nearest-neighbor bonds.^{10,11} These chains are aligned in the $[001]$ direction and packed so as to give the orthorhombic symmetry of the unit cell. Choosing *A* as the origin, the nearest atoms are *C, C'* at $(0, 2y, \frac{1}{2})$, the second-nearest are at position *B*, $(1, 0, 0)$, the third-nearest at *D*, $(\frac{1}{2}, \frac{1}{2}, 0)$ and the fourth nearest at *E*, $(\frac{1}{2}, \frac{1}{2} - 2y, \frac{1}{2})$. The mechanism we are proposing is based on speculation of the *y*-parameter change (now under study) and is as follows: As the crystal is cooled, the c_0 parameter decreases and the *y* parameter increases so as to decrease the angle between the *AC* and *AC'* bonds and, most important, to decrease the fourth-neighbor distance *AE*. The latter effect begins to weaken the *A*-to-*B* bonding in the range of 300°K, as indicated by the c_{11} and $[100]$ direction compressibility data. In the range of 90°K, the temperature coefficient for the *y* parameter change increases markedly, the "squashing"

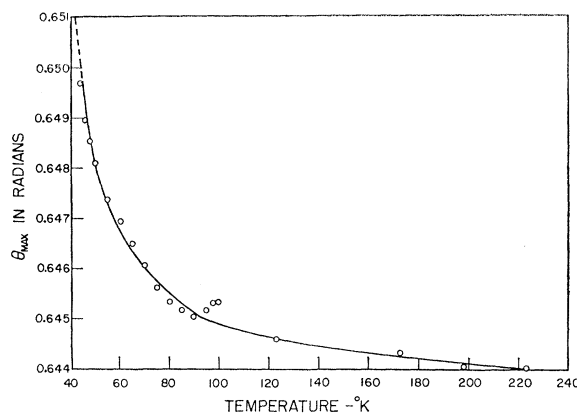


FIG. 8. Variation with temperature of the direction for maximum stiffness, which remains in the (100) plane and inclined to $[001]$ direction by θ_{\max} .

of the chains causing an increasing temperature coefficient for the $[001]$ compressibility (Fig. 4). At the transition, the *AB* bond instability is complete and the *A-B* distance begins to increase to accommodate the more symmetrical electron distribution caused by the packing arrangement. The anomalies in the Hall coefficient, electrical conductivity, and thermoelectric power would then be the result of changes in the band structure at the transition and a gradual reformation of a new stable configuration on cooling to about 20°K.

Further measurements of the lattice parameter changes through the transition temperature will assist in checking the course of the proposed atom movements. The negative thermal expansion for the a_0 parameter is already indicated in reference 3. Changes in the *y* parameter in the low-temperature range are not available, as yet. We do, however, have some further basis for the proposed mechanism from the correlation between the directions of the maximum elastic stiffness, $(c_{33}')_{\max}$, and the nearest neighbor bond, which has been discussed previously.^{1,12} The direction for $(c_{33}')_{\max}$ is in the (100) plane, inclined about 37° to the $[001]$. The changes in inclination angle, which we call θ_{\max} , with temperature is shown in Fig. 8. The increase on cooling from 220° to 90°K may be within the error in the modulus values involved in the computations but the 0.9% change between 90° and 44°K along a relatively smooth curve indicates a significant change in θ_{\max} and implies an increase in either the *y* or the b_0 parameter of over 0.1%. The b_0 increase seems inconsistent with the known data.³

ACKNOWLEDGMENTS

We gratefully acknowledge the participation of T. B. Bateman in carrying out the ultrasonic measurements. We wish to thank Dr. T. G. Berlincourt (Atomics International, Inc.) for supplying the analysis of his electrical resistivity data.

¹⁰ C. W. Jacob and B. E. Warren, J. Am. Chem. Soc. **59**, 2588 (1937).

¹¹ Lattice parameter values given in Fig. 7 are unpublished values of A. Cooper and W. L. Bond.

¹² E. S. Fisher and H. J. McSkimin, J. Appl. Phys. **29**, 1473 (1958).