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# Elastic Moduli and Phase Transition in Uranium at $T < 43^{\circ}K^*$

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The elastic moduli of single crystals of  $\alpha$ -U have been measured with some success at temperatures between 2 and 43°K. Minima in the shear moduli  $c_{55}$  and  $c_{66}$  are observed at 18°K on cooling and at 22.5°K on heating with high acoustic attenuation at  $T < 43^{\circ}$ K. Hysteresis is also observed in the  $c_{11}$  modulus at  $10.5^{\circ}\text{K} < T < 35^{\circ}\text{K}$ . It is concluded that an  $\alpha_0 \rightleftharpoons \alpha$  structural phase change occurs at some temperature between 35 and 43°K and that the two phases are very similar in structure, thus explaining the absence of a heat-capacity anomaly and the coexistence of  $\alpha_0$  and  $\alpha$  over a wide temperature range. It is proposed that the filamentary superconductivity at  $T < 2^{\circ}K$  and the excess electrical resistance at  $4^{\circ}K$  are produced by the  $\alpha$ phase retained by fast cooling.

#### INTRODUCTION

IN a 1961 publication, evidence was presented for a phase transition in α-U at some temperature between 40 and 43°K. At that time the measurements of the single-crystal elastic moduli were the only direct and unambiguous evidence of this transition.

It has since been shown that the volume-expansion coefficient is negative at T < 43°K primarily because of a severe anomaly in the temperature dependence of the  $a_0$  lattice constant of the orthorhombic unit cell.<sup>2</sup> In the present work we have extended the elasticmoduli measurements to include the temperature range 2-43°K. The results indicate that a structural phase change occurs at 37±2°K and that the linear compressibility in the [100] direction of the low-temperature phase is almost twice as large as that in the  $\alpha$  phase.

# EXPERIMENTAL PROCEDURE

The earlier elastic modulus studies in the 43°K range were hampered by fracturing of the cements that were used to acoustically couple the uranium single crystals to the piezoelectric quartz transducers. As a result, only one  $(c_{11})$  of the nine independent elastic moduli could be measured at temperatures below 30°K. A careful search for the possibility of hysteresis effects in  $c_{11}$  was not possible because of the coupling problem. During recent experiments we have found that an acoustic coupling made from Dow Corning Silicone high-vacuum grease can be cooled by an appropriate technique, so that the stresses produced by anisotropic thermal expansion will not fracture the bond. This discovery has enabled the completion of measurements of the nine elastic moduli in the temperature range 44-2°K.

The ultrasonic technique and the preparation of the single-crystal samples have been described in several previous papers.3,4 The measurements were carried out in a He4 cryostat with pumping connections. Temperatures were measured with a calibrated copper-constantan thermocouple.

Although the coupling problem was solved, there remained considerable acoustic attenuation in measurements associated with [100] direction shear displacements at temperatures below 24°K. The [100] direction is coincident with the second-nearest-neighbor bond directions, as shown in Fig. 1. The pure longitudinal waves with displacements along  $\lceil 100 \rceil$ ,  $\lceil 0k0 \rceil$ , and  $\lceil 001 \rceil$ directions, respectively, giving direct measurements of  $c_{11}$ ,  $c_{22}$ , and  $c_{33}$ , respectively, produced no attenuation difficulties at temperatures below 39°K. Similarly, the pure  $c_{44}$  shear mode, which produces a distortion within the (h00) planes, give no attenuation problems. The pure  $c_{55}$  and  $c_{66}$  shear modes, which distort the (00l)

<sup>\*</sup> Work performed under the auspices of the U. S. Atomic Energy Commission.

<sup>&</sup>lt;sup>1</sup> E. S. Fisher and H. J. McSkimin, Phys. Rev. 124, 67 (1961). <sup>2</sup> C. S. Barrett, M. H. Mueller, and R. L. Hitterman, Phys. Rev. 129, 625 (1963).

<sup>&</sup>lt;sup>8</sup> E. S. Fisher and H. J. McSkimin, J. Appl. Phys. 29, 1473 (1958).
<sup>4</sup> H. J. McSkimin and E. S. Fisher, J. Appl. Phys. 31, 1627

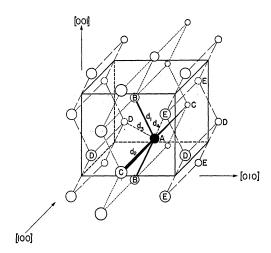


Fig. 1. Crystal structure of  $\alpha$ -U. The (h00) planes contain nearest-neighbor atoms separated by  $d_1$ .  $d_2$  is second neighbor distance [separate (100) planes].  $d_2 > d_1$  by 3.5%,  $d_3 > d_1$  by 18%, and  $d_4 > d_1$  by 21%.

and (0k0) planes, respectively, produced severe acoustic attenuation at temperatures lower than  $24^{\circ}$ K. To measure  $c_{55}$  and  $c_{66}$  at these temperatures it was necessary to prepare single-crystal faces so that pure shear modes could be propagated along directions close to the [001] axis. Thus the crystal designated D', for example, was prepared so that the propagation direction was in the (0k0) plane and inclined 8.2° from the [001] direction. The velocity of the pure shear mode was primarily that of the unattenuated  $c_{44}$  mode but contained a small component of the  $c_{66}$  mode. In contrast, crystal D was oriented for propagation in a direction inclined  $45^{\circ}$  to [001]. The displacements in D contained too much  $c_{66}$  component to permit velocity measurements below  $24^{\circ}$ K.

The attenuation of the  $c_{55}$  and  $c_{66}$  components also caused difficulties in measuring the velocities of the quasilongitudinal modes with propagation directions in the (0k0) or (00l) planes. Thus the cross-coupling moduli  $c_{12}$  and  $c_{13}$  could not be determined at  $4.2 < T < 24^{\circ}\text{K}$  by the most accurate route (from directions inclined  $45^{\circ}$  to the principal axes) but were obtained from the quasilongitudinal modes of crystals D' and F'. At  $4.2^{\circ}\text{K}$ , however, we obtained measurements of the quasilongitudinal and quasishear modes in crystal D that permit a check on  $c_{55}$ , as computed from F', and an accurate evaluation of  $c_{13}$ .

#### RESULTS

 $c_{11}$ 

The complex nature of the results is perhaps best shown in the results of a detailed study of the effects of the heating and cooling cycle on  $c_{11}$ , as summarized in Fig. 2. The precipitous decrease in  $c_{11}$  upon cooling to the 43°K transformation is shown on the right side of the figure. The measurements are interrupted be-

tween 46 and 38°K by attenuation difficulties. It is clear that  $c_{11}$  decreases from a maximum of 2.15 dyn/cm² at 250°K to a minimum less than 0.8 dyn/cm² and that the temperature cycle has no significant affect above 35°K. Upon further cooling  $c_{11}$  decreases as shown by the curve with arrows pointing left. There is a slight minimum at 20°K and a smooth curve between 16 and 2°K. Upon heating from 2°K the curve is reproduced up to approximately 10.5°K at which point the heating curve begins to deviate. The heating curve shows no fine structure between 2 and 22.5°K. At 22.5°K there is an abrupt change to a positive slope which decreases smoothly and becomes negative again above 25°K. The heating and cooling curves coincide at 35±1°K.

These solid lines are perfectly reproducible if the heating and cooling cycles start at 10.5 and 35°K, respectively. When, however, the temperature cycles begin at intermediate points the measurements fall along lines that are schematically represented by the dashed lines lying within the bounds of the full cycle lines.

#### $c_{22}$ and $c_{33}$

As in the case of the upper transition ( $\sim$ 43°K), the effects of the lower transitions on the elastic moduli are markedly anisotropic. The  $c_{22}$  modulus is apparently not affected by the lower transitions, as is shown in the basic data plots of Fig. 3. The ordinate in Fig. 3 is the wave velocity relative to that at 77°K when the dimensional changes are neglected. The dots correspond to data obtained during cooling and the open circles are the points obtained during heating. For  $c_{22}$  the upper transition occurs sharply at 40.5°K and the total change in wave velocity during cooling to 2°K is only 1%, in contrast to >10% velocity change for the  $c_{11}$  mode.

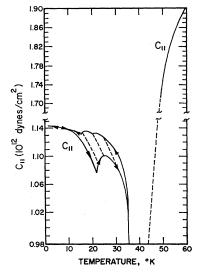


Fig. 2. Temperature dependence of  $c_{11}$  on cooling ( $\leftarrow$ ) and heating ( $\rightarrow$ ). Small dash lines schematically indicate data obtained during interupted thermal cycle.

The indicated hysteresis is extremely small and could be the result of a slight  $c_{11}$  component caused by a  $\pm \frac{1}{4}^{\circ}$  error in orienting the wave-propagation direction.

The  $c_{33}$  data (Fig. 3) do, however, show small but significant effects of the lower transitions, with the upper transitions indicated at 41.5°K. A significant change in slope occurs at  $\sim 38$ °K during both the heating and cooling cycles. No further deviations from a smooth curve are indicated in the cooling data. The heating data, however, show a well-defined change in slope at 22.5°K.

The data shown in the bottom two sections of Fig 3. are from longitudinal waves propagated in two different intermediate directions,  $E_{QL}$  deviating 35.5° from [001] in the (100) plane and  $D_{QL'}$  deviating only 8.2° from [001] in the (010) plane. Both sets of data show the slope change at 38°K that was observed in the  $c_{33}$  data. The  $D_{QL'}$  data show several additional points of interest: (a) The upper transition involves a minimum at 43°K and a sudden shift at 41°K, (b) an abrupt change in slope at 22.5°K on cooling as well as heating, and (c) a well-defined reversal in slope of the cooling curve at 18°K.

#### Shear Moduli

The data obtained for the pure  $c_{44}$  mode and for the pure shear modes that were primarily  $c_{44}$  but contained  $c_{55}$  and  $c_{66}$  components, respectively, are shown in Fig. 4. The pure  $c_{44}$  mode velocity has only a slight dependence on temperature below 43°K and a slight hysteresis

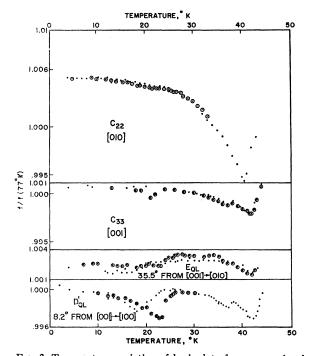


Fig. 3. Temperature variation of basic data for compressional modes  $c_{22}$ ,  $c_{33}$ ,  $\rho V_{E^2}(E_{QL})$ , and  $\rho V_{D^2}(D_{QL'})$ . Dots and circles represent data obtained during heating and cooling, respectively.

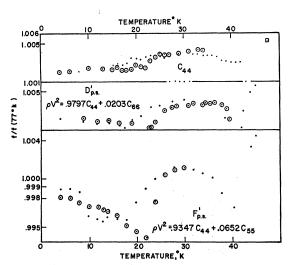


Fig. 4. Temperature dependence of basic data for shear moduli, Dots and circles represent data obtained during heating and cooling, respectively.

between 18 and 24°K. With a  $c_{66}$  contribution,  $D_{PS}'$ , there is clearly a hysteresis between 18 and 30°K and well-defined minima at 18°K on cooling and 22°K on heating. These same features are even more distinct in  $F_{PS}$ , where the  $c_{55}$  component is present. In addition, there appears to be a sudden jump in velocity on cooling below 9°K. The values of  $c_{55}$  computed from these data are shown in Fig. 5. The errors in  $c_{55}$  at temperatures between 18 and 24°K are considerable because of slight uncertainties in the temperature dependence of  $c_{44}$ . Nevertheless, the form of the curve seems clear: There is a maximum at 28°K that is at least 20% greater than the  $40^{\circ}K$  value and at least 30% greater than the minima at 18 and 22°K. There is a sharp increase in  $c_{55}$  below 9°K. The curve of  $c_{66}$ versus temperature (Fig. 6) cannot be defined between 36 and 41°K. Otherwise it appears similar in form to the  $c_{55}$  curve with sharp troughs at 18 and 22°K, on cooling and heating, respectively. It appears that there is also the abrupt increase on cooling below 9°K.

In regard to the accuracy of the  $c_{55}$  and  $c_{66}$  moduli as computed from the data of Fig. 4, an analysis of the probable errors indicates that  $c_{55}$  has a probable error of approximately 10% and the  $c_{66}$  probable error is about 31%, assuming that both  $c_{44}$  and  $\rho V^2$  are known to within 0.3%. The crosschecks at T>24°K, shown in Figs. 5 and 6, indicate, however, that the errors are probably less than 5% in this temperature range. At 4.2°K the hysteresis and the relatively large sensitivity to temperature probably gives rise to greater uncertainties in both  $c_{55}$  and  $c_{66}$ . Nevertheless, the uncertainties are probably less than 10%, as is indicated in the  $c_{55}$  calculations:  $c_{55} = 0.85 \times 10^{12}$  dyn/cm<sup>2</sup> on cooling to 4.2°K and decreases to 0.82×10<sup>12</sup> dyn/cm<sup>2</sup> on warming to 5°K. In addition, the crosscheck on  $c_{55}$ , obtained from 4.2°K measurements of the quasilongitudinal and quasishear modes of crystal D, give a value of 0.817

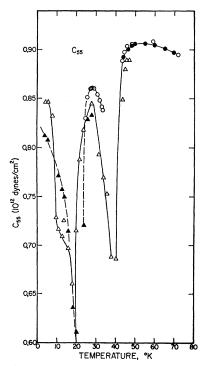


Fig. 5. Variation of  $c_{55}$  shear modulus with temperature. Filled and open triangles represent  $c_{55}$  calculated from  $F^{7}$  data of Fig. 4. Circles at T>43°K calculated from pure  $c_{55}$  mode; circles at T<40°K are from  $\frac{1}{2}(c_{55}+c_{44})$  shear mode.

 $\times 10^{12}$  dyn/cm<sup>2</sup> with a calculated probable error of less than 2%. Although we have no crosscheck on  $c_{66}$  at 4.2°K, the uncertainty in the value calculated from the cooling data of Fig. 4 is probably less than 10%, as in the case of  $c_{55}$ . In Table I, however, the indicated probable errors are obtained from a standard-error analysis.

### $c_{12}$ , $c_{13}$ , and $c_{23}$

The equations for computing the cross-coupling moduli are given in Ref. 4. These moduli are necessary for calculating the compressibility parameters. There is no difficulty in computing  $c_{23}$  at any temperature since this computation involves  $c_{22}$ ,  $c_{23}$ ,  $c_{44}$ , and  $\rho V_{E^2}$ , all of which are well established, with no significant hysteresis. On the other hand, the computation of  $c_{12}$ involves  $c_{11}$ ,  $c_{22}$ ,  $c_{66}$ , and either a quasilongitudal or quasishear wave propagated in the (001) plane. Although we were able to obtain the quasishear velocities in a direction inclined 45° to [100] at T < 38°K, the computation of  $c_{12}$  at  $10^{\circ}\text{K} < T < 23^{\circ}\text{K}$  was subject to considerable error because of the very large uncertainties in  $c_{66}$  and the hysterisis in  $c_{11}$ . For  $c_{13}$  there are similarly large uncertainties in this temperature range. At 4.2°K, however, where the hysterisis in  $c_{11}$  does not exist, the calculated  $c_{12}$  and  $c_{13}$  values are probably accurate and reproducible to within 5%. The probable errors listed in Table I are obtained from standard-error analyses. The linear and volume compressibilities at 4.2°K are also given in Table I.

Table I. Elastic moduli of  $\alpha$ -U at 4.2°K.

Stiffness moduli	Compressibilities
(10¹² dyn/cm²)	(10 <sup>-12</sup> cm <sup>2</sup> /dyn)
$\begin{array}{c} c_{11}=1.143\pm0.3\%\\ c_{22}=2.111\pm0.3\%\\ c_{33}=2.860\pm0.3\%\\ c_{12}=0.286\pm27\%\\ c_{13}=0.347\pm5\%\\ c_{22}=1.129\pm0.5\%\\ c_{44}=1.396\pm0.3\%\\ c_{55}=0.820\pm2\%\\ c_{66}=0.892\pm31\%\\ \end{array}$	$eta_{100} = 0.758 \pm 7\% \ eta_{010} = 0.296 \pm 16\% \ eta_{001} = 0.141 \pm 16\% \ eta_{v} = 1.195 \pm 6\%$

The compressibility-versus-temperature curves are shown in Fig. 7, with the dashed lines indicating that the calculated probable errors in  $c_{12}$  and  $c_{13}$  were larger than 50%. From interpolation it appears that  $\beta_{100}$ , i.e., linear compressibility in the [100] direction, has a sharp peak only on heating (22.5°K) and a very high peak between 38 and 44°K.  $\beta_{010}$  has only slight variations with temperature, whereas  $\beta_{001}$  shows two troughs, at 41 and 22.5°K, respectively. The volume compressibility curve reflects  $\beta_{100}$  primarily. It should be noted that cooling through the upper transition increases  $\beta_{100}$  by almost a factor of 2, whereas the lower transitions have only a relatively small effect on the compressibilities.

#### Debye @ at 4°K

In the Debye theory, the lattice contribution to the specific heat increases with the third power of the parameter (T/Q);

$$C_v \sim (T/\Theta)^3$$
, (1)

where  $\Theta$ , the Debye temperature, is a single parameter

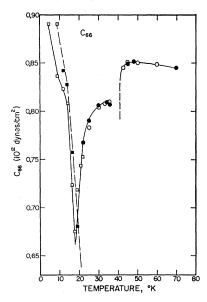


Fig. 6. Variation of  $c_{66}$  shear modulus with temperature. Filled and open squares represent  $c_{66}$  calculated from D' data of Fig. 4. Circles at T>43°K calculated from pure  $c_{66}$  mode; circles at T<40°K are from  $\frac{1}{2}(c_{66}+c_{44})$  shear mode.

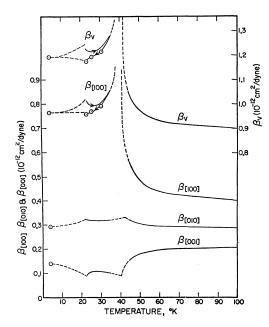


Fig. 7. Temperature dependence of linear and volume compressibilities. Dashed lines indicate uncertainties greater than 3% in ordinate.

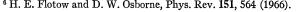
characteristic of the average vibrational frequency at  $0^{\circ}$ K. The Debye  $\Theta$  can be computed directly from an averaging of the acoustic wave velocities and can be determined experimentally from heat-capacity data. The agreement between the two results for a given material is generally within 2% when the computations use the elastic moduli measured at 4.2°K and the heat capacities have been accurately measured at sufficiently low temperatures. The Debye  $\Theta$  for  $\alpha$ -U has been computed by Neighbours<sup>5</sup> from the elastic moduli given in Table I using a computer averaging program. Neighbours's Debye  $\Theta$ , averaging over 30 000 wave-propagation directions is 248.17°, assuming no errors in elastic moduli. This is approximately 12% higher than the 222°K Debye Θ evaluated from the recently published data of Flotow and Osborne.6

This large deviation between  $\Theta_e$  (elastic) and  $\Theta_s$ (calorimetric) indicate that there are significant contributions to the lattice heat capacity other than the acoustical modes. There remains the possibility, however, that the deviations arise because of either accidental errors in the modulus measurements or that the moduli at 4.2°K are not reproducible because of the observed hysteresis. These possibilities appear unlikely in view of the following evidence.

The value of  $c_{11}$  at  $4.2^{\circ}$ K noted in Table I represents at least eight different complete runs, starting from room temperatures, with two different crystals. Two of the runs were actually carried out by McSkimin in 1961, with different equipment and different coupling

<sup>&</sup>lt;sup>5</sup> J. R. Neighbours, U. S. Naval Post Graduate School, Monterey, Calif. (unpublished).

<sup>6</sup> H. E. Flotow and D. W. Osborne, Phys. Rev. **151**, 564 (1966).



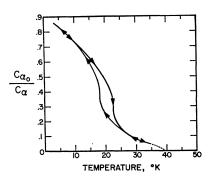


Fig. 8. Schematic representation of the relative concentrations of  $\alpha$  and  $\alpha_0$  phase uranium at T < 43°K, as suggested by elastic moduli.

cements than used in the present measurements. All of the  $c_{11}$  measurements at 4.2°K agree within 0.5%. The estimated 0.3% probable error allows for the accumulation of small corrections, noted in Ref. 4. The same probable error is assigned to  $c_{22}$ ,  $c_{33}$ , and  $c_{44}$ , all of which are direct measurements and show no evidence of hysteresis at  $T < 20^{\circ}$ K. The uncertainties in  $c_{23}$ ,  $c_{55}$ ,  $c_{66}$ ,  $c_{12}$ , and  $c_{13}$  are discussed above.

A straightforward analysis of the effects of errors in the moduli on the Debye  $\Theta$  can be obtained from Anderson's method<sup>7</sup> of computing the average wave velocity. This method gives a value of  $253\pm4^{\circ}$ K for  $\Theta_{e}$ calculated from the moduli and probable errors of Table I. Although this value differs from that given by the computer technique, because it represents a poorer statistical average, the error of  $\pm 4^{\circ}$ K would apply to the 248°K value of  $\Theta_e$  given by the computer method. It is thus unlikely that the 26°K deviation between  $\Theta_{\epsilon}$  and  $\Theta_{\epsilon}$  can be accounted for by accidental errors or by uncertainties caused by the hysteresis in the measurements.

# DISCUSSION OF RESULTS

# Interpretation of Elasticity Results

On the basis of the x-ray diffraction measurements of Barrett et al.,2 and several studies6-8 of the heat capacity in U, it has been assumed that the phase transition at 43°K does not involve a structural transformation. It appears from the present data, however, that a structural transformation does in fact occur at temperatures between 35 and 43°K. From the absence of observed x-ray diffraction and heat-capacity evidence and the absence of effects on the  $c_{22}$  and  $c_{44}$  elastic moduli, it may be surmised that the  $\alpha$  structure and the lowtemperature structure, henceforth referred to as  $\alpha_0$ , are extremely similar in crystal symmetry, lattice constants, and total entropy. We would then expect a very sluggish transformation with a strong coherency between the  $\alpha$ 

<sup>&</sup>lt;sup>7</sup> O. L. Anderson, J. Phys. Chem. Solids 24, 909 (1963) <sup>8</sup> B. B. Goodman, J. Hillairet, J. J. Veyssie, and L. Weill, in Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960 (University of Toronto Press, Toronto, 1961), p. 350.

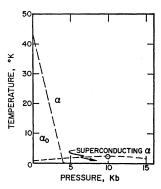


Fig. 9. Generalized temperature-pressure equilibrium-phase diagram constructed on the basis of theory for the pressure dependence of superconductivity in (Ref. 13).

and  $\alpha_0$  crystal lattices. We would also expect the effects of the transformation to be observed over a wide range of low temperatures, thus accounting for the hysterisis observed in the present work as well as the effects of quenching and reheating on the dilatation<sup>9</sup> and electrical resistance. 10 The following discussion presents a qualitative interpretation of the anomalies in the elastic moduli, based on the presumed strong coherency between coexisting phases and a sluggish transformation. It appears from the thermal-expansion data and the present measurements that the  $\alpha$  and  $\alpha_0$  phases differ primarily in the  $a_0$  lattice constant, the linear thermal expansion coefficient  $\alpha_{100}$ , and the linear compressibility  $\beta_{100}$ . From the fact that the hysterisis in  $c_{11}$ begins at 35°K on cooling and from the observed slight anomalies in the c<sub>33</sub> data at 38°K we presume that the  $\alpha_0$  phase, i.e., the low-temperature crystal structure, begins to form as coherent nuclei within the  $\alpha$  matrix upon cooling to the temperature range of  $37\pm2^{\circ}$ K. We presume that  $a_0$  lattice constant has a thermal expansion coefficient  $\alpha_{100}$  that is very large and negative relative to  $\alpha_{010}$  and  $\alpha_{001}$  and is also larger than  $\alpha_{100}$  of the  $\alpha$ phase. During further cooling, elastic shear stresses develop because of coherency in  $\{0k1\}$  planes in  $\langle 100 \rangle$ directions. There is then an internal elastic relaxation superimposed on the externally produced  $c_{55}$  and  $c_{66}$ shear displacements. As this effect increases with decreasing temperature, the measured  $c_{55}$  and  $c_{66}$  moduli reach a maximum and begin to decrease sharply in the range 36-30°K. In addition, the acoustic attentuation for both the  $c_{55}$  and  $c_{66}$  shear modes increases sharply. In contrast, the  $c_{44}$  shear modulus would be unaffected,

The sharp changes in slope of the  $c_{55}$  and  $c_{66}$  curves at 18°K apparently reflect the relief of the internal stresses by either the loss of complete coherency and the development of defects between (0k1) planes of the two phases, or by the accelerated growth of coherent  $\alpha_0$ plates as the elastic constraints decrease. The acoustic

attenuation would not necessarily be relieved by either mechanism, because of relaxation associated with either dislocations or point-defect dipoles. The dilatation measurements9 indicate that the interface movement is probably involved, i.e., the [010] and [001] directions continue to expand and contract, respectively, when the crystals are slow cooled from 25°K, whereas thermal expansion is inhibited in fast-cooled samples.

The coherency stresses between the two phases apparently create extensional strains in the [100] direction of the  $\alpha$  phase during cooling, as well as shear strains. The relaxation of the extensional strains during heating is presumed to be partially responsible for the hysteresis in  $c_{11}$  between 10.5 and 35°K. Similar to the case of the shear moduli, the relaxation effect (the difference between cooling and heating values of  $c_{11}$ ) reaches a maximum at 22.5°K as the  $\alpha_0$  domains begin to expand and decreases gradually to zero at 10.5°K. The dilatation measurements indicate that  $\alpha_{100}$  of both phases decrease rapidly upon cooling below this temperature: Thus we should expect the heating and cooling curves of  $c_{11}$  to coincide at T < 10.5°K, without regard to the relative concentrations of  $\alpha$  and  $\alpha_0$ . There are indications, however, that the coincidence of the curves at T < 10.5°K may be the result of almost complete transformation to  $\alpha_0$ . The fine structure, i.e., the small anomalies, in the cooling curve of  $c_{11}$  at T < 24°K, suggest that the ratio of phase concentrations may be changing rapidly during a slow cool from 24°K and that the  $\alpha \rightarrow \alpha_0$  transition is almost complete at T < 16°K. The  $c_{11}$  curve obtained on warming from T < 10.5 to 22.5°K may then represent the temperature dependence of  $c_{11}$  in pure  $\alpha_0$ . The change in slope at 22.5°K on warming can reasonably be taken as the beginning of the  $\alpha_0 \rightarrow \alpha$  transformation, which is almost complete near 35°K.

# CONCLUSIONS

On the basis of the elastic modulus measurements we conclude that coherent nuclei of an  $\alpha_0$  phase, that differs slightly in crystal structure from  $\alpha$ -U, are present within the  $\alpha$  matrix at temperatures that are within 5-8°K below the electronic transition at 43°K. Since the 43°K transition is presumed11 to be similar in character to that in  $\gamma \rightleftharpoons \alpha$  cerium, the existence of a structural change is to be expected. The growth in concentration of the  $\alpha_0$  phase as a function of temperature is presumed to follow the schematic diagram given in Fig. 8. Between ~38 and ~20°K (18 on cooling and 22.5°K on warming), the α<sub>0</sub> phase remains tightly coherent with the  $\alpha$  matrix and produces elastic stresses that result in shear distortions in (100) directions of  $\{0k1\}$  planes and in extensional strains in  $\langle 100 \rangle$  directions. At  $T < 10^{\circ}$ K the  $\alpha_0$  phase grows rapidly and becomes the predominant phase on slow cooling to 10.5°K.

K. Andres, following paper, Phys. Rev. 170, 614 (1968).
 J. C. Jousset, Acta Met. 14, 193 (1966).

<sup>&</sup>lt;sup>11</sup> T. H. Geballe, B. T. Matthies, D. Andres, E. S. Fisher, T. F. Smith, and W. H. Zachariesen, Science 152, 755 (1966).

The reversion to a predominant concentration of  $\alpha$ begins at 22.5°K on warming.

Because of the very small entropy difference between  $\alpha$  and  $\alpha_0$  and the relatively large elastic restraints at T < 10.5°K, it is presumed that the  $\alpha \rightarrow \alpha_0$  transition does not go to completion and, consequently, metastable  $\alpha$  phase and crystalline defects exist at very low temperatures. If we assume that the  $\alpha$  phase is the bulk superconductor produced under high pressures, 12 the superconducting filaments that are apparently present at ambient pressures may be the metastable  $\alpha$  phase. In a sluggish transformation it is not uncommon to find that the degree of transformation depends on the stress within the sample prior to transforming. The observed dependence of the filamentary superconducting transition temperature on metallurgical history of uranium samples<sup>13</sup> could be directly related to the stress concentration around the  $\alpha$ -phase particles remaining at T < 1.5°K.

With regard to the pressure-induced bulk superconductivity, it was previously assumed that this was brought about by a reduction in volume without a crystal-structure transition.12 The present results suggest that the  $\alpha_0 \rightarrow \alpha$  transition does occur at some pressure below 10 kbar, as indicated in the proposed equilibrium T-P diagram of Fig. 9. Elastic moduli measurements under pressure at T < 43°K are planned to establish the validity of the  $\alpha/\alpha_0$  phase-boundary

It was noted above that the Debye  $\Theta$  as computed from the 4°K elastic moduli is at least 12% higher than that determined from several sets of heat-capacity data  $\Theta_s$ . The agreement between  $\Theta_s$  and  $\Theta_e$  in other metals is invariably less than 5%, when the heat capacity is obtained at very low T. Thus we believe that the deviation in uranium is significant and reflects the contribution of the phase change and/or of defects in the lattice<sup>14</sup> to the vibrational heat capacity.

Jousset et al. 10 reported the observation of an excess electrical resistance in uranium wires quenched from above 22.5°K. The excess resistance is gradually annealed out by pulse heating to T < 22.5°K. These results are quite similar to the dilatation measurements of Andres,9 where rapid cooling inhibited thermal expansion. It appears that both sets of observations can be explained as a quenching in of the strained lattice formed by the fine coherent  $\alpha_0$  phase. The annealing effects are produced by the growth of the  $\alpha_0$  domains and dimunition of elastic stresses as T approaches 22.5°K.

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<sup>13</sup> W. E. Gardner and T. F. Smith, Phys. Rev. 154, 309 (1967).

<sup>&</sup>lt;sup>14</sup> H. B. Rosenstock, J. Phys. Chem. Solids **12**, 41 (1959).