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Thermal Expansion of Alpha-Uranium below 10°K

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The thermal-expansion coefficient of α-U (orthorhombic) remains negative in the a and b directions and positive in the c direction below 43°K, the reported temperature for a suggested phase transition. Below 5°K, the temperature dependence of the three expansion coefficients can be described by

$$\alpha_1=(1/a)\partial a/\partial T=-21\times10^{-8}T-27\times10^{-10}T^3,$$
$$\alpha_2=(1/b)\partial b/\partial T=-3.7\times10^{-8}T-3.1\times10^{-10}T^3,$$
$$\alpha_3=(1/c)\partial c/\partial T=+5.0\times10^{-8}T+3.2\times10^{-10}T^3.$$

It is shown that these results are thermodynamically consistent with the pressure dependence of the specific heat observed by Ho *et al.* Hysteretic behavior is observed in that the linear dimension of the crystal at 0°K depends on the speed of cooling in the range 25–15°K.

I. INTRODUCTION

RECENT studies of the superconducting properties of α-U single crystals[1] and α-U under pressure[2] have shed new light on the mechanism of the transition which this material undergoes below 43°K and which has been observed first by studies of the elastic properties of the crystal[3] and then also by x-ray analysis.[4] According to the latter work, the transition manifests itself by an anomalously large increase in the a and b parameters (0.3 and 0.045%, respectively) and a corresponding decrease in the c parameter (−0.08%) below 43°K down to absolute zero, the symmetry of the unit cell remaining apparently unchanged. Neutron-diffraction studies show extra lines in the whole temperature range below room temperature, which eventually could be accounted for by the presence of a sublattice of magnetic moments.[4] However, no evidence for a magnetic-ordering phenomenon is so far available from magnetic-susceptibility measurements. The compressional as well as the shear elastic moduli show sharp decreases at 43°K. These constants increase again below this temperature and show further anomalies below 25°K. The recent work of Ho *et al.*[2] has demonstrated the extreme strain sensitivity of the superconducting transition temperature and the electronic specific heat. A hydrostatic pressure of 10 kbar applied to a polycrystalline sample increased the transition temperature to 2°K and also increased the electronic specific heat by 18%.[2] While superconductivity was detected at 0.2°K in some unstrained crystals,[1] an anomalous rise in the specific heat below 0.7°K at zero pressure, which could not be accounted for by a hyperfine contribution of U^{235}, disappeared at 10 kbar. All these phenomena are qualitatively consistent with the hypothesis that below 43°K a certain fraction of conduction electrons gradually condenses into $5f$-like states, thereby reducing the cohesive energy.[1,5] Studies of the thermal expansion at low temperatures, on which we report in this paper, were undertaken with the aim of determining whether the expansion anomaly below 43°K is due to an extreme strain sensitivity of mainly the cohesive energy or the lattice vibrations.

II. EXPERIMENTAL TECHNIQUE

The measurements were made using the capacitor technique described by White.[6] The crystals used were kindly furnished by E. Fisher from Argonne National Laboratory. They were typically of a size 2×3×5 mm. Copper endpieces were glued to the crystals with epoxy resin, and the composite sample was then screwed to the bottom plate of the capacitor cell. The gap between the upper copper endpiece and the top plate of the cell was typically 4 mil at low temperatures, corresponding to a capacity of 7 pF. The thermal expansion was thus measured relative to copper. A calibrated Ge thermometer is used to monitor the temperature of the cell. A superconducting solenoid around the cell permits fields up to 30 kOe to be generated in order to study magnetostrictive effects.

III. EXPERIMENTAL RESULTS

In the temperature range below 25°K, the thermal expansion shows hysteretic behavior in all three directions. The a and b dimensions reach their largest values at 1°K either after cooling slowly (several minutes) from 25°K or after repeated thermal cycling between 1 and about 13°K. The c dimension reaches its smallest value in this way. Observed relative changes in length below 15°K in the three principal directions are shown in Fig. 1. The cooling curves were taken slowly; the warming curves were taken after a fast cooldown

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[1] T. H. Geballe, B. T. Matthias, K. Andres, E. S. Fisher, T. F. Smith, and W. H. Zachariasen, Science **152**, 755 (1966).

[2] J. C. Ho, N. E. Phillips, and T. F. Smith, Phys. Rev. Letters **17**, 694 (1966).

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[6] G. K. White, Cryogenics **1**, 151 (1961).

(~30 sec) from 30°K. The hysteresis effects in the lattice parameters are $\Delta a/a=5.6\times10^{-5}$, $\Delta b/b=1.1\times10^{-5}$, and $\Delta c/c=-1.2\times10^{-5}$. From the work of Barrett *et al.*, one estimates that the lattice parameter changes from 43°K down to absolute zero are $\Delta a/a=3\times10^{-3}$, $\Delta b/b=4.5\times10^{-4}$, and $\Delta c/c=-8\times10^{-4}$. The observed hysteresis effects therefore suggest that at least 2% of the crystal remains untransformed upon rapid cooling. It should be pointed out that Fisher *et al.*[7] also have observed hysteretic behavior in the elastic constants in the temperature range 10–35°K. These authors, in fact, find evidence for still another structural transformation which occurs between 35 and 43°K but which involves only an extremely small symmetry change.

The thermal-expansion data between 1.5 and 10°K were always taken after slow cooling and were reversible. These data then must be characteristic of the completely transformed crystal, for the following two reasons: First, because of the reversibility, any remaining untransformed material (less than 2% according to the aforementioned) remains untransformed in this temperature range. Secondly, the thermal-expansion contribution of this untransformed material would be negligibly small, since the untransformed crystal must have a much smaller (presumably positive) thermal-expansion coefficient. The results are shown in Fig. 2, where the relative change in length from 0°K, divided by T^2, is plotted against T^2 for three principal directions. The data actually represent the difference in expansion between the sample and the copper cell, the latter, however, being almost negligible. The changes in length from 0 to 1.5°K have been obtained by extrapolating the expansion coefficient from above 1.5°K to zero and integrating back to 1.5°K. The deviations from the straight lines at low temperatures shown in Fig. 2 largely stem from errors of this extrapolation.

It can be seen that below 7°K, $\Delta l/lT^2$ can reasonably well be fitted to a temperature dependence of the form

$$\Delta l/lT^2=\tfrac{1}{2}a+\tfrac{1}{4}bT^2, \qquad (1)$$

(straight lines in Fig. 2), where a and b are the coefficients of the electronic and lattice thermal expansion, respectively. The expansion of the copper cell can be described by[8]

$$(\Delta l/lT^2)_{\mathrm{Cu}}=1\times10^{-10}+0.7\times10^{-11}T^2.$$

Including this small correction due to the cell expansion, the expansion coefficients of α-U are, below 7°K, well represented by

$$\alpha_1=(1/a)\partial a/\partial T=-21\times10^{-8}T-27\times10^{-10}T^3,$$
$$\alpha_2=(1/b)\partial b/\partial T=-3.7\times10^{-8}T-3.1\times10^{-10}T^3,$$
$$\alpha_3=(1/c)\partial c/\partial T=+5.0\times10^{-8}T+3.2\times10^{-10}T^3.$$

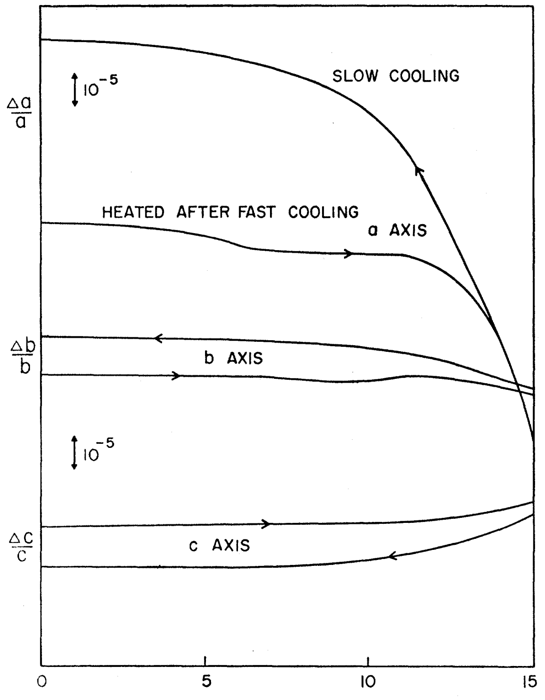

FIG. 1. Observed changes in the three lattice parameters upon slow cooling and upon slow heating after fast cooling.

Above 7°K, α_1 and α_2 go more strongly negative than described above. No magnetostriction in fields up to 30 kOe was detected at all temperatures.

IV. DISCUSSION

The results in Fig. 2 show that below 7°K, the linear terms in the temperature dependence of all the three principal expansion coefficients dominate. This means that in this temperature range, the thermal expansion is predominantly due to the conduction electrons. The ratio of the three coefficients of the linear terms in Eq. (1) ($-21:-3.7:+5\times10^{-8}/°\mathrm{K}^2$) is similar to the lattice parameter changes between 0 and 43°K observed

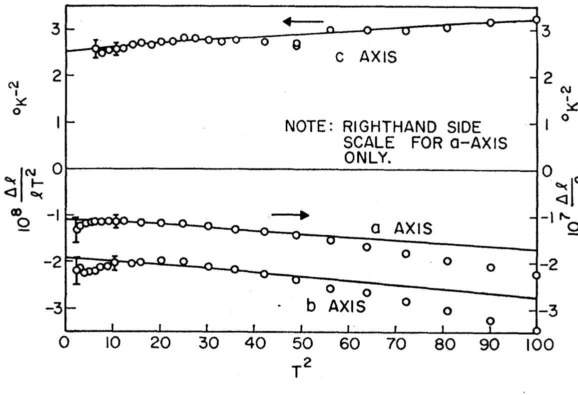

FIG. 2. Observed relative length changes, divided by T^2, in the three principal directions of α-U, plotted against T^2.

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by Barrett *et al.*[4] ($-30:-4.5:-8\times10^{-4}$). This suggests that the whole change is mainly an electronic effect which arises from an unusually large strain dependence of the energy of some electron states near the Fermi surface. It is useful to compute the Grüneisen parameters out of the thermal expansion coefficients, the elastic constants, and the specific heat. They are a measure of the strain dependence of the specific heat[9,10] and allow a comparison of the thermal expansion results with specific-heat measurements under pressure as well as a comparison with Grüneisen parameters of other materials. In a temperature range where the electronic and lattice contributions to the thermal expansion and the specific heat can be separated from each other, both the strain dependence of the electronic and lattice specific heat can be computed. This is done in Sec. V.

In the Voigt notation, the stress-strain relations are

$$\epsilon_i=\sum_j s_{ij}\sigma_j;\quad \sigma_i=\sum_j c_{ij}\epsilon_j,\quad i,j=1,\cdots,6. \qquad (2)$$

For orthorhombic symmetry, the nonzero components of C are c_{11}, c_{22}, c_{33}, c_{44}, c_{55}, c_{66}, c_{12}, c_{13}, and c_{23}. The thermal expansion coefficient in the three principal directions is given by[9]

$$\frac{V}{c}\alpha_i=\sum_j s_{ij}\Gamma_j,\quad i,j=1,\cdots,3 \qquad (3)$$

where V is the molar volume and c is the molar specific heat. Γ_j is the Grüneisen parameter which is a thermal average of the strain dependence of the electronic specific heat $[\Gamma_{e,j}=\partial(\ln c_e)/\partial\epsilon_j]$ and the phonon vibration frequencies $[\Gamma_{l,j}=-\langle\partial(\ln\omega_k)/\partial\epsilon_j\rangle]$ with respect to strain ϵ_j. s_{ij} in Eq. (3) is zero for $i=1,\cdots,3$, $j=4,\cdots,6$, so that only $\Gamma_1,\cdots,\Gamma_3$ enter in the thermal expansion. By analogy with Eq. (2), Eq. (3) can be solved for Γ_1;

$$\Gamma_i=\sum_j \frac{V}{c}c_{ij}\alpha_j,\quad i,j=1,\cdots,3. \qquad (4)$$

At low temperatures, both c and α can be separated into a contribution from the electrons (varying linearly with temperature) and a contribution from the phonons (changing with the cube of the temperature). Thus an electronic as well as a "lattice" Grüneisen parameter can be defined, in the following way:

$$\Gamma_{e,i}=\sum_j \frac{V}{c_e}c_{ij}\alpha_{e,j},\quad \Gamma_{l,i}=\sum_u \frac{V}{c_l}c_{ij}\alpha_{l,j},$$

where

$$\Gamma_{e,i}=\partial(\ln\gamma_e)/\partial\epsilon_i,$$
$$\Gamma_{l,i}=-\partial(\ln\Theta)/\partial\epsilon_i.$$

Most of the nine elastic constants are known in the whole temperature range 4–923°K through the extensive work of Fisher *et al.*[3,7,11–13] The cross coupling moduli are known only down to 45°K, and their values at 0°K have been estimated by extrapolation. The values of the six elastic constants of interest at 0°K are (in units of 10^{12} dyn/cm^2)

$$c_{11}=1.14,\qquad c_{22}=2.11\pm2\%,$$
$$c_{33}=2.86\pm2\%,\quad c_{13}=0.35\pm5\%,$$
$$c_{12}=0.29\pm5\%,\quad c_{23}=1.13\pm2\%.$$

With these values, the data in Eq. (1), and the specific-heat data of Ho *et al.*[2] ($c=10.3T+0.323T^3$ mJ/°K^2 mole) and using Eq. (4), we compute the following electronic and lattice Grüneisen parameters at low temperatures:

$$\begin{aligned}\Gamma_{e,1}&=-27.2, & \Gamma_{l,1}&=-11.1,\\ \Gamma_{e,2}&=-4.6, & \Gamma_{l,2}&=3.2,\\ \Gamma_{e,3}&=+3.2, & \Gamma_{l,3}&=+0.5.\end{aligned} \qquad (5)$$

The Grüneisen parameter for a hydrostatic deformation is given by

$$\Gamma_v=\sum_i\frac{\beta_i}{\beta}\Gamma_i,\quad i=1,\cdots,3 \qquad (6)$$

where β_i are linear compressibilities and $\beta=\sum\beta_i$ is the volume compressibility. With the values of β_i given by Fisher at 4°K[7] ($\beta_1=0.76$, $\beta_2=0.29$, $\beta_3=0.14$, $\beta=1.20\times10^{-12}$ cm^2/dyn), we compute

$$\Gamma_{ev}=-17.9=\partial(\ln\gamma_e)/\partial\ln V, \qquad (7)$$
$$\Gamma_{lv}=-7.8=-\partial(\ln\Theta)/\partial\ln V, \qquad (8)$$

where γ_e is the electronic specific heat and Θ is the Debye temperature). Ho *et al.* have measured the specific heat of α-U both at zero pressure and at 10 kbar. They observe an increase in γ_e from 10.3 to 12.2 in J/°K^2 mole, a possible change of the Debye temperature being outside their detection limit. Using Fisher's compressibility value at 4°K,[7] this increase corresponds to a mean value of Γ_e of -18 in this pressure range, which is in good agreement with the value of 17.9 [Eq. (7)] deduced from thermal expansion.

Negative values of Γ_e of this order of magnitude have so far been found only in antiferromagnetic materials such as β-Ce (hcp) ($\Gamma_e\sim-15$)[10] and chromium ($\Gamma_e=-8.5$).[9] In both these cases, the Néel temperature T_N decreases under pressure.[10,14] The negative value of Γ_e and the positive value of $\partial(\ln T_N)/\partial\ln V=+22$ for Cr have recently been interpreted as being due to a change with volume of the fraction of elec-

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trons on the Fermi surface which condense into the spin-wave state,[15] where they no longer contribute to the linear terms in the specific heat and the thermal expansion coefficient. In β-Ce it is well known that the number of $4f$ states can be decreased to zero by raising their energy above the Fermi level with a pressure of the order of 10 kbar.[16] The similarity of the thermal-expansion anomalies in β-Ce (relative volume increase of 2.1×10^{-4} below the Néel temperature of 13°K) and α-U (relative volume increase of 2.6×10^{-3} below the phase transition temperature of 43°K) suggests that in α-U, too, conduction-electron states condense into $5f$-like states which order antiferromagnetically, as has been proposed before by various authors.[3–5] By analogy, one would predict that the phase transition temperature of α-U also decreases under pressure. However, as mentioned before, no clear evidence of an antiferromagnetic state has so far been offered. According to theory,[17] spin-wave excitations from an antiferromagnetic ground state (in the absence of magnetocrystalline anisotropy) should contribute a T^3 term to both the specific heat and the thermal-expansion coefficient. The fact that $\Gamma_{l,v}$ [Eq. (8)] is negative may be an indication for the presence of such a term. Otherwise this negative value could also be explained by the observations of Fisher *et al.* that most of the elastic constants increase below 43°K. If we assume a negative pressure dependence of this phase transition temperature, this would lead to a negative pressure dependence of these elastic constants below the transition. This in turn would mean negative pressure dependencies of certain acoustic phonon frequencies and possibly a negative lattice Grüneisen parameter at low temperatures.

V. CONCLUSIONS

The negative thermal expansion of α-U below 7°K is mainly electronic in origin. The negative electronic Grüneisen parameter deduced from it is in agreement with the pressure dependence of the electronic specific heat observed by Ho *et al.* The fact that the anisotropy of the electronic thermal expansion is the same as the anisotropy of the total lattice parameter changes between 0 and 43°K indicates that these lattice-parameter changes are mainly caused by a change in the cohesive energy of the conduction electrons rather than by lattice dynamics. Analogies to cerium and chromium suggest that the phase transition may consist in a condensation of conduction electrons into $5f$-like states which are antiferromagnetically ordered.

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