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Impurity Effects on Low-Temperature
Physical Properties of Uranium

by

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ABSTRACT

Dips in low temperature heat capacity results for nomi-
nal high-purity uranium can be attributed to heat evolution
from the U which is acting like a quenched martensite. Be-
cause of its martensite-like properties, the cooling rate
through the $\beta \rightarrow \alpha$ -phase transformation can affect the low-
temperature physical properties of α-phase U.

Published information suggests that there will be no
structural modification in very pure U below room tempera-
ture. A single change, thought to be structural, is observed
at 36 K in U of nominal high purity. It is ascribed to
Fermi surface-Brillouin zone boundary interactions. Phenomena
observed at 250 K and 338 K are seemingly associated with
the 36 K structural modification.

The appearance of as many as three low temperature heat
capacity transitions, reported in this work for low-purity
U, is attributed to impurity content. The observation of
three low temperature transitions in single-crystal U, as
reported in the literature, may be due to the grain-coars-
ening method of preparation of single crystals through Si
addition.

Heat capacity results presented here are considered
to be a function of the impurity content and microstructure
of a particular U specimen at the time of C_p measurement.

I. INTRODUCTION

The major interest in the α-phase of uranium in
recent years has arisen because of the unusual dis-
agreement concerning its superconducting transition
temperature (T_c). Reported values of T_c have ranged
from 0.15 to 1.5 K.[1] Most of the physical properties
of α-U, the allotropic form of the metal stable to
~ 934 K, show anomalous behavior below 350 K and in
particular below 60 K. There appears to be a time-
temperature dependence in results for many of the
measurements made on α-U at low temperatures, which
is suggestive of an ordering phenomenon.[2,3,4] The
form of ordering may be complex, and various possi-
bilities are discussed later. In addition, physical
property results appear to have an impurity[5] and
microstructural[6] dependence.

A number of transitions have been found below
60 K. The temperature at which they are observed
seems to depend upon whether the U test specimen
has been prepared from high-purity, polycrystalline
metal or from single-crystal material. A single
transition has been noted between 37 and 43 K when
physical property measurements were made on poly-
crystalline U,[5,7] but a temperature of 55-60 K was
reported for what is probably the same transition
when thermoelectric power measurements were per-
formed. Transitions at 23, 37 and 43 K have been
observed with single-crystal U specimens,[8,9] but

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other workers have reported only a single transition at 43 K.[10,11] British workers[12] found in their thermal expansion studies that they could suppress the 43 K transformation in polycrystalline U by quenching from above 50 K.

Higher temperature ranges reported for the appearance of what may be the same phenomenon are as follows: 70-100 K,[6,13] 250-280 K[2,4,10,13] and 325-350 K.[14]

The authors of a recently published paper note that the $\beta \to \alpha$ transformation in pure U is peculiar and not, as yet, understood.[15] They note that the best evidence available for the transformation during a quench from the β-phase suggests a shear transformation analogous to the martensitic (diffusionless) transformation in U-Cr alloys.[15] They also note, however, that the near-equilibrium transformation in pure U (cooled very slowly through the transformation range) may be comparable to dilute U-C alloy transformations and be diffusion controlled. The cooling rate of U from the β-phase can thus affect the microstructure, because stacking faults, dislocations and quenched-in vacancies can be a function of the cooling rate as well as be influenced by stresses during martensitic transformations. Thus the quench and near-equilibrium transformations of normal purity U might be comparable to those of U alloys. Uranium (α-phase) is classified as a metallic alloy by Pearson,[16] even in the absence of impurity elements.

Berlincourt[5] studied the low temperature Hall coefficient, (R), of two polycrystalline U specimens of different purity. The higher purity specimen showed a sharp drop in Hall coefficient at ~ 40 K, while the coefficient of reactor grade U decreased slowly between 100 K and 60 K and dropped off more rapidly below ~ 60 K. The value of R of the reactor grade sample became negative at ~ 20 K. His work thus shows the sensitivity of U behavior to impurities.

A domain structure has been found in single crystals of U by neutron diffraction measurements.[17] The domain size decreased by about a factor of two on cooling from room temperature to 10 K. The presence of domains suggests an antiphase ordered structure or a modulated stacking ordered structure.

Models for electronic changes during low temperature phase transitions have been discussed by

Smith and Fisher.[1] Three of these mechanisms were considered by Ross and Lam[18] in attempting to explain their magnetic susceptibility results for single-crystal α-U: (a) localized 5f electrons, (b) spin-density waves and (c) Fermi surface-Brillouin zone boundary interactions.

The question arises as to whether the low temperature physical property behavior of U should be attributed only to any one or more of the suggested mechanisms or models, or whether it is also partially and significantly dependent on purity, microstructure or a form of order-disorder.

We have studied the low temperature heat capacity of polycrystalline ^{235}U and ^{238}U of known purity with the hope that careful measurements on U of different microstructures would clarify the mechanisms involved. It was further hoped that the physical property changes at ~ 250 K and 325-350 K could be correlated with the presence or absence of low temperature phase transitions.

II. SURVEY OF PRIOR RESEARCH

A phase transition in U at approximately 42 K was first reported by Fisher and McSkimin[10] from single-crystal elastic moduli measurements. Schuch and Laquer[19] had earlier shown a minimum in the thermal expansion of polycrystalline U at about this temperature, the minimum corresponding to a maximum in density.

X-ray analysis of single-crystal U by Barrett et al[11] showed an anomaly at 43 K, which was manifested by a rapid increase of the a_o and b_o cell dimensions below this temperature. The c_o dimension contracted on cooling to 43 K and decreased even more rapidly below this temperature. They reported additional neutron diffraction reflections at low temperatures which could have been indicative of magnetic ordering, but susceptibility measurements by Ross and Lam[18] tend to disprove this.

Fisher and Dever[20] measured the elastic moduli of single crystals of U between 2 and 77 K and observed minima in the shear moduli at 18 K on cooling and at 22.5 K on heating. There was a high acoustical attenuation at T < 43 K. They concluded that there was a structural phase change between 35 and 43 K, and that the two phases had similar structures. The phase change was found to occur at 37 ± 2 K. Indications for three phases below 50 K were reported

by Steinitz et al,[8] using semiconductor strain gauges on single-crystal U. Abrupt discontinuities in length were observed at 23 and 37 K, while a sharp change in slope was seen at 43 K.

Indications for the existence of low temperature phases in U by heat capacity measurements have been reported. Lee et al[7] observed a small heat capacity anomaly at ~ 43 K in high-purity, polycrystalline U. Crangle and Temporal[9] measured the heat capacity of two polycrystalline specimens and one "pseudo single crystal" of U between 2 and 70 K. An anomaly in C_p vs T was seen in all of the samples at 43 K, but only the "pseudo single crystal" exhibited anomalies at 22 and 37 K.

Evidence for a phase transition at a temperature as high as ~ 55 K was presented by Sze and Meaden.[2] They measured the thermoelectric power, (S), of "unannealed" and annealed high-purity polycrystalline U at various warming rates following various cool-down rates. Changes in slope of the S vs T curves were seen after fast or slow cooling rates if the subsequent warming conditions were dynamic. The changes of slope were seen at approximately 20, 30, 40 and 55 K. Measurements taken under conditions approaching equilibrium, when there was a delay of 25 to 40 min preceding each measurement, gave a smooth S vs T curve with a minimum at about 50 K in both annealed and "unannealed" U and following either fast or slow cooling. Their interpretation was that very slow reheating permitted transformation of retained, metastable α-phase to the properly stable low temperature phase for temperatures below ~ 50 K. Faster warming permits the formation of one or more metastable low temperature phases. They not only have shown how one can get evidence for slight anomalies at ~ 20, 30 and 40 K due to the possible existence of phase mixtures, but also have suggested another possible transition at 50-55 K under certain conditions.

The resistivity study of Arajs and Colvin[3] also indicated resistivity changes at ~ 50 K, and especially for a lower purity U sample which had been held in liquid nitrogen at ~ 75 K for 8 days prior to the test. Holding for this length of time caused a decrease in the resistivity compared to that obtained upon normal warming from ~ 4 K. The decrease persisted upon cooling until 48 K was reached, at which temperature the lower (cooling) resistivity curve joined the upper (warming) curve. Their work indicates the importance of another temperature, 75 K, and presents possible evidence for a form of ordering in U which takes place slowly in the vicinity of this temperature.

The very slight dip in susceptibility found by Fournier[4] between 80 and 280 K for polycrystalline α-U could also be considered as evidence for a form of ordering which was not magnetic in character, but due only to structure. His work introduces another significant temperature for α-U, namely ~ 280 K. Other workers have noted slight changes in α-U properties at this approximate temperature. Rosen[13] reported that the longitudinal acoustical attenuation of U displayed a small hump centered at 250 K, while Sze and Meaden[2] found a thermoelectric power anomaly at the same temperature. Fisher and McSkimin[10] noted that the stiffness modulus, c_{11}, of single-crystal U changed anomalously between 78 and 573 K and had a maximum value at 265 K.

Rosen[13] studied Young's modulus, shear moduli, acoustical attenuation, adiabatic compressibility and θ_D behavior of U containing 200 ppm impurities. Young's modulus showed a maximum at 100 K and decreased with decreasing temperature to a minimum at ~ 36 K. Armstrong et al[6] studied the elastic moduli of the different phases of polycrystalline U, and of α-U down to low temperatures to determine the influence of crystal structure. They found that the elastic moduli of α-U were very sensitive to the degree of preferred grain orientation. The wide range in reported values for Young's modulus at 70 K, the temperature at which the modulus reaches a maximum, is shown in their Fig. 3. The structural transition temperature of 37 K for U coincides with their temperature of the minimum in Young's modulus.

It was noted above that certain experimental results indicate the possibility of a form of ordering in α-U. Weisberg and Quimby[21] have reported that length, electrical resistivity and the elastic moduli all decrease with increasing crystallographic order, but that Young's modulus, which is a reciprocal function of the elastic constants, increases with increasing order. The Young's modulus (E) of U increases with decreasing temperature and reaches a maximum at ~ 70 K.[6] This behavior is compatible with a form of order in U, and a variable degree of

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order attained would explain the difference in values observed for E at 70 K.

Abnormal changes in the temperature dependence of certain shear moduli and Young's modulus of α-U above 350 K have been noted by Fisher.[14] He suggests that the causes for the high attenuation for the different shear modes above 325 K may be related to twinning dislocations, since twinning in α-U is very difficult to prevent. Twinning is a form of order, and twins can be formed in U by deformation (or plastic strain) and even during heating and cooling, because of the anisotropy of thermal expansion in the different crystallographic directions.

Douglass and Bronisz[22] studied cold-worked and recrystallized α-U by transmission electron microscopy. The dislocation array, shown in their Fig. 3, for 3.5 per cent deformation by cold rolling, shows a few of the irregular closed loops similar to those which are seen as light or dark bands in the observation of antiphase boundaries.[23]

III. SPECIMEN DESCRIPTION

The specimens of ^{235}U and ^{238}U, to be used for heat capacity studies reported here, were machined from nominal high-purity buttons. These had been prepared by bomb reduction of the uranium tetrafluoride with calcium by the method of Kewish et al.[24] The metal reductions for the two materials were done by different operators in different reduction furnaces, because of the radioactivity of the ^{235}U. Chemical and spectrographic analyses of the original buttons are shown in Table I. Six specimens, 41.28 mm long and blunted 60° triangular cross section at the ends, were machined from each button. The longitudinal base of each specimen had a width of 8.687 mm and a top width of 3.175 mm. The height was 4.763 mm. The specimens were designed to fit snugly against the separating walls of a six-vaned calorimeter can. The machined specimens were annealed for

0.5 hr at 873 K in vacuum and were allowed to cool slowly overnight.

The experiment was designed to determine the influence of microstructure on the heat capacity of metal of each isotope. Thus, after the first set of measurements, the ^{238}U specimens were heavily cold worked by pressing the flat base of each blunt-edged triangular specimen into a mold having a radius of curvature of 12.32 mm, the radius of the interior wall of the calorimeter can. The actual reduction in height of the triangular cross section was only from 4.763 mm to 4.547 mm, but the major deformation was in shaping the flat base of each specimen into a partial cylindrical shape. The second set of C_p measurments were made on the cold-worked metal.

A third set of heat capacity measurements was made on the ^{238}U specimens after annealing for one hr at 873 K, and a fourth set after an additional heat treatment at 898 K for 144 hr.

After initial measurements, the ^{235}U specimens were refrigerated in their sealed calorimeter can for one year. They were then remeasured to determine the effects of self-irradiation damage. Differences in heat capacity should be due solely to microstructural changes.

The annealed ^{238}U specimens showed slight twinning after the first set of heat capacity measurements. The ^{235}U specimens were not examined metallographically until after completion of all heat capacity measurements, but they also showed only slight twinning. This twinning could have arisen from stresses due to: (a) metallographic polishing, (b) temperature cycling or (c) the β → α-phase transformation during casting of the original button. The cold-worked ^{238}U specimens had a very high twin density and appeared to be deformed uniformly. The grain size was about the same in both the ^{235}U and ^{238}U specimens, but of a duplex nature, i.e., a mixture of large and small grains.

TABLE I

IMPURITY CONTENT OF ^{235}U AND OF ^{238}U

Element (ppm by mass)	Al	Mg	Si	Ca	Mn	Fe	Co	Ni	Cu	H	N	O	C
^{235}U	5	20	15	<2	2	30	--	20	2	-	-	-	50
^{238}U	2	15	30	<2	3	15	<5	20	5	<10	<10	75	50

The average size was about A.S.T.M. Std. No.-1 for all specimens. The surface of one of the [235]U specimens showed some recrystallization, which must have occurred during the original heat treatment, and was indicative of cold work caused by surface machining with a dull tool. The fine grain size in the recrystallized areas was about A.S.T.M. Std. No. 8. There were a considerable number of oxide inclusions in the [235]U specimens, while the [238]U specimens were relatively free of inclusions.

The heat capacity of a low-purity [235]U specimen had been investigated prior to the measurements on the nominal high-purity specimens. The low-purity specimen was a cylindrical rod 6.35 mm O.D. and weighed 12.79 g. The rod had been prepared by swaging and machining, and was then annealed for two hr at 898 K. The major impurities were: C, 410; Si, 180; Al, 40 and Fe, 35 ppm by mass.

The nominal high-purity [235]U specimens actually contained 93.18 mass per cent [235]U. The balance was assumed to be [238]U in calculating a gram formula mass (molar mass) of 235.2 to be used to derive the thermodynamic functions. The molar mass used to calculate the thermodynamic functions of [238]U was 238.07.

IV. EXPERIMENTAL

Apparatus

The adiabatic-type continuous calorimetry system, including a description of the calorimeter cans, platinum resistance thermometer, temperature scale, 10-channel data log and timer-triggering circuit, has already been described in considerable detail.[25]

Method

The method of making heat capacity measurements has also been described in detail previously.[25] The six annealed [235]U specimens were placed in a six-vaned calorimeter can and pushed snugly against the 60° angled vanes. Copper shot was poured behind each specimen to fill up the space in the calorimeter can to the top of the specimen. The Cu shot was used as a heat exchanger between the specimen and the exterior wall of the can and to insure that the [235]U specimens were kept in continuous contact with the separating vanes of the can. The masses of the [235]U, Cu shot and calorimeter can assembly were 131.732 g, 47.273 g and 119.580 g, respectively.

The annealed [238]U specimens were inserted in an identical calorimeter can in the same manner. Slightly more Cu shot was added, and the initial masses of the [238]U specimens, Cu shot and calorimeter can assembly were 136.140 g, 58.940 g and 119.580 g, respectively.

Each calorimeter can, with its threaded cover tightly screwed into place, was evacuated through a Cu tube previously silver soldered into the cover and back-filled six times with dry He gas before sealing with In+Sn solder. The two calorimeter can assemblies were again evacuated and back-filled six more times with dry He gas before clipping off each Cu tubulation and soldering its seam.

In the second set of measurements, the cold-worked [238]U specimens were replaced in the calorimeter can with their now rounded base against the outer wall of the can. Copper shot was poured into the narrower part of the volume of each of the six compartments, thus insuring heat exchange between a specimen and the vaned walls of the can. Heat capacities were then determined. The cold-worked specimens of [238]U were annealed for one hr at 873 K and the C_p vs T was remeasured. The specimens were then given an additional 144 hr anneal at 898 K, and the heat capacity was measured again. Heat capacity measurements were thus made on the [238]U in four different microstructural states.

Since the radioactive contamination of equipment was a problem with the [235]U, the specimens were held in the sealed can in a household-type refrigerator for one year in order to evaluate the effects of self-irradiation damage. First measurements on the [235]U (after holding) were followed by others made at random intervals for a period of three months. The heat capacity results for the [235]U were therefore representative of the annealed metal and for the metal after 12 to 15 months of self-irradiation damage. The microstructure in the damaged state should have been representative of the effects of vacancies and interstitials resulting from Frenkel pair production for slightly over one year. Nothing unusual was seen by optical metallographic examination of the damaged [235]U after all measurements were completed.

V. RESULTS

^{235}U (Low-Purity Metal)

Heat capacity measurements were made on a swaged and annealed specimen of low-purity ^{235}U. Evidence for a phase transition was clearly seen at about 22 K in the first run of a series, or for other runs when the specimen had been warmed above 60 K before starting a run again at 4 K. If an adiabatic heat capacity run was stopped below 43 K, then the peak originally at 22 K occurred at a higher temperature with each repeat run until it was at 32 to 43 K. Only a slight hump was seen at ~ 19 K. Slight peaking was also seen from 60 to 70 K whenever a repeat run was continued above 43 K. Measurements were discontinued after four series because there was no reproducibility in the data, i.e., no decision could be made as to a clear-cut phase transition temperature or if one truly existed. The peaking in heat capacity seemed to depend on the processing. The thermoelectric power vs temperature curves for dynamic runs made on polycrystalline U, as reported by Sze and Meaden[2] and shown on their Figs. 1 and 3, have the multiple peaks occurring at slightly different temperatures. These are like the C_p vs T data obtained with the low-purity ^{235}U, which suggested several low temperature transitions.

^{238}U (Polycrystalline)

The C_p vs T data for ^{238}U specimens in the cast and annealed state and for the subsequent heavily cold-worked state are shown on Fig. 1 along with the data of Flotow and Lohr[26] for high-purity ^{238}U. Curve A of Fig. 1 shows the best average of the low temperature data for the annealed polycrystalline U. No evidence for low temperature phases was detected by heat capacity measurements. The data were comparable, within experimental error, to those of Flotow and Lohr (curve C) up to 36 K. Curve A diverged from curve C at 36 K and continued at a lower C_p level with increasing temperature to about 250 K. Curve A and the data of curve C were the same from 250 to 322K, where curve A turned upward to peak at 338 K. It returned to the curve of previously reported data at 352 K. The apparent heat evolution between 36 and 250 K in curve A of Fig. 1 seems to be supporting evidence for some form of ordering in ^{238}U, with possible disordering at 338 K.

Curve B, Fig. 1, indicates an entirely different behavior for the heavily cold-worked metal. Although some runs showed dips between 38 and 45 K and between 45 and 50 K, the majority of the data was the same as that for curve C within experimental error up to 50 K. Above this temperature, the data for curve B are higher than those for curve C, but the two curves coincide again at ~ 175 K. The data for the cold-worked metal, curve B, were quite consistent with those of curve C from 175 K up to 350 K.

The cold-worked ^{238}U specimens were annealed for one hr at 873 K and remeasured. The C_p vs T curve for the specimens in this microstructural state was similar to curve C up to 50 K, where it dipped slightly. Repeated runs yielded a wide band of data between 100 K and 373 K due to
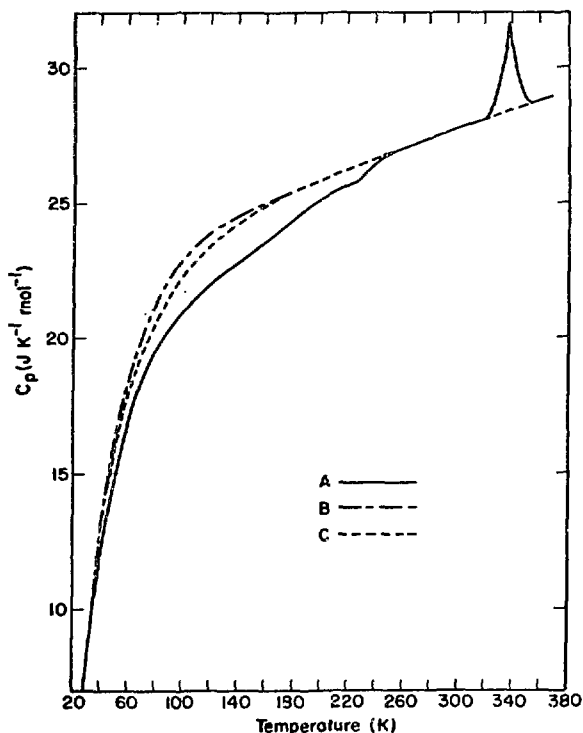

Fig. 1. Heat capacity vs temperature for nominal high-purity ^{238}U in different microstructural states. (Smoothed curves.) Comparison with ^{238}U data of Flotow and Lohr.[26] A. Machined from reduction button and annealed 0.5 hr at 873 K. B. Specimens described under (A), but heavily cold worked. C. Results of Flotow and Lohr. (Swaged rods annealed 0.5 hr at 873-923 K.)

TABLE II

SMOOTHED ENTROPY VALUES FOR ^{238}U IN DIFFERENT MICROSTRUCTURAL STATES

(Molar mass = 238.07 g Mole^{-1}; Cal$_{th}$ = 4.184 J)

T(K)	Cast and annealed	Cold worked	Cold worked plus Annealed 1 hr at 873 K	Cold worked plus Annealed 144 hr at 898 K	Data from Flotow and Lohr[26]	
	J K^{-1} Mole^{-1}					Cal$_{th}$ K^{-1} Mole^{-1}
30	3.35	3.35	3.39	3.35	3.23	0.772
50	9.37	9.50	9.67	9.67	9.46	2.261
70	14.98	15.52	15.48	15.48	15.34	3.666
90	19.83	20.75	20.63	20.63	20.46	4.891
110	24.02	25.23	25.02	24.98	24.92	5.955
130	27.74	29.12	28.95	28.83	28.82	6.887
150	31.00	32.63	32.51	32.22	32.28	7.715
200	37.99	39.92	39.62	39.50	39.53	9.448
250	43.72	46.19	45.73	45.73	45.40	10.851
300	48.66	51.25	50.75	51.09	50.36	12.037
350	53.09	55.81	55.35	55.98	54.67	13.006
273.15	46.07(±.08)	48.58(±.24)	48.03(±.24)	48.33(±.20)	47.78(±.08)	11.42(±.02)
298.15	48.49(±.08)	51.13(±.24)	50.62(±.28)	50.88(±.25)	50.21(±.08)	12.00(±.02)
373.15	54.85(±.16)	57.40(±.32)	57.11(±.32)	57.73(±.40)	---	---

non-reproducible oscillations in the results. Thermodynamic function values were calculated for each run.

The ^{238}U specimens were then annealed for an additional 144 hr at 898 K. Measurements indicated that slight additional changes had taken place. The C_p vs T curve was essentially that of curve C, Fig. 1, up to 45 K, where a slight dip occurred. Repeated runs again showed oscillations in results and gave a wide band to the C_p vs T curve between 100 and 373 K. All measurements after the 144 hr anneal showed a slight consistent increase in C_p above 300 K, when compared with the data for the other microstructural states.

The entropy values obtained from the low temperature heat capacity measurements on the ^{238}U in four different microstructural states are shown in Table II. The data are compared with values reported by Flotow and Lohr[26] for the same temperatures. The enthalpy values calculated from the same data are shown in Table III and are again compared with the data of Flotow and Lohr for the same temperatures.

^{235}U (Polycrystalline)

The heat capacity data for the ^{235}U (curve A) are compared with data of Flotow and Lohr (curve C) for ^{238}U on Fig. 2. Curve A shows the best average of the results obtained with the cast and annealed ^{235}U specimens approximately two months after machining and annealing. The curve starts dipping away from curve C at 36 K. There is a change of slope in curve A at 50 K, and the curve returns to curve C at ~ 70 K. The C_p vs T curve again dips away from curve C beginning at ~ 70 K and returns again to that curve by 120 K. No evidence for transitions below 36 K was seen by heat capacity peaking. The data were extremely consistent in all heat capacity runs in the temperature range up to 70 K. Scatter in the data increased above 70 K, but the C_p vs T curve obtained had a relatively narrow band width and nothing unusual was discernible from 120 K up to 373 K.

Curve B of Fig. 2 illustrates the effect of self-irradiation damage in ^{235}U held at ~ 278 K for 12 months. The data for most runs started at 4 K fell on curve C up to 40 K. The curve fell away from curve C at 40 K, crossed over it at ~ 58 K

T(K)	Cast and annealed	Cold worked	Cold worked plus Annealed 1 hr at 873 K	Annealed 144 hr at 898 K	Data from Flotow and Lohr[26]	Cal$_{th}$ Mole^{-1}
			J Mole^{-1}			
30	71.13	71.13	73.20	75.30	70.46	16.84
50	310	322	324	326	320.9	76.70
70	649	678	669	669	672.3	160.69
90	1033	1096	1079	1079	1081	258.44
110	1452	1544	1515	1502	1526	364.61
130	1900	2017	1987	1966	1992	476.21
150	2356	2498	2464	2435	2477	591.94
200	3565	3778	3728	3707	3739	893.57
250	4828	5121	5054	5113	5055	1208.1
300	6197	6502	6460	6552	6417	1533.6
350	7636	7937	7899	8125	7825	1870.2
273.15	5452($\pm$24)	5761($\pm$40)	5690($\pm$40)	5761($\pm$48)	5682($\pm$12)	1358($\pm$3)
298.15	6143($\pm$32)	6456($\pm$48)	6410($\pm$40)	6502($\pm$48)	6364($\pm$12)	1521($\pm$3)
373.15	8276($\pm$40)	8590($\pm$60)	8548($\pm$48)	8920($\pm$48)	---	---

and showed slight peaking at 63 K and 75 K. Above 85 K, the C_p data were consistently higher than those of curve C. The same tendency for oscillations in data was seen in the self-damaged ^{235}U as was seen with heavily cold-worked ^{238}U that had been annealed for one hr at 873 K. Repeated runs were made in order to get reasonably accurate thermodynamic function values.

The entropy values for the ^{235}U in its two different microstructural states are compared in Table IV at several temperatures with data of Flotow and Lohr. The enthalpy data for the ^{235}U at the same temperatures is listed in Table V along with the enthalpy data of Flotow and Lohr.

Runs started at 75 K (^{235}U and ^{238}U)

Several heat capacity runs were made with both the ^{233}U and ^{238}U in their different microstructural states after liquid nitrogen cooling and holding for 30 min at ~ 75 K. All curves started at lower C_p values than were observed with continuous adiabatic runs after additional liquid He cooling. The C_p vs T curves for liquid N_2 cooling and holds at ~ 75 K are shown for two different microstructures of both

isotopes of U of Fig. 3, along with the C_p vs T curve of Flotow and Lohr. Curve A, for specimens machined from cast and annealed ^{238}U, is much lower than curve C for specimens machined from cast and annealed ^{235}U. Curves A and C are both appreciably lower than curve E of Flotow and Lohr. Cold working the ^{238}U raised the C_p curve noticeably. The data for cold-worked ^{238}U are shown as curve B. It starts 1.5 percent above curve E, as compared to starting ~ 6.5 percent lower than curve E in the cast and annealed state.

The heat capacity curve for the ^{235}U held for 12 to 15 months is curve D on Fig. 3. The curve for the self-damaged metal starts slightly below curve E at 82 K, but crosses over and goes above curve B by 100 K. Self-irradiation damage to ^{235}U for slightly over one year has an effect similar to cold working ^{238}U insofar as its effect on heat capacity behavior is concerned.

The results of Flotow and Lohr[26] were chosen as the reference curve for Figs. 1 through 3 and as reference values for Tables II through V because their results were for truly high-purity U prepared in the standard manner, i.e., swaged and then
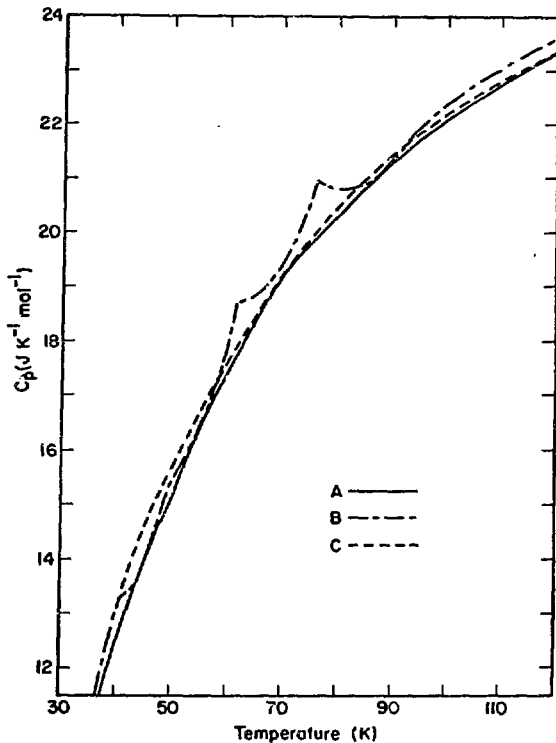
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Fig. 2. Heat capacity vs temperature for nominal high-purity [235]U in different microstructural states. (Smoothed curves.) Comparison with [238]U data of Flotow and Lohr.[26] A. Machined from reduction button and annealed 0.5 hr at 873 K. B. Specimens described under (A), but self-damaged by holding for 12 months at ~ 278 K. C. Results of Flotow and Lohr.

annealed for 0.5 hr at 873 to 923 K. In addition the data from all microstructural states of [235]U and [238]U matched their data within experimental error over several temperature ranges.

VI. DISCUSSION OF RESULTS

Low Temperature Phases

Although the single-crystal U studies of Steinitz et al[8] and Crangle and Temporal[9] indicate possible phase changes at 22, 37 and 43 K, and Smith and Fisher[1] report phases designated as α_1, α_2 and α_3 from their high pressure work on single-cryst: U, it is difficult to reconcile anything but a slight transition at ~ 36 K with the low temperature heat capacity results presented here for cast polycrystalline material. The heat capacity of the
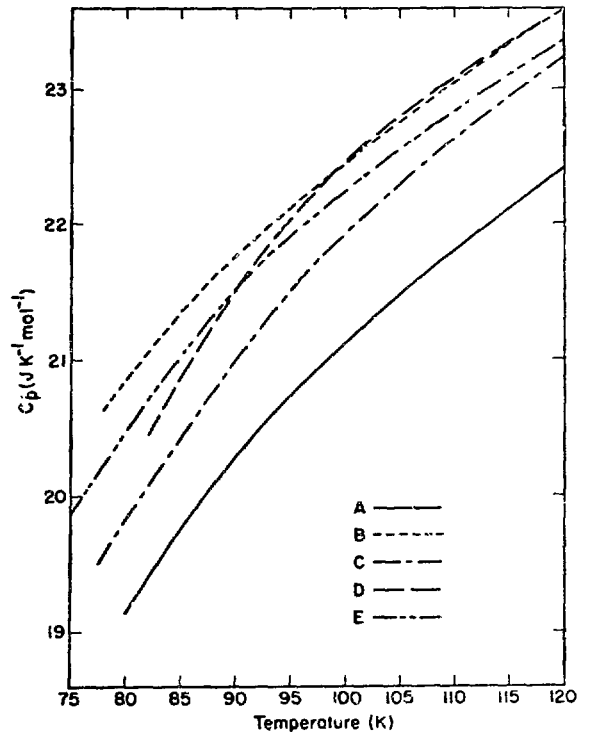

Fig. 3. Heat capacity vs temperature for nominal high-purity [235]U and [238]U in different microstructural states. (Smoothed curves.) Data taken after liquid nitrogen cooling followed by 0.5 hr hold. A. Machined from [238]U reduction button and annealed 0.5 hr at 873 K. B. Specimens described under (A), but heavily cold worked. C. Machined from [235]U reduction button and annealed 0.5 hr at 873 K. D. Specimens described under (C), but self-damaged by 12 months storage at ~ 278 K. E. Results of Flotow and Lohr.[26]

calorimeter can and Cu shot below 90 K was so small compared with that of the mass of the [235]U or [238]U that it is unlikely that any first order transition would be missed under the adiabatic conditions of our experiment. There were no arrests in either the specimen temperature-time plots or in the shield temperature-time plots below 36 K.

Confirmation for a single transition at ~ 43 K, with supposedly very pure polycrystalline U, was presented by Lee et al[7] from their heat capacity study. The thermoelectric power study of Szc and Meaden[2] on high-purity polycrystalline U indicated a transition at 50 to 60 K under conditions approaching equilibrium.

TABLE IV
SMOOTHED ENTROPY VALUES FOR ^{235}U IN DIFFERENT MICROSTRUCTURAL STATES
(Molar mass = 235.2 g Mole^{-1}; Cal$_{th}$ = 4.184 J)

T(K)	Cast and annealed	15 months self damage		Data from Flotow and Lohr[26]
	J K^{-1} Mole^{-1}			Cal$_{th}$ K^{-1} Mole^{-1}
30	3.26	3.51	3.23	0.772
50	9.33	9.71	9.46	2.261
70	15.10	15.64	15.34	3.666
90	20.13	20.79	20.46	4.891
110	24.56	25.27	24.92	5.955
130	28.33	29.16	28.82	6.897
150	31.71	32.68	32.28	7.715
200	38.95	39.96	39.53	9.448
250	44.77	46.15	45.40	10.851
300	49.83	51.17	50.36	12.037
350	54.22	55.73	54.67	13.066
273.15	47.20(±.12)	48.62(±.12)	47.78(±.08)	11.42(±.02)
298.15	49.66(±.16)	51.00(±.24)	50.21(±.08)	12.00(±.02)
373.15	56.07(±.20)	57.36(±.30)	----	----

TABLE V
SMOOTHED ENTHALPY VALUES FOR ^{235}U IN DIFFERENT MICROSTRUCTURAL STATES
(Molar mass = 235.2 g Mole^{-1}; Cal$_{th}$ = 4.184 J)

T (K)	Cast and annealed	15 months self damage		Data from Flotow and Lohr[26]
	J Mole^{-1}			Cal$_{th}$ Mole^{-1}
30	70.29	74.48	70.46	16.84
50	313.4	324.3	320.9	76.70
70	656.9	682.0	672.3	160.69
90	1063	1096	1081	258.44
110	1502	1540	1526	364.61
130	1962	2008	1992	476.21
150	2439	2489	2477	591.94
200	3686	3770	3739	893.57
250	4996	5134	5055	1208.1
300	6360	6569	6417	1533.6
350	7791	9012	7825	1870.2
273.15	5619(±20)	5803(±24)	5682(±12)	1358(±3)
298.15	6309(±20)	6514(±28)	6364(±12)	1521(±3)
373.15	8431(±25)	8765(±40)	---	---

Our heat capacity results showing a 22 K transition in low-purity ^{235}U suggested that this transition was due to impurities, principally C and Si. Other transitions at 32 to 43 K and from 60 to 70 K were also found for the less pure ^{235}U. The swaging and annealing of our low-purity ^{235}U gave results surprisingly close to those presented by Crangle and Temporal[9] for "pseudo single-crystal" U, except for the presence of a C_p spike at 60-70 K.

The U specimens of Flotow and Lohr[26] had been prepared by swaging, which was followed by annealing for 0.5 hr at 873-923 K. The specimens contained the following major impurities in ppm: C, 18; Si, 12 and O, 15. They did not report any low temperature phase transformation. This suggests that there will be no low temperature structural change occurring in U of sufficiently high purity. There can be the indication of a low temperature structural modification, which appears at ~ 36 K, if the C, Si and O impurity contents are as high as shown in Table I (C, 50 ppm; Si, 15 to 30 ppm and O, 75 ppm). The observation of low temperature phases in U, and their number, appears to depend upon metal purity and very possibly on the C and Si content.

FCC Phase in Uranium

A recent paper by Tudja and Ban[27] shows that a fcc phase can exist in U at room temperature. It is stabilized by small amounts of N, S, Se, Te, P, As, Sb, Bi, C or Si. With S as the stabilizing element, the composition of this fcc phase ranges between $U_{20}S$ and U_8S. If the atomic ratio of impurity to U was kept very low (~ $UX_{0.1}$), the same fcc U phase appeared with almost identical lattice parameters for most of the elements listed above. Only the proportion of α-U and fcc U differed from sample to sample.

The low-purity ^{235}U investigated by heat capacity measurements contained 410 ppm C and 160 ppm Si by mass. The atomic per cent of these two elements combined would be ~ 1.0. Assuming that their effect would be similar to that for S, this could permit the presence of considerable fcc phase mixed in with the predominantly α-phase, similar to the results of Tudja and Ban, who obtained mixtures of these phases with sulfur compositions varying from only $US_{0.02}$ to $US_{0.40}$.

The fcc structure for U, which has been shown to exist in the presence of certain impurity elements and at certain atomic ratios, may be really only a rediscovery. Early x-ray studies by McLennan and McKay[28] on what may have been rather impure metal suggested a cubic cell with a_o = 3.43 Å (indexed at 45° from Tudja and Ban). As the U was prepared in a purer and purer state, a monoclinic structure was proposed, and this was finally followed by the orthorhombic structure accepted today.[29]

The methods used in preparation of single crystals of U have been discussed by Gittus.[30] One of these methods, the grain-coarsening method, starts with high-purity U to which a controlled amount of a suitable impurity such as Si is added by diffusion.[31] Swaging and annealing follow the siliconizing heat treatment. If only a 10 to 20 ppm overall increase in Si content was sufficient to prepare single crystals of α-U, then the Si content of Fisher's single crystals[31] was slightly higher than listed in Table I for the nominal high-purity ^{235}U and ^{238}U.

The low-purity ^{235}U specimen mentioned above had a high Si content. It had been swaged and annealed. The latter two steps are part of the method used to promote grain growth for conversion to a single crystal. The heat capacity results for this low-purity ^{235}U indicated the presence of several low temperature phases including one with a transition at 19 to 22 K. The appearance of the three low temperature phases may then be due to microstructural effects which were not eliminated by the annealing treatment, i.e., "banding" (Fisher's terminology)[31] remaining from the swaging operation. Actually only small amounts of Si may be required to set up islands of a stacking fault orientation of the fcc phase in the presence of a regularly banded microstructure.

Although classified as orthorhombic, the α-U structure can also be described as deformed close-packed hexagonal. The resemblance is to that of a hexagonal metal in which successive basal planes have been shifted out of line with their neighbors. The structure has the appearance of a series of corrugations. It is realized today that stacking faults in metallic solid solutions play a considerable role in the explanation of properties such as phase

morphology and crystallography of phase transformations, particularly in fcc and cph structures. A stacking fault consists of a sliver or island of mismatched material equivalent to cph stacking in a fcc crystal and vice versa. Impurities present in sufficient quantity to stabilize the fcc phase of U might play an important role in the appearance of phases (Smith and Fisher)[1] on application of pressure to supposedly single-crystal U. The martensitic nature of the $\beta \rightarrow \alpha$-phase transformation in U could insure the presence of stacking faults. Increasing pressure might force the appearance of the structures which are known to be possible in U because a stacking fault is a factor in the stability of one phase with respect to another.

Domain Structure in Single-Crystal U

A domain structure for single-crystal U was determined by the neutron diffraction study of Lander and Mueller.[17] The size of the perfect domains was reduced by about a factor of two in cooling from room temperature to 11 K. Their work thus implies a domain structure from 11 K up to above room temperature.

A recent paper by Roitburd[32] can help to explain the formation of domain structures in the presence of internal stresses in α-U. The differences in the thermal dilation of the orthorhombic α-U structure would induce severe strains in the metal on cooling or quenching to low temperatures. There could be formation of a new phase in order to lower the elastic energy of internal stresses and the fragmentation of the new phase into domains. There could also be the formation of ensembles of the crystals or regions of new phases arranged regularly inside the parent phase. This could thus explain the appearance of low temperature phases in U.

It is also possible that the deformed matrix of the swaged U rods, i.e., the banded structure of swaged material, may exist even after recrystallization into a single crystal. The presence of dislocations and stacking faults along with the banded array might allow a domain structure to form easily on cooling single-crystal U to low temperatures. The suggestion that swaging, Si diffusion and recrystallization play a role in domain formation seems plausible. One can speculate that the domain structure present in single-crystal U between 11 K

and room temperature[17] would be a modification of a long period stacking order. Stacking fault boundaries are a form of low energy boundary like antiphase boundaries which can modulate a close-packed structure. Thus a stacking modulated structure can become more stable than an unmodulated one. Modulated stacking ordered structures can even be stabilized in pure metals.[33]

If sufficient Si was present for formation of slivers of fcc phase in U, then this could be a way of introducing basal planes of fcc structure into the orthorhombic unit cell. This could be a source of stacking-order modulation as a modified form of a long period superlattice[33] in U. Orthorhombic modulated structures and their notation have been discussed by Pearson.[34]

Structures Below 36 K in Polycrystalline U

The results reported here for polycrystalline ^{235}U and ^{238}U, and shown on Figs. 1 and 2, show that the heat capacity behavior below ~ 36 K is the same regardless of microstructure. This requires an explanation, because the experimental results presented above indicate that C_p values found above ~ 36 K are strongly dependent upon microstructure. The C_p vs T curves of Figs. 1 and 2 for ^{238}U and ^{235}U match that of Flotow and Lohr[26] for high-purity U below 36 K. No low temperature phases were detected by them although their specimens were prepared by swaging and annealing. What one observes in the physical property behavior of U below 36 K must then depend almost entirely on purity. The implication of Flotow and Lohr's result is that there is no low temperature transition in high-purity U. It is thus doubtful if a domain structure can even exist in α-U of sufficiently high purity when the specimen has been slowly cooled from the β-phase under diffusion-controlled conditions, because there will be a minimum of stacking faults.

Uranium Martensites

The heat evolution and its effect on the "apparent" heat capacity of quenched martensites has recently been discussed for iron-base alloys by Mogutnov and Shwartzman.[35] Complexity of the aging processes, metastability of low temperature precipitates and influence of lattice imperfections were covered in their survey. They show that energy is evolved in raising the temperature of a quenched

martensite. This causes dips in C_p vs T curves of the type visible in curves A of Figs. 1 and 2. There is thus the possibility that U can be showing the physical property behavior of a quenched martensite in its heat evolution below 250 K.

The effects of impurities on the kinetics of the $\beta \rightarrow \alpha$ transformation in U have been discussed by Rechtien and Nelson.[15] The low temperature transformation in U-Cr alloys is considered to be martensitic, while higher temperature transitions are bainitic and pearlitic. The three modes of transformations are thus analogous to those in the Fe-C systems. The survey of Rechtien and Nelson suggests that the presence of small amounts of certain impurities may be sufficient to impart the characteristics of an alloy to U, and influence the martensitic nature of the $\beta \rightarrow \alpha$ transformation.

Elements other than Cr might also cause the formation of metastable martensites of U. The consequence of this could be seen as low temperature phase transitions. The temperature at which a phase appeared could depend upon the metastable martensitic character imparted to the α-phase by the impurity elements present.

The heat capacity results shown in Figs. 1 through 3 suggest that the impurities (listed in Table I) in the ^{235}U and ^{238}U specimens may be sufficient to cause an alloy-like behavior. The decomposition of a metastable martensitic alloy could give changes in the C_p behavior which would be indicative of a phase transition, but it should not do it reproducibly on cooling from 373 K back to 4 K unless FS-BZ boundary interactions were involved. The reproducibility of appearance of the dip in C_p vs T curves at ~ 36 K shown by the polycrystalline U isotopes should not be possible if the ^{235}U and ^{238}U were showing only the properties of a metastable martensite.

Results of recently reported electron microscopy studies of tempered Cu-Al martensites by Lefever and Delaey[36] indicate the presence of an antiphase (long period superlattice) structure. The heat evolution noted on warming quenched martensites could thus be indicative of the appearance of an antiphase ordered structure and suggests that antiphase structures may be quite common in martensites.

Evidence for an Antiphase Structure in U

It has been noted above that small amounts of impurity elements may give U an alloy-like character, and that Pearson[16] classifies α-U as a metallic alloy. Ordering in an alloy, with domain formation, is required for appearance of an antiphase structure. It was developed in the introductory sections that there was published information suggesting ordering in U at low temperatures. Barrett et al[11] reported additional reflections in neutron diffraction patterns of single-crystal U. These could be indicative of a form of order that was not magnetic.

Evidence for a difference in the degree of ordering at ~ 80 K, dependent upon microstructure of the U, appears in the data of Fig. 3. The data shown on this figure were taken after holding for ~ 30 min in liquid N_2 and seem to show the effect of some form of order. The curve for the ^{238}U (A) is lower than the one for ^{235}U (C) and both are lower than the data of Flotow and Lohr (E). Cold working (curve B) or self damage (curve D) changed the heat capacity results drastically. The dislocation pile up from cold work must prevent the ordering of dislocations and stacking faults into an antiphase structure at the temperature where it would normally appear. Small dips in C_p of cold-worked ^{238}U and self-damaged ^{235}U at higher temperatures could be from energy release due to step-wise ordering and give the wide band of data reported above.

Sato and Toth[37] have established that the creation of new Brillouin zone boundaries at the Fermi surface can reduce the energy of the conduction electrons. This usually requires the creation of superperiods in the crystal lattice, and the superperiod arises by the periodic introduction of antiphase boundaries. Complex superdislocation configurations can make up an antiphase domain structure. These complicated structures composed of extended dislocations, antiphase boundaries and stacking faults have been discussed by Marcinkowski et al[38] for the case of superlattice dislocations in Cu_3Au. Such a complicated antiphase structure should be expected in U because of the nature of its martensitic $\beta \rightarrow \alpha$-phase transformation.

The explanation for the drop-off in C_p at 36 K, as shown for cast and annealed polycrystalline ^{238}U by curve A of Fig. 1, may be through the appearance of an antiphase structure at this temperature. Such

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a dip has been seen in heat capacity by Taylor et al[39] in a Pu-Ga (δ-phase stabilized fcc) alloy on a first low temperature heat capacity run. A second low temperature run after self-irradiation damage to the specimen showed a double dip in heat capacity which has been interpreted by Sandenaw and Harbur[40] as evidence for an antiphase structure. They have also suggested that there is evidence for an antiphase structure in Pu.

The C_p vs T curve for an antiphase structure shows a double dip due to energy release in domain formation. The reason for this was explained as follows by Sykes and Jones[41] for Cu_3Au: (a) the emergence of domains leads to a decrease in heat capacity through the liberation of energy by ordering within domains, (b) the liberation of energy falls off when the domains grow in size to contact each other, and the heat capacity rises toward a normal value and (c) energy release starts on further warming, which again causes a lowering of heat capacity. The second energy evolution is attributed to disappearance of domain boundaries as the size of the remaining domains increases. Evolution of heat again stops when only a single ordered domain remains. There would be a temperature range of order above the antiphase structure range. This may be followed by another temperature range of disordering of atoms.

The heat capacity curve A of Fig. 1 does not show a clear-cut double dip which can be attributed to an antiphase structure, but there is a change in curvature at ~ 145 K and at ~ 225 K. A slight maximum at ~ 210 K is a possibility. Return of curve A to match curve C at ~ 250 K followed by peaking at ~ 338 K could be construed as reasonable evidence for an antiphase structure in the ^{238}U. The end of the antiphase domain structure at ~ 250 K could explain the anomalies noted in thermoelectric power,[2] susceptibility,[4] acoustical attenuation[13] and stiffness modulus, c_{11},[10] at this approximate temperature. The total breakup of a complicated order would account for the peaking at ~ 338 K shown by curve A, Fig. 1, and would explain the high attenuation of different shear modes noted by Fisher.[14]

An explanation has to be given as to why the C_p vs T curve for the ^{235}U did not show as low a dip as was seen with ^{238}U, although both specimens were machined from cast polycrystalline material of about the same purity and annealed identically. The partial answer may be in the stacking fault, dislocation and vacancy concentrations. These would affect ordering, especially if in antiphase or modulated stacking ordered structures. One of the operators involved in bomb reduction of the U isotopes pointed out that the ^{235}U button was cooled from the molten state at a very slow rate. The ^{238}U button was cooled rapidly. Slow cooling through the β → α phase transition could give a smaller stacking fault and dislocation concentration than rapid cooling through the same transition, particularly since it is martensitic.

Domain hardening can be evidence of an antiphase structure in an alloy. This point is presented here because development of an increasing hardness in α-U on cooling below room temperature could be evidence for an antiphase structure. If there was indeed a maximum of order in U at ~ 70 K, as suggested by Young's modulus measurements, then there could be a considerable decrease in hardness at the lower temperature and a much lower flow stress. Gittus[42] shows the Brinell hardness of as-cast U (500 ppm C) increasing down to 201 K where measurements ended. Leteurtre and Quere[43] note that slip becomes easy in α-U at a temperature between liquid N_2 and room temperature, which is strongly dependent on the impurity content. These two bits of evidence seem to strengthen the argument for the possibility of both ordering and an antiphase structure below room temperature in U.

FS-BZ Boundary Interactions in U

If the dips in the C_p vs T curves for cast and annealed ^{235}U and ^{238}U shown on Figs. 1 and 2 were due to formation of martensite caused by the alloying effect of the impurities, then the reproducibility in the levels of the curves would seem to be an impossibility. This would only happen if there were FS-BZ boundary interactions which forced a reproducible antiphase ordered structure in the martensite. If the impurity atoms present in U can influence the physical properties as greatly as they seem to do, then they must contribute to electron/atom or electrons/unit cell ratios of the resulting dilute alloys. Depending upon the impurity atom and its electron contribution, one could expect FS-BZ boundary interactions to show up at slightly different temperatures. Whether a structural modification takes

place at 36, 37, 43 or 55 K could depend entirely on the impurity atoms present and their concentrations. This would explain the variability in observed transition temperatures.

The suggestion given by Ross and Lam[18] that FS-BZ boundary interactions could explain their susceptibility results seems to give the best explanation for the low temperature behavior of U.

Factors Influencing Superconductivity

The above discussion suggests that there can be several factors influencing the temperature (T_c) at which superconductivity is observed in U. The variability in superconducting transition temperature of U could depend upon: (a) impurity content, (b) martensitic nature of an impurity alloy depending upon β → α-phase cooling rate, (c) the particular phase existing at T_c under the circumstances (orthorhombic, cph or perhaps fcc), (d) a phase mixture under some conditions of cooling and (e) domain size in a possible modulated stacking ordered structure.

Radiation Damage vs Cold Work

Lattice defects can be produced by quenching, cold work and particle bombardment. The latter would produce lattice defects in ^{235}U with its own α-particle activity. A comparison of the C_p vs T curves for cold-worked and self-damaged U, Figs. 1 and 2, indicates that the effects are very much alike in U above 50 to 60 K. The C_p vs T curves after cold work and self damage are higher than in their original cast and annealed state. This also shows up in Fig. 3, but the defects resulting from self damage give a different heat capacity response below 100 K than defects produced by cold work.

Thermodynamic Function Values

The heat capacity behavior shown in Figs. 1 through 3, for the cast and annealed U isotopes, is most likely representative only of metal with the impurity content shown in Table I. Higher concentrations of C and Si (as well as other elements like Cr) may change the martensitic character of the dilute alloy formed and give deeper dips in a C_p vs T curve. The thermodynamic function values listed in Tables II through V may be only representative of the ^{235}U and ^{238}U in the presence of the impurities indicated.

The entropy values for the ^{238}U in the various microstructural states are shown for several temperatures in Table II. The entropy at 298.15 K is lower for the cast state by 1.72 J K^{-1} Mole^{-1} (3.4 percent) than the value reported by Flotow and Lohr,[26] but the $S^o(298)$ value for the cold-worked state is 0.92 J K^{-1} Mole^{-1} (1.8 percent) higher. Annealing the cold-worked ^{238}U lowered the $S^o(298)$ value by one percent and the 144 hr anneal at 898 K seemed to cause an increase in $S^o(T)$ particularly at 350 K and above. The same trend in entropy values was noted with the ^{235}U sample. The value of $S^o(298)$, Table IV, for the cast and annealed ^{235}U was 1.1 percent lower than the value reported by Flotow and Lohr, but the value for the self-damaged state was higher by 1.6 percent.

The enthalpy values for the ^{238}U in the various microstructural states are given in Table III as a function of temperature. The value of enthalpy at 298.15 K for cast and annealed ^{238}U is 4.8 percent lower than that for the cold-worked state at the same temperature. Repeated annealing of the previously cold-worked state did not bring the value of $\{H^o(298) - H^o(0)\}$ down to the value reported for 298.15 K by Flotow and Lohr. The highest value of enthalpy at 298.15 K is shown by self-damaged ^{235}U (Table V).

Tables II and IV show that $S^o(298)$ values are comparable for cold-worked ^{238}U and self-damaged ^{235}U, thus showing that the two different defect structures have a very similar effect on C_p and must be quite similar. The difference in enthalpy between cold-worked ^{238}U and self-damaged ^{235}U at 298.15 K is ~ 0.9 percent.

SUMMARY

Dilute alloys of U form at very low impurity levels. These may have a high ratio of U atoms to impurity atom. Low concentrations of C and Si (among other elements) apparently have as great an effect on physical property behavior of U as small amounts of C addition have on the physical properties of steels.

The β → α-phase transformation of U may either be martensitic or diffusion controlled depending upon cooling rate. The metal appears to have the properties of a martensite even in very dilute alloys. The cooling rate from the β-phase is thus very

important in the development of martensitic charac-
teristics. The difference was noticeable in dips in
C_p vs T curves of ^{235}U and ^{238}U when reduction but-
tons of the isotopes were cooled at different rates
from the molten state.

There appears to be a type of crystallographic
order in dilute U alloys, and the simple model of
order-disorder may not be applicable. It is suggest-
ed that the ordering is complex and such that an
antiphase ordered structure or a modulated stacking
ordered structure is formed. These different order-
ed structures are postulated for different tempera-
ture ranges.

Evolution of heat with increasing temperature
is a property of quenched martensites. The dips in
C_p vs T curves of ^{235}U and ^{238}U which were found
experimentally could be explained by the martensitic
nature of dilute U alloys. It is instead postulated
that the reproducibility of starts in heat capacity
dips at 36 K and the reproducibility in levels of C_p
curves between 36 K and 250 K are more representa-
tive of the appearance of an antiphase ordered
structure.

FS-BZ boundary interactions are considered to
be the source of transitions observed in low-purity
U. It is suggested that electron contributions
from impurity elements present in dilute U alloys
affect the temperature at which low temperature
structural modifications appear.

Heat capacity curves presented and the thermo-
dynamic values tabulated for cast and annealed ^{235}U
and ^{238}U are considered to be only valid for metal
with the impurity content listed. Complete conver-
sion to an antiphase structure would require a much
higher impurity concentration. The tendency towards
a complex form of order can explain the wide band of
C_p vs T data above 100 K for self-damaged ^{235}U and
for cold-worked and annealed ^{238}U.

Several low temperature phases were noted in
low-purity ^{235}U by heat capacity measurements. Im-
purity elements known to stabilize a fcc phase of U
and the banding resulting from swaging are consid-
ered to be the sources of these low temperature
phases.

The difference between S^o(298) of cold-worked
^{238}U and S^o(298) for transition-free U (Flotow and
Lohr) is 0.92 J K^{-1} Mole^{-1}. The difference between
S^o(298) values for cold-worked ^{238}U and self-

damaged ^{235}U (after 12 to 15 months) is only 0.13
J K^{-1} Mole^{-1}. The difference in enthalpy values
for cold-worked ^{238}U and transition-free U (Flotow
and Lohr) at 298.15 K is 92 J Mole^{-1} (22 cal Mole^{-1}).

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