concludes that the velocity of the center of mass of tracer is given by

$$dx/dt = D(2B/\lambda + \partial \log D/\partial x - \partial \log \gamma/\partial x),$$

where B is a factor that measures the vacancy flux, λ is the jump distance, and γ is the activity coefficient of the diffusing specie. Since the second and third terms on the right are small in the proposed experiment, there would appear to be an excellent chance of directly measuring the quantity B. Such experiments are now in progress.

III. CONCLUSIONS

The main conclusions reached from this experiment are as follows. Firstly, uncertainties in temperature measurement, rather than sectioning errors, limit the accuracy of determination. Secondly, the migration entropy of a vacancy decreases linearly with composition by 1.5 R from pure silver to pure gold, and in any given composition both tracers have almost identical entropies of activation. Thirdly, although we do not yet have a diffusion theory which can provide a comprehensive description of a system as simple as silver-gold, several discussions are compatible with substantial portions of the experimental observations. In particular, the treatments of Lidiard and of Manning can be applied to the data to obtain detailed information concerning individual jump frequencies and correlation factors.

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Crystal Structure Variations in Alpha Uranium at Low Temperatures*

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The unusual temperature dependence of the elastic moduli and other physical properties of alpha uranium near 43°K which have been previously reported are found to be correlated with changes in atomic position and with cell dimensions. The atom position parameter, y, decreases to a minimum at 43°K and then rapidly rises on further cooling, as shown both by x-ray and neutron data. The a_0 and b_0 cell dimensions decrease to a minimum at 43°K and then rapidly increase, giving a large negative linear expansion coefficient in the range 43–18°K; the c_0 dimension contracts on cooling to 43°K and decreases even more rapidly below this temperature thus giving a higher positive linear expansion coefficient in the 43–18°K range. Neutron diffraction experiments disclose the existence of additional reflections at the lower temperatures which are presumably due to a magnetic moment arrangement.

INTRODUCTION

THE cusps in the curves for the elastic moduli of α uranium near 43°K,[1] and the unusual temperature dependence of various physical properties in the low-temperature region have emphasized the need for precise crystal-structure data for it down to liquid-helium temperatures. Accordingly, determinations have been made of the atom position parameter, unit cell dimensions, and expansion coefficients throughout the low-temperature range with a precision x-ray diffractometer and cryostat unit using single crystals of high purity. The atom position parameter was also determined in an independent series of experiments using neutron diffraction. Single crystals were used in these studies to avoid the effects of elastic strains that arise from the differential thermal contraction of adjoining regions of different orientation in any measurements made on polycrystalline or twinned material, and perhaps to some extent even on crystals containing lineage structure. The use of single crystals is also desirable because of the high precision in lattice constants and the high diffracted intensities that can be obtained with them when modern techniques are employed.

MATERIALS AND METHODS

The single-crystal samples used in both the x-ray and neutron investigations were rectangular blocks 1 to 3 mm on a side, furnished by Lloyd, which had been previously prepared for thermal expansion studies.[2]

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[1] E. S. Fisher and H. J. McSkimin, Phys. Rev. 124, 67 (1961).

[2] L. T. Lloyd, J. Nucl. Mater. 3, 67 (1961).

These crystals had been grown from high-purity uranium by the grain-coarsening techniques described by Fisher[3] and were isolated from other grains and formed into rectangular blocks by metallographic procedures. The orientation of the electropolished surfaces were within a $\frac{1}{2}$° of the principal planes as determined by Laue back reflection photograms and the crystals appeared to be free from lineage boundaries.

The crystals for the x-ray study were mounted in holes in copper blocks, and secured by flat brass leaf springs. The copper blocks were fastened to the lower end of the helium container in the x-ray cryostat unit[4,5] and surrounded by heat shields, the inner one at the temperature of the specimen and the outer one at the temperature of the surrounding container, namely, 78°K. Temperatures were measured by a copper-Constantan thermocouple clamped to the copper block surrounding the specimen.

Lattice constants at fixed temperatures of 4.2, 78, and 298°K were measured by determining peak positions of high angle reflections on two sides of the incident beam, after the procedure described by Bond.[6] It was judged unnecessary to apply corrections for beam divergence, index of refraction, or other factors since we were concerned mainly with the relative changes in the lattice constants. Lattice constants were measured at intermediate temperatures by permitting the sample to gradually warm up from 4.2 or from 78°K; the diffraction angles were measured by scanning the chosen peak on one side of the direct beam. Each scanning took 2 to 3 min, using a scanning rate of 0.25°/min, during which time the rate of heating was 1 to 2°C/min. Each peak center was determined on the chart from a series of positions near the half-maximum intensity; the width of the peaks at half-height was 0.20°–0.25°.

The atomic position parameter, y, was determined by measuring the integrated intensities of selected $0k0$ reflections since the structure factor for these reflections is $F=4f\cos 2\pi ky$. The x-ray technique consisted in using a beam of Mo $K\alpha$ filtered radiation, collimated by a 0.010-in. pinhole and a 0.010-in. slit, striking the center of the electropolished (010) face of the single crystal mounted as described above for lattice constant measurements. The reflections were scanned using a scintillation counter connected to a pulse-height analyzer which was set to exclude the half-wavelength component.

The copper block containing the specimen was rigidly fastened to the helium container of the cryostat when runs were made at liquid-helium and liquid-nitrogen temperatures; other temperatures were reached by partially insulating the copper block and applying current to a heating wire wrapped around the connecting bar between the helium container and the specimen holder.

TABLE I. Lattice constants and volume of alpha uranium.

Temperature (°K)	a_0 (Å)	b_0 (Å)	c_0 (Å)	V (Å^3)
4.2	2.8444	5.8689	4.9316	82.3256
50.0	2.8364	5.8666	4.9363	82.1401
78.0	2.8377	5.8672	4.9377	82.2095
298.0	2.8537	5.8695	4.9548	82.9918
298.0[a]	2.85360	5.86984	4.95552	83.0058

[a] Ann S. Cooper, Acta Cryst. **15**, 578 (1962).

Although the 020 and 040 intensities were measured, they were very strong and judged to be of doubtful value because of extinction; 060 was borderline in this respect; 0, 12, 0, was too weak in many of the runs to be of value in computing the parameter. The parameters were computed from the integrated intensities of $0k0$ with $k=8$, 10, 14, and 16; several computations included also $k=6$ or $k=12$, chiefly as an aid in estimating the probable errors in the determinations.

The Busing-Levy least-squares program[7] on an IBM-704 computer was used in computing y with the scattering factors listed by Dauben and Templeton.[8] A few computations were also made using the scattering factors listed by Roof[9]; the results with these did not differ significantly from the former results for y although a considerable change occurred in the temperature factor, as expected. It was necessary in many cases to treat the temperature factor as a constant, using estimated values (which were, however, believed to be approximately correct), since the computer otherwise called for negative values, especially in the lower range of temperatures.

For the neutron diffraction runs the crystals were held in a copper block with cadmium-covered jaws. This block was attached to the lower part of a cryostat and surrounded by aluminum heat shields (which have low absorption for thermal neutrons); one shield at the sample temperature and the other at liquid nitrogen temperature. Cadmium (which has a very high absorption for thermal neutrons) was used as a mask around the copper jaws.

With the crystal properly oriented, intensities were obtained for the even orders of the $0k0$ reflections from 2 through 10 using a neutron wavelength of 0.98 Å and stepwise scanning over the peaks. A least-squares calculation was carried out as described above omitting the 020 because of extinction and using an estimated temperature factor at the lower temperatures.

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[3] E. S. Fisher, Trans. Am. Inst. Mining. Met. Petrol Engrs. **209**, 882 (1957).

[4] C. S. Barrett, Acta Cryst. **9**, 621 (1956).

[5] C. S. Barrett, Trans. Am. Soc. Metals **49**, 53 (1957).

[6] W. L. Bond, Acta Cryst. **13**, 814 (1960).

[7] W. R. Busing and H. A. Levy, Oak Ridge National Laboratory, Report 59-4-37, 1959 (unpublished).

[8] C. H. Dauben and D. H. Templeton, Acta Cryst. **8**, 841 (1955).

[9] R. B. Roof, Acta Cryst. **14**, 934 (1961).

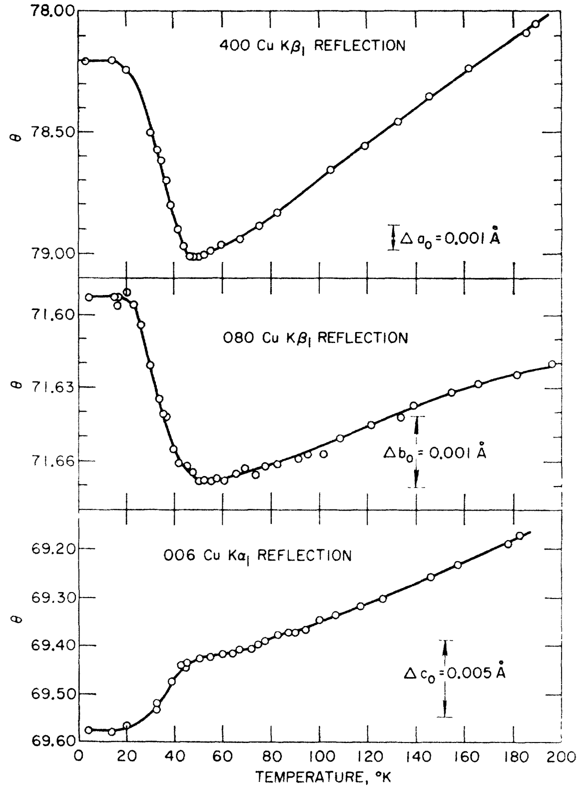

FIG. 1. Relative change of 400, 080, and 006 reflections for alpha uranium as a function of temperature. Angle θ in degrees.

RESULTS

Lattice Constant

The lattice constants at several temperatures are reported in Table I. They are based on the wavelengths Cu $K\alpha_1 = 1.54050$ Å and Cu $K\beta_1 = 1.39217$ Å. From duplicated runs, reverse-direction scanning runs, and consideration of crystal perfection, the estimated accuracy of the constants is of the order of 1 part in 10 000. Results of the most precise previous investigation converted to angstroms are also included.

In Fig. 1 are plotted the diffraction angle, θ, vs temperature during slow warming experiments; corresponding changes in lattice constants are indicated (approximately) in the figure by the distances Δa_0, Δb_0, and Δc_0.

TABLE II. Mean linear and volume expansion coefficients of alpha uranium.

Temperature range (°K)	$\Delta a/a$[a] (10^{-6} per deg C)	$\Delta b/b$ (10^{-6} per deg C)	$\Delta c/c$ (10^{-6} per deg C)	$\Delta V/V$ (10^{-6} per deg C)
32–40	−136.0	−28.2	52.1	−112.1
81–100	27.9	2.89	10.6	41.4
152–179	24.7	2.09	13.7	40.5
78–298	25.6	1.78	15.7	43.0

[a] $\Delta a/a = (1/a)[(a_2 - a_1)/(T_2 - T_1)]$ where a_2, T_2 refer to the higher temperature. The other coefficients were calculated similarly.

TABLE III. X-ray determinations of α-uranium parameter.

Temp. (°K)	Run	k	y	B	R
4.2	1/2	6, 8, 10, 14, 16	0.10228	0.009	0.032
4.2	1/2	8, 10, 14, 16	0.10250	0.005[a]	0.032
4.2	1/24	8, 10, 14	0.10249	0.003[a]	0.003
19.5	1/18	6, 8, 10, 14, 16	0.10225	0.038	0.021
19.5	1/18	8, 10, 14, 16	0.10211	0.01[a]	0.040
23.3	1/25	8, 10, 14, 16	0.10205	0.01[a]	0.036
25.0	1/31	8, 10, 12, 16	0.10199	0.01[a]	0.039
31.4	1/16	6, 8, 10, 14, 16	0.10186	0.01[a]	0.013
36.0	1/31	8, 10, 12, 14, 16	0.10197	0.01[a]	0.017
36.0	1/31	8, 10, 14, 16	0.10204	0.01[a]	0.004
38.1	1/16	8, 10, 14, 16	0.10169	0.01[a]	0.020
49.0	1/16	8, 10, 14, 16	0.10187	0.015[a]	0.037
66.0	1/31	8, 10, 14, 16	0.10195	0.02[a]	0.013
66.0	1/31	8, 10, 12, 14, 16	0.10194	0.02[a]	0.016
78.0	1/24	8, 10, 14, 16	0.10199	0.20[a]	0.088
78.0	1/24	8, 10, 14, 16	0.10204	0.025[a]	0.016
82.0	1/17	8, 10, 14, 16	0.10191	0.20	0.099
82.0	1/17	8, 10, 14, 16	0.10193	0.03[a]	0.024
165.0	1/20	8, 10, 14, 16	0.10199	0.07[a]	0.012
165.0	1/20	6, 8, 10, 14, 16	0.10205	0.049	0.012
297.0	1/18	8, 10, 14, 16	0.10235	0.41	0.015
297.0	1/18	6, 8, 10, 14, 16	0.10257	0.27[a]	0.032
297.0	1/18	8, 10, 14, 16	0.10247	0.27[a]	0.057
298.0	1/23	8, 10, 14, 16	0.10239	0.27[a]	0.028

[a] B held invariant at value indicated.

The changes in diffraction angle correspond to large negative linear expansion coefficients below 46°K for the a_0 and b_0 unit cell dimensions, followed by smaller positive coefficients in the range 46–298°K. The increase in a_0 below 46°K is in agreement with the observation reported previously[10] in cooling from 63 to 20°K. The c_0 dimension has positive expansion coefficients throughout, but higher values below 45°K than above this temperature. The expansion of all three axes is negligible below 18°K. The corresponding change in volume is plotted in Fig. 2. Some values for these coefficients, computed from the curves, are listed in Table II. Some negative expansion coefficients were expected from the

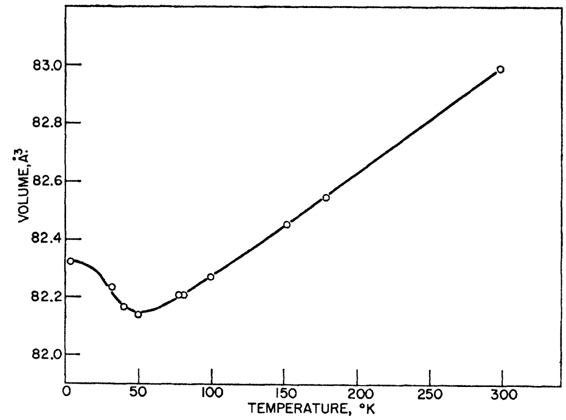

FIG. 2. Volume change for alpha uranium as determined from the lattice constants.

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[10] J. R. Bridge, C. M. Schwartz, and D. A. Vaughn, Trans. Am. Inst. Mining, Met. Petrol. Engrs. **206**, 1282 (1956).

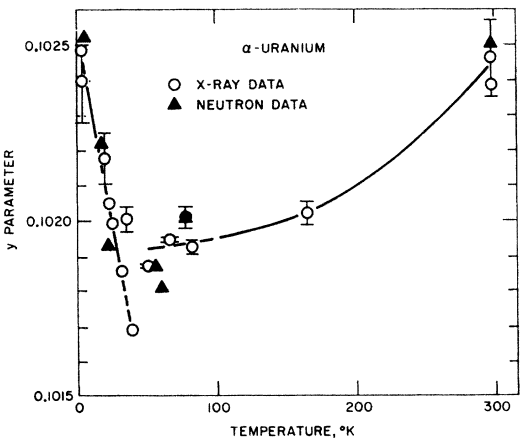

FIG. 3. The atomic position parameter, y, of alpha uranium as a function of temperature.

previous publications of dilatometer curves for polycrystalline samples;[11,12] as these have indicated negative coefficients below about 45°K with most rapid changes near 35°K. They are in good agreement with calculations from the present single-crystal results, and with the total maximum contraction at 45°K and expansion to 4.2°K as shown in Table I and Fig. 2.

Parameters

All x-ray runs with acceptable internal consistency are listed in Table III. Some runs were computed in more than one way, with the use of different lists of reflections or with different temperature factors, B. The results of the computations are plotted in Fig. 3. When different computations of the data from a given run were available, the range of uncertainty indicated by these has been shown in the figure—the range thus determined should be an overestimate since data of borderline credibility were included in one of the computations that was used judging the uncertainty. The results at room temperature are in excellent agreement with the most accurate previous determination.[13]

TABLE IV. Neutron determination of an α-uranium y parameter.

Temp. (°K)	Run	k	y	B	R
16	B345	4, 6, 8, 10	0.10259	0.01[a]	0.018
16	B345	2, 4, 6, 8, 10	0.10205	0.01[a]	0.030
25	B341	4, 6, 8	0.10194	0.01[a]	0.014
25	B341	2, 4, 6, 8	0.10167	0.02	0.042
26	B373	2, 4, 6, 8, 10	0.10218	0.01[a]	0.056
48	B323	4, 6, 8, 10	0.10187	0.015[a]	0.048
48	B323	2, 4, 6, 8, 10	0.10164	0.015[a]	0.061
78	B344	4, 6, 8, 10	0.10225	0.1[a]	0.118
78	B344	2, 4, 6, 8, 10	0.10167	0.1[a]	0.138
78	B372	4, 6, 8, 10	0.10203	0.025[a]	0.038
78	B372	2, 4, 6, 8, 10	0.10180	0.025[a]	0.052
78	B343	4, 6, 8, 10	0.10209	0.025[a]	0.084
298	B327	4, 6, 8, 10	0.10229	0.27	0.063
298	B327	2, 4, 6, 8, 10	0.10235	0.215	0.062
298	B340	2, 4, 6, 8, 10	0.10227	0.27[a]	0.090
298	B340	4, 6, 8, 10	0.10250	0.27[a]	0.079

[a] B held invariant at value indicated.

TABLE V. Interatomic distances (A) and angles for α U as defined in Fig. 4.

Temp. (°K)	AC and DE	AB (a_0)	AD and CE	AE	Angle CAC'
298	2.7539	2.8537	3.2632	3.3427	128.21°
78	2.7438	2.8377	3.2587	3.3352	128.26°
50	2.7423	2.8364	3.2581	3.3352	128.32°
4.2	2.7432	2.8444	3.2609	3.3322	128.02°

The results of the neutron experiments are listed in Table IV and are compared with the x-ray results and previous neutron results at room temperature[14] in Fig. 3. The uncertainty within a run was in the same range as the x-ray results although it is not indicated in Fig. 3. It is immediately obvious that the y parameter decreases from room temperature to a minimum near 43°K and rapidly increases between this temperature and 4.2°K. The shape of the curve between 300 and 43°K has not been accurately determined.

There is obviously no appreciable discontinuity in the y parameter as the temperature varies through the 43°K neighborhood, although an abrupt change of 1 part in 500 or 1000 may exist; there is a large discontinuity, however, in the slope of the curve.

Neutron diffraction studies of single crystals have disclosed the existence of several additional reflections which are not permitted with the present alpha uranium structure. These increase in intensity from room temperature to the lower temperatures; however, they have not been observed in the x-ray pattern. The 001 and 003 reflections are detected together with several other more general reflections with intensities several times

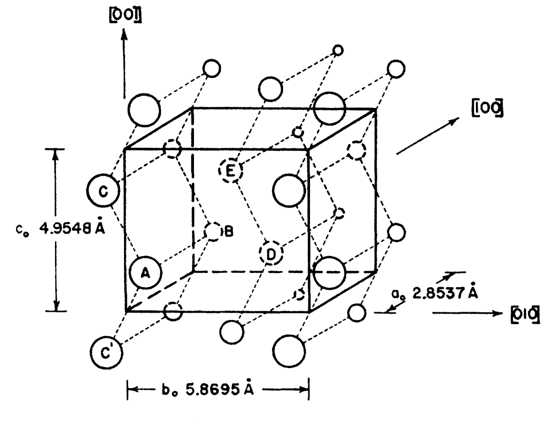

FIG. 4. Atomic arrangement in alpha uranium with room-temperature lattice constants.

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[11] A. F. Schuck and H. L. Laquer, Phys. Rev. **86**, 803 (1952).

[12] H. L. Laquer, Los Alamos Scientific Laboratory Report AECD-3706, 1952 (unpublished).

[13] E. F. Sturcken and B. Post, Acta Cryst. **13**, 852 (1960).

[14] M. H. Mueller, R. L. Hitterman, and H. W. Knott, Acta Cryst. **15**, 422 (1962).

that attributable to the $\lambda/2$ component of the beam. Possible causes for their existence are briefly discussed later.

DISCUSSION

The four nearest-neighbor distances and angles along the chain were calculated from the results of the lattice constants and from the value of y. These results are shown in Table V and identified in Fig. 4. It can be seen that upon cooling, the first three distances decrease to the 40–50°K region and then increase and that the fourth distance, AE, steadily decreases over the entire range. The greatest percentage change occurs in the AB distance. It can also be noted that there is very little change in the bonding angle along the chains over the entire low-temperature range.

Fisher and McSkimin have concluded that the anomalies in physical properties do not imply a first-order phase change, and we find no evidence of one. They have ascribed the changes in physical properties to changes in the number of bonding electrons or the number of available bonding electrons localized to the AB bond, which is the second nearest-neighbor bond. Arguing from elastic coefficients and compressibilities they proposed that on cooling near 300°K the c_0 dimension decreases and the y parameter should increase so as to decrease the angle between the AC and AC' bonds and also the fourth-neighbor distance AE. We have found the following: The c_0 does decrease with lower temperature; the y, however, does not increase until the 40–50°K region; the angle CAC' is quite stable and the AE distance does decrease. At 43°K they proposed that the AB bond would become unstable and would begin to increase below this temperature region.

The anomalous expansion characteristics below 43°K can be considered on the basis of the Grüneisen factor γ, as has been suggested by Gibbons[15]; on this basis an understanding of the negative volume expansion coefficient should be sought in a detailed analysis of the modes of vibration of the structure. By analogy with the covalent crystals Si, InSb,[15] and Ge,[16] which also have a "open" type structure, it might be expected that some transverse modes of vibration in uranium may increase in frequency with increasing volume and thus contribute terms that lead to negative rather than positive values of γ and the expansivity at very low temperatures.

However, since there are extra reflections in the neutron pattern, an explanation of their existence may well have a bearing on the explanation of the structure changes and physical properties at low temperatures. These have not been observed up to the present with x rays and yet are observed with thermal neutrons even when a Pu filter is used which eliminates most of the $\lambda/2$ component; their intensities with the filtered beam precludes explaining them as $\lambda/2$ reflections.

We have considered other possible causes such as impurities, multiple crystals, multiple Bragg scattering, and magnetic scattering. We tentatively conclude that in addition to multiple Bragg scattering a magnetic contribution must be present, but the nature of the magnetic arrangement has not yet been determined and further work is in progress.

Magnetic-susceptibility measurements are also being carried out on single crystals by Lam at the Argonne National Laboratory in order to investigate further a preliminary observation of magnetic anisotropy in a single crystal of uranium at 77°K.

ACKNOWLEDGMENTS

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[15] D. F. Gibbons, Phys. Rev. **112**, 136 (1958).

[16] W. B. Daniels, Phys. Rev. Letters **8**, 3 (1962).