STUDIES IN X-RAY CRYSTALLOGRAPHY

I The Allotropic Forms of Cerium

II The Structure of Urea Oxalate

Thesis by

Adam Frank Schuch

In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1950

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help and encouragement I have received from others in these studies. Professor J. H. Sturdivant taught me the principles and methods of X-ray crystallography and supervised my researches. I am especially grateful to him for the continuing interest he has taken in me and for his guidance and many suggestions. Professor Linus Pauling suggested the study of cerium to me. Dr. Jerry Donohue instructed me in calculating Fourier projections and gave me many hints when I was determining the structure of urea oxalate. I am very much indebted to my wife, Edith, for her help with many laborious calculations.

ABSTRACT

I The Allotropic Forms of Cerium

The crystal structure of elementary cerium has been investigated by X-ray diffraction at temperatures from room temperature to that of liquid nitrogen. Despite a variety of heat treatments, I have been able to obtain at room temperature only a cubic closest-packed structure with $a_0 = 5.139$ Kx. No evidence could be found to confirm the existence of a hexagonal closest-packed structure.

When stresses are produced in cerium, as for example by quenching from 250°C. or higher, and it is then rapidly cooled with liquid air, a new form is obtained which also has the cubic closest-packed arrangement but with $a_0 = 4.82$ Kx. If the cerium is annealed or free of stresses then no allotropic change takes place.

In the new structure it is believed that the 4f electron has moved into hybridized 5d 6s orbitals to take part in bond formation. This experimental work confirms in part the predictions of Trombe.

II The Structure of Urea Oxalate

Urea oxalate crystallizes monoclinic prismatic, $P\,2_1/c$, $A_1 = 5.218$ Å., $A_2 = 12.404$ Å., $A_3 = 11.576$ Å., and $\beta = 143^\circ 1'$. There are two formula weights per unit cell. The structure is a layer one with the molecules almost parallel to (100). The layers are held together by van der Waals forces. There is no discrete urea oxalate molecule. Each layer is a network of urea and oxalic acid molecules held together by hydrogen bonds. One extremely short $O - H \cdot O$ distance of 2.47 Å. was found.

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THE ALLOTROPIC FORMS OF CERIUM

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Introduction

In the first X-ray diffraction investigation (1) of the structure of cerium the metal was reported to crystallize at room temperature in both the hexagonal closest-packed and the cubic closest-packed arrangements, but in later X-ray studies only the cubic form has been found. The phase behavior at low and high temperatures also has been examined by dilatometric, magnetic, and other methods, not including X-ray diffraction. The results have shown a strong dependence on the history of the specimen, but they have also indicated that cerium might have altogether four allotropic forms. The most interesting transition is evidenced by a 10% contraction in volume at 109° K.

A. The Structure of Cerium at Room Temperature.

1. Historical

In 1921 A. W. Hull (1) after making the first X-ray diffraction investigation of cerium reported as follows on its structure. "Cerium thus appears to be composed of the hexagonal and cubic forms of close packed arrangements of atoms, like cobalt. The effect of annealing has not been tried. It is possible, however, that the apparent dimorphism is due to impurity, as the sample, though supposed to be very pure, has not been analyzed, and its pattern was almost identical with that of 'misch metal' which contains about 8% iron."

Hull found the cell dimensions of the hexagonal structure to be a_o = 3.65 Å., c_o = 5.96 Å., c/a = 1.633; and of the cubic structure a_o = 5.12 Å. With these dimensions the densities of the hexagonal and cubic forms are 6.72 gm/cm^3 and 6.88 gm/cm^3 respectively. No other data than the cell dimensions were published by Hull, but recently he has kindly given Professor Linus Pauling a photostat of his original data. I have used it to prepare Table 2.

Since Hull, other authors (2), (3), (4), (5) have reported the results of X-ray diffraction investigations of cerium. They all found the cubic form. Of these Klemm and Bommer found besides the cubic diffraction maxima two additional faint lines which they could index as reflections from the (101) and(103) faces of hexagonal closest-packed cerium. No other X-ray evidence of the existence of the hexagonal structure has been published.

In a microscopic study of a cerium casting Schumacher and Lucas (6) found only the cubic structure.

Jaeger, Bottema, and Rosenbohm (7) studied the variation of specific and electrical resistance from room temperature to 540° C. When their specimen was freshly cast, the curves were irregular and non-reproducible, and remained so until the specimen had been cycled some eight times from 150°to 540° C. The resistance curve for the cycled specimen indicated transitions at 393° and 440° C. Their deductions as to the structures of cerium are not of interest.

Trombe and Foex (8) in dilatometric studies also found that the density of cerium is dependent upon its history, but becomes reproducible after prolonged annealing cycles between 500° C. and the temperature of liquid nitrogen. In their dilatometric curve they observed no discontinuities at 393° and 440° C., but they found one at 150° C. When the cerium was slowly cooled from 150° C. its density at 20° C. was 6.72 gm/cm^3, and when it was quenched from 150° C. its density was 6.77 gm/cm^3. By comparison with the densities calculated for Hull's two structures Trombe assigned the hexagonal structure to the annealed cerium and the cubic structure to the quenched cerium.

2. Experimental

The cerium used in the present investigation was a small casting obtained from F. H. Spedding. He listed the impurities as 0.2% calcium, 0.2% magnesium, and 0.04% beryllium.

By a spectrographic analysis I found the sample free of other rare earths.

The specimens for the X-ray diffraction investigation were prepared in an argon atmosphere by sifting 200-mesh filings from the casting into thin-wall glass capillary tubes. The tubes were then sometimes evacuated and sealed, and at other times sealed at once without removing the argon. All heat treating was done after the sample was thus prepared. When the specimens were quenched it was by directing onto them a blast of air. This gave immediate cooling, because the thin-wall capillaries were only 0.3 mm. to 0.4 mm. in diameter. The X-ray powder photographs were taken in a camera of radius 5 cm. with copper radiation filtered through nickel foil 100 μ thick.

I first found that unannealed filings from the casting gave the pattern corresponding to face-centered cubic cerium. I then attempted to prepare hexagonal cerium.

According to the reports of Trombe or of Jaeger, respectively, phase transitions occur at 150° or at 393° and 440° C. Both agree that at room temperature hexagonal cerium is the stable form. In the attempt to get hexagonal cerium I heated specimens to different temperatures up to as high as 420° C. and slowly cooled them to room temperature. Other samples I cooled past the purported transition points and then quenched. On the supposition that hexagonal cerium is stable at high temperature I quenched still other samples from as high as 575° C. I even applied a low-temperature heat treatment by repeatedly dipping a specimen in liquid air, because Trombe reported that this favors the formation of hexagonal cerium. Finally, I also remelted a portion of the original casting and repeated some of the above thermal experiments on it. Altogether, I never found so much as a trace of hexagonal closest-packed cerium. I always got the cubic closest-packed structure.

The detailed heat treatments given the samples are shown in Table 1. Those samples designated by a common letter are the same specimen; the numerals indicate a sequence of heat treatments.

I found the unit cell edge of quenched cerium to vary from 5.132 Kx. to 5.148 Kx. To obtain a reproducible value of the lattice constant I determined it on two carefully annealed specimens. The two values are:

Sample	a_0
E-2	5.139 Kx.
L-5	5.138 Kx.

I determined the constants in the following manner. First, I found the value of a_0 represented by each reflection that occurred at a high

Table 1

Summary of Heat Treatments*

Sample	Heat Treatment
E-1	Cooled from 208° to 130° at 10°/hr.; held 12 hours at 130°; cooled to room temp. at 30°/hr.
E-2	Cooled from 420° to 300° at 20°/hr.; held 18 hours at 300°; cooled to 135° at 20°/hr. Held 12 hours at 135°; cooled to room temp. at 12°/hr.
G-1	Quenched from 525°.
G-2	Held 2 days at 320° and quenched.
J-1	Held 2 hours at 300° and quenched.
K-1	Held 6 weeks at 105° and quenched.
K-2	Held 4 weeks at 340° and quenched.
L-2	Slowly cooled from 490° to 430°; held 30 hours at 430°; quenched.
L-3	Held 10 days at 375° and quenched.
L-4	Held 11 days at 330° and quenched.
L-5	Cooled from 320° to 0° at 10°/hr.
L-6	Dipped four times in liquid air.
M-1	Slowly cooled from 490° to 430°; held 30 hours at 430°; slowly cooled to 335°; held 17 hours at 335°; quenched.
O-1	Held 45 min. at 575° and quenched.
P-1	Held 1 day at 340° and quenched.
T-1	Part of original casting remelted, cooled in furnace; sampled.
U-1	Specimen from remelted casting; cooled from 300° to room temp. at 50°/hr.
V-1	Specimen from remelted casting; held 2 hours at 300°; quenched.

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*Temperatures are degrees Centigrade. Samples with a common letter are the same specimen, but the numerals show a sequence of heat treatments.

Bragg angle. Thus with sample L-5 I got these values:

hkℓ	Radiation	Sine θ	a_0
511	K α_1	.77832	5.131 Kx.
440	K α_1	.84725	5.132
531	K α_1	.88574	5.134
531	K α_2	.88769	5.135
600	K α_1	.89799	5.135
600	K α_2	.90027	5.135
620	K α_1	.94640	5.136
620	K α_2	.94879	5.136

I then plotted the values of a_0 against the Nelson and Riley (9) function,

$$\tfrac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right),$$

and extrapolated them to $\theta = 90^\circ$. The value of a_0 at 90° I took to be the true value. Nelson and Riley in a study of extrapolation methods have shown that this is the best function to use when absorption is high, which is the case with cerium.

The points were all nearly on a straight line, and the extrapolated values are in error by less than 0.002 Kx. The two values of a_0 I obtained agree well with the values of 5.138 and 5.140 Kx. reported by Zintl and Neumayr (3) and 5.140 Kx. ± .002 reported by Klemm and Bommer (5).

I calibrated the camera with sodium chloride whose cell edge I took to be 5.626 Kx. The data were always corrected for the shrinkage of the film. Before development two marks were indented on the film with an instrument which had two prongs at a known distance apart. When the pattern on the film was measured the distance between the two marks was also measured, and the shrinkage was thus found. The wavelengths I used for the copper radiation are:

$K\alpha_1$	1.5374 Kx.
$K\alpha_2$	1.5412
$K\alpha$	1.5387

3. Discussion.

In view of my own inability and that of others to get hexagonal cerium I have studied Hull's data in some detail. In Table 2 I compare the intensities and interplanar spacings he observed with those that hexagonal and cubic closest-packed cerium should have according to my computations. There are three maxima which cannot be indexed on the hexagonal or the cubic lattice. They may be due to some impurity. The agreement in intensities is somewhat haphazard but cannot with propriety be appraised by present standards. On the whole I am inclined to accept that Hull's sample had a hexagonal structure. But in view of the lack of an analysis of the specimen, and the similarity of its diffraction pattern with that of misch metal, an alloy containing only about 50% cerium (10), I question whether the hexagonal structure was that of cerium.

Table 2

Observed and Calculated Interplanar Spacings for Cerium

Calculated Hexagonal closest-packing $a_o = 3.56$ Å. $c_o = 5.96$			Observed Hull - 1921		Calculated Cubic closest-packing $a_o = 5.14$ Å.		
hkℓ	d	I	d	I	hkℓ	d	I
100	3.16	2.2	3.03	2			
002	2.98	2.5	2.92	2	111	2.97	2.5
101	2.79	9.0	2.79	12			
			2.555	1	200	2.57	1.1
			2.455	1			
102	2.17	1.4	2.185	?½			
			1.880	??¼			
110	1.825	1.6	1.824	8			
					220	1.817	0.8
103	1.682	1.8	1.668	2			
200	1.581	0.3					
112	1.556	1.9	1.555	10wide	311	1.550	0.8
201	1.527	1.3					
004	1.49	0.2	1.478	2	222	1.484	0.2
202	1.396	0.3	1.393	??½			
104	1.348	0.3	1.326	??¼			
					400	1.285	0.1
203	1.236	0.6	1.232	½			
120	1.195	0.2	1.182	2			
					331	1.179	0.4
121	1.171	1.1	1.154	3	420	1.15	0.3
122	1.109	0.3					
300	1.054	0.3	1.065	??¼			
					422	1.049	0.3
123	1.024	0.7	1.03	?¼			
302	0.993	0.5	0.997	?½	511	0.989	0.4
205	0.953	0.4	0.954	??¼			
			0.939	??¼			
220	0.913	1.0	0.918	?½			
310	0.877	0.1	0.878	½			
222	0.873	0.5	0.871	½			
					531	0.864	0.6

B. The Structure of Cerium at Low Temperature

1. Historical

In 1934 Trombe (11) discovered an hysteresis in the magnetic susceptibility curve of cerium at the temperature of liquid nitrogen. This phenomenon was also observed by Klemm and Bommer (5). Others (12) (13) were unable to observe any such effect. Later Trombe and Foex (8) after an extensive dilitometric, magnetic, and electrical study of cerium published the conditions under which this phenomenon could be observed.

If the cerium had been recently cast, or if it had been quenched from 200° C. to room temperature, then upon cooling it to the temperature of liquid nitrogen, they obtained the dilatometric and magnetic susceptibility curves shown in Figures 1 and 2 on the next page. The density and magnetic susceptibility changed sharply at 109° K. when the temperature was lowered, and they again changed together at 175° K. At 109° K. the decrease in length is 3.36%, which corresponds to a decrease in volume slightly greater than 10%.

When however the cerium was slowly cooled at about 50° per hour from 500° C., or even from 200° C., to room temperature, then upon cooling it to the temperature of liquid nitrogen they obtained a curve similar to the one shown in Figure 3. This time there was a smaller change in density at 109° K., but the curve was not reproducible. Successive cooling and heating cycles between room temperature and liquid nitrogen continuously contracted the hysteresis loop until with the sixth cycle the reproducible curve "β" in Figure 4 was obtained. This figure best summarizes how quenched and annealed cerium undergo different dilatometric changes at 109° K.

The behavior of annealed cerium at 150° C. is also curious. It contracts when heated past this temperature. Trombe reports that this is the

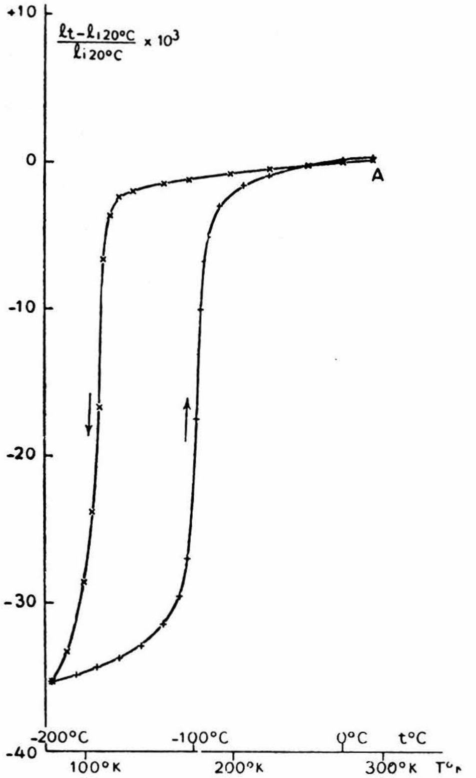

Figure 1

The thermal expansion coefficient
of quenched cerium

Figure from Ann. chim. 19, 424 (1944)

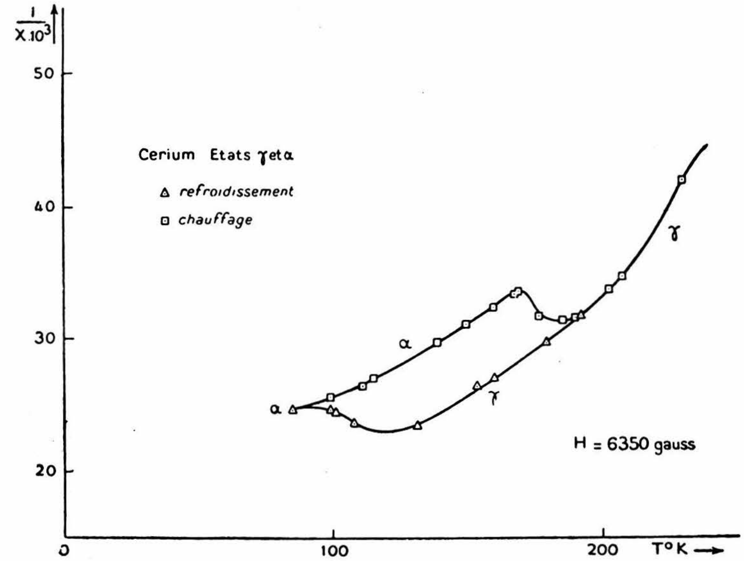

Figure 2

The magnetic susceptibility of quenched cerium

Figure from Ann. chim., 19, 434 (1944)

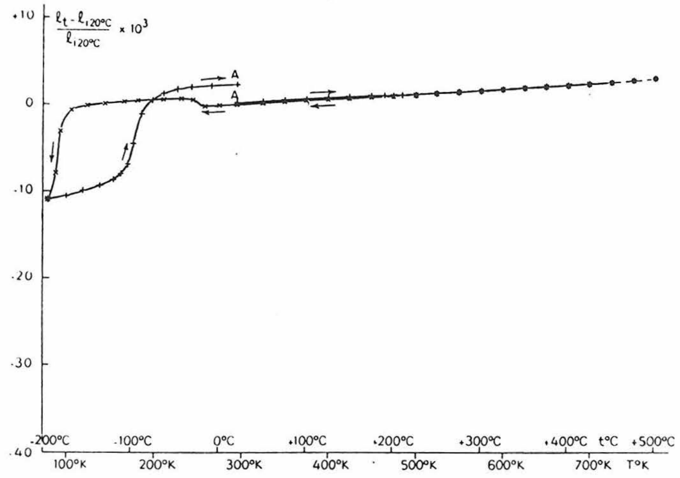

Fig. 4. — Etude dilatométrique. Chauffage de 20° C à 500° C, refroidissement lent de 500° C à — 195° C et retour à la température ordinaire.

Figure 3

The thermal expansion coefficient of annealed cerium

Figure from Ann. chim., 19, 425 (1944)

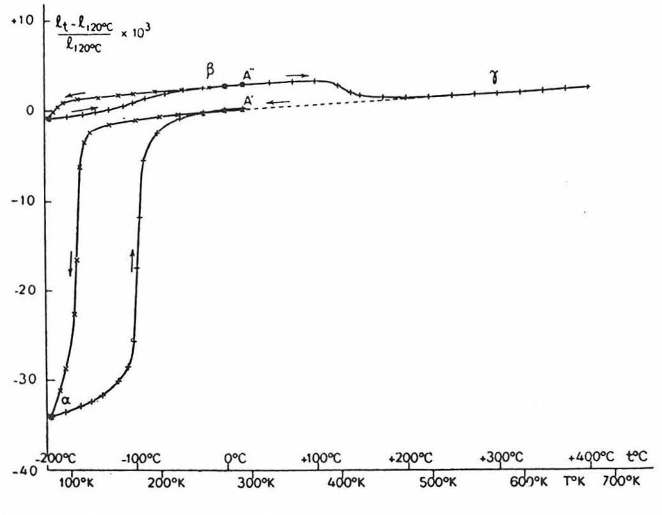

Fig. 6. — Etude dilatométrique. Sixième refroidissement lent de 20° C à — 195° C, chauffage de — 195° C à 400° C et refroidissement de 400° C à — 195° C.

Figure 4

Upper curve: dilatometric changes upon the sixth cooling of annealed cerium to -195° followed by heating to 400° C.
Lower curve: dilatometric changes in quenched cerium

Figure from Ann. chim., 19, 428 (1944)

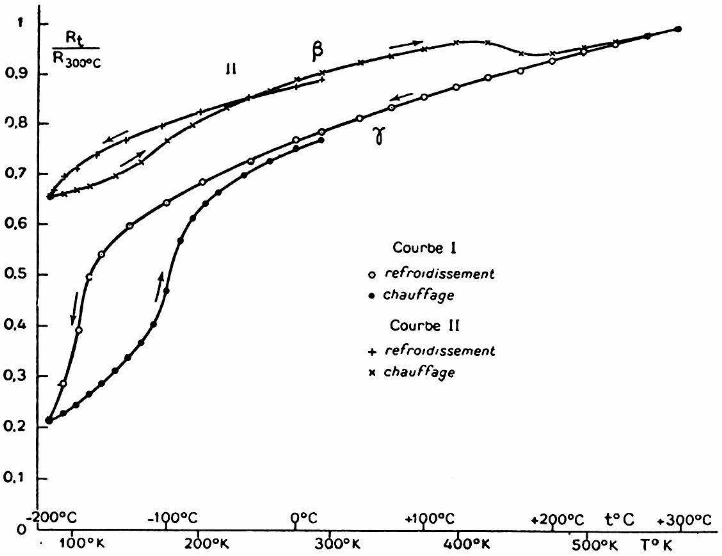

Figure 5

The electrical resistance of annealed (β) and quenched (γ) cerium

Figure from Ann chim., 19, 440 (1944)

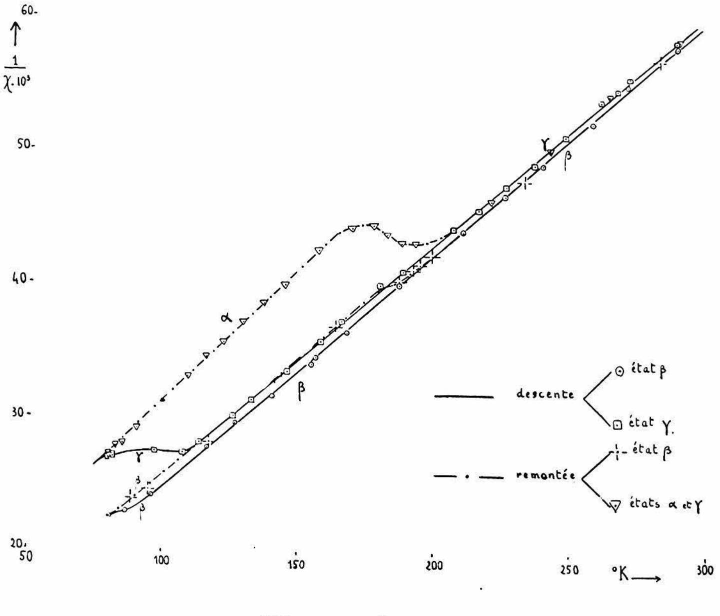

Figure 6

A magnetic susceptibility study by LaBlanchetais of annealed (β) and quenched (γ) cerium. The course of the curve α indicates a new structure.

Figure from Compt. rend., 220, 392 (1945) critical temperature from which by cooling or quenching one can get cerium with either of two different properties.

The differnce between annealed and quenched cerium is also shown by the electrical resistivity curve, Figure 5. Quenched cerium undergoes a great increase in conductivity at 109° K.

Figure 6 is an independent magnetic study of the two kinds of cerium (14).

Trombe concluded from these results that he was dealing with three allotropic forms of cerium as follows:

(1) The γ form is stable above 150° C., but it can be brought to room temperature by quenching. A newly cast piece of cerium is apt to be in this form.

(2) The α form is obtained at 109° K. from γ cerium. Once formed it is stable upto 165° K., where it reverts to the γ form. The $\gamma \rightarrow \alpha$ transition is accompanied by a decrease in volume of 10%.

(3) The β form is stable at room temperature. It is obtained by slowly cooling γ cerium from 135° C. Should the transition to β cerium not be complete when room temperature is reached, it can be made so by subjecting the sample to cycles of slow cooling and heating between liquid nitrogen and room temperature. The transitions $\beta \rightleftarrows \alpha$ do not take place.

Additional observations by Trombe and other French workers which will be referred to are the following:

a. If the cerium is pure, then the γ form can be kept at room temperature at least a year, and upon cooling it will give the α form (8).

b. The most effective way of producing γ cerium is to quench it from 425° C. with liquid nitrogen. (8).

c. A commercial specimen of cerium containing 0.22% Fe, 0.15% Ca, and 0.08% Al, when put into the γ form, changed spontaneously in 5 months to the β form (15).

d. The contraction of quenched cerium at 109° K. was decreased by magnesium and disappeared entirely when the magnesium content reached 1% (16).

Trombe has not determined the structure of α, β, or γ cerium. However, as I have described earlier, after comparing their densities with those of Hull's two structures, he assumed that β cerium has the hexagonal closest-packed structure and that γ cerium has the face-centered cubic structure. This assumption was all the more reasonable because Klemm and Bommer (5) found from their own X-ray diffraction work that the cerium which showed a magnetic anomaly at low temperature was face-centered cubic at room temperature.

2. Investigation of the Structure at Low Temperatures.

To determine the structure of α cerium an apparatus for cooling the sample was built similar to the one described by Hume-Rothery and Strawbridge (17). It cooled the sample by blowing over it the vapor from boiling liquid air. A sketch of it is shown in Figure 7. The lowest operating temperature that could be reached with it was 109° K., which is just the temperature at which the γ → α transition takes place.

Runs were made on two different samples, but no allotropic changes were found. The diffraction lines remained sharp, and within the limits of my measurements only one of the samples showed a slight contraction

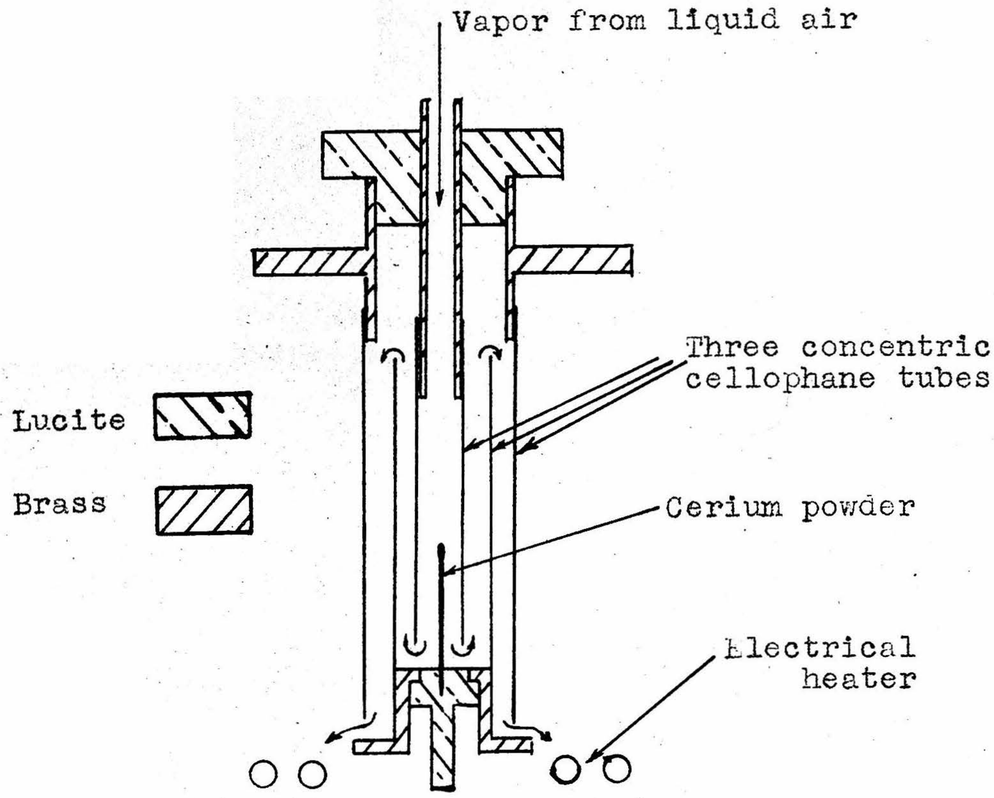

Figure 7

An apparatus for cooling a powder specimen to low temperatures for X-ray diffraction

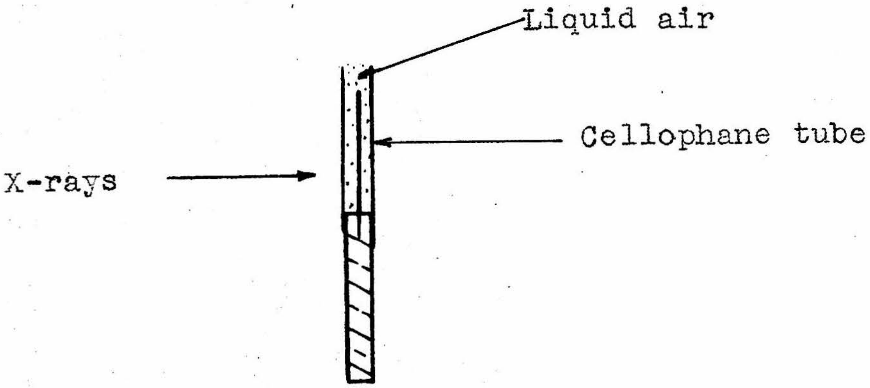

Figure 8

Another apparatus for cooling a powder specimen to low temperatures for X-ray diffraction at 109° K. The results are given here.

Sample	a_0	Temperature
J-1	5.137 Kx.	Room temperature
J-2	5.123	109° K.
P-1	5.132	Room temperature
P-2	5.134	109° K.
P-3	5.143	Room temperature

The decrease in the density of cerium at room temperature after having been cooled to 109° K. which is shown by sample P-3 has already been observed by Trombe and is illustrated in Figure 3. Sample J was quenched from 300° and P from 340° C. In each case it required an hour to reach 109° K. from room temperature.

For a temperature as low as -100° C. this apparatus is very efficient and I recommend it highly. However, I found it very difficult to reach and hold 109° K. Therefore, I built a different apparatus. It was a small lucite cup in the center of which the glass tube containing the sample was erected. A continuous stream of liquid air was allowed to flow down over the sample tube and fill and overflow the cup.

Three samples, one of them annealed, were photographed. None showed a change, and as before the diffraction lines remained sharp.

Next a piece of the original casting was remelted under vacuum. During the remelting a mirror formed on the cold part of the apparatus above the melt. A spectrographic analysis showed the mirror to be calcium and magnesium.

Low-temperature photographs of specimens from the remelted casting were taken. For the first time evidence of some change was found. Most of the diffraction lines of the old cubic structure had disappeared. The only reflections still definitely present were 220 and 311, but their interplanar spacings had increased slightly. The 511 and 531 reflections may also have been present but it was hard to tell because of the many diffraction lines from ice that were present. Even if they were counted as present there were still nine reflections missing. On a photograph taken at room temperature immediately afterwards the lines were diffuse and weak. With subsequent photographs I continued to have trouble with ice. I therefore devised another method of taking a low-temperature photograph.

In this last and successful method the entire sample tube was placed inside a column of liquid air, and the photographs were taken with the X-rays passing through the column. The arrangement is shown in Figure 8. A continuous stream of liquid air kept the cellophane tube full, and the overflow washed the outside free of ice. Since the X-rays had to pass through 3 mm. of liquid air it was necessary to use molybdenum radiation.

For the investigation by this method a sample T from the remelted casting was quenched from 300° C. The first low temperature photograph, T-3, showed that at last I had a new structure. A print from it is shown in Figure 9 along with prints from a room temperature photograph and another low-temperature photograph.

They clearly show that a change has taken place at the lower temperature. To make sure that the new diffraction lines are not due to ice, cellophane, or some condition of the experiment I ran a blank and this photograph had no diffraction lines. When I indexed the lines I found that the cerium is a mixture of the old and new structures. The new structure is also face-centered cubic but the size of the unit cell is smaller. The

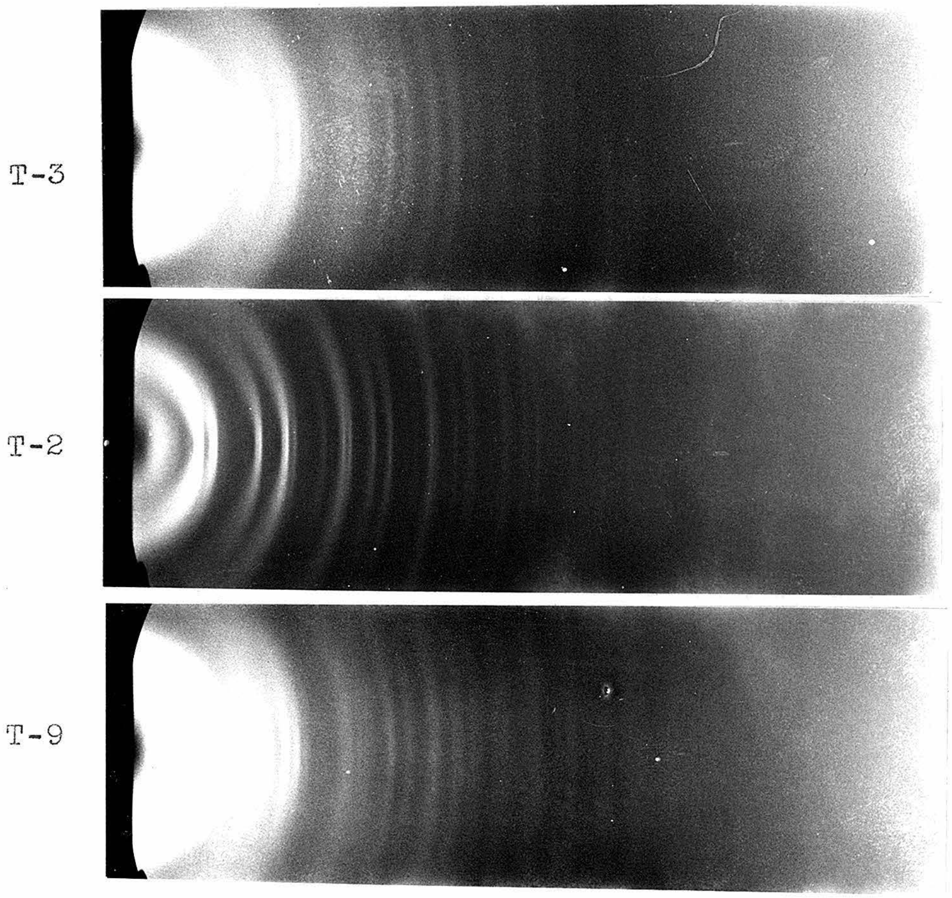

Figure 9

X-ray diffraction photographs of cerium powder.

T-2 was taken at room temperature, T-3 and T-9 at the temperature of liquid air. The diffraction lines of two coexisting structures appear in the low-temperature photographs.

prints do not show detail as well as the negatives, but in T-9 the lines of the old structure are relatively stronger with respect to those of the new structure than they are in T-3. Now in taking T-3 the sample was cooled for the first time with liquid air and for the fourth time when taking T-9. Thus it can be seen that repeated cooling with liquid air favors the retention of the old structure.

Tables 3 and 4 give the interplanar spacings and the indices of the lines of T-3 and T-9. Another photograph, T-7, also showing the new structure is not included because it does not give any additional information.

With the cell edge of the old structure equal to 5.14 Kx. and that of the new equal to 4.82 Kx. the decrease in volume is 17.54%.

3. Discussion of the Low-Temperature Form of Cerium.

I obtained the new dense form only after the cerium had been remelted and the magnesium and calcium sublimed. Hahn (16) has shown that magnesium inhibits the transition to the α form. But apparently the prerequisite for the phase transition in pure cerium is that the specimen be strained, as for example by quenching. Then upon cooling with liquid air the strains are increased and the transition takes place. It is strains which cause β and γ cerium to have different properties. They do not have different structures, as I have proved by many X-ray diffraction experiments. We recall an observation by Trombe that the transition at 109° K. is obtained most easily when the sample is quenched from 425° C. with liquid nitrogen. On the other hand, he also reports and I have found that repeated cooling with liquid air, which is a form of annealing, inhibits this transition.

The metal at 109° K. is a mixture of the old and new structures.

Table 3

Indices of the Diffraction Lines on Photo T-3

			Old Structure		New Structure	
Line	Intensity	$d_{hk\ell}$	$hk\ell$	a_0	$hk\ell$	a_0
1	Str	2.76			111	4.780 Kx.
2	Str	2.40			200	4.800
3	Str-wide	1.813	220	5.128 Kx.		
4	Str-wide	1.703			220	4.817
5	Str-wide	1.549	311	5.138		
6	Str-wide	1.457			311	4.832
7	Wk-wide	1.396			222	4.836
8	Very Wk	?				
9	Very Wk	?				
10	Wk	1.106			331	4.821
11	Wk	1.077			420	4.816
12	Str-wide	0.986	511	5.123	422	4.830
13	M-wide	0.927			511	4.817
14	Str-wide	0.860	531	5.088		
15	Str-wide	0.812	620	5.135	531	4.803
16	V. Wk-wide	.772	622	5.121		
17	Wk	?				
18	M-wide	0.673			711 640	4.806 4.853
19	V. Wk	0.644			642	4.819
20	Wk	0.628			731	4.824
			Average*	5.117 Kx.		4.823 Kx.

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*In both cases the first two reflections are not included in the average.

Table 4

Indices of the Diffraction Lines on Photo T-9

Line	Intensity	$d_{hk\ell}$	Old Structure $hk\ell$	 a_0	New Structure $hk\ell$	 a_0
1	V. Str	2.755			111	4.770 Kx.
2	Str	2.408			200	4.816
3	V. Str	1.826	220	5.165 Kx.		
4	V. Str	1.699			220	4.810
5	V. Str	1.546	311	5.128		
6	V. Str	1.457			311	4.832
7	Wk	1.392			222	4.822
8	Str-wide	1.171	331	5.104		
9	Str-wide	1.142	420	5.107		
10	Wk	1.105			331	4.817
11	Wk	1.077			420	4.816
12	Str	0.983	511	5.109	422	4.817
13	M	0.929			511	4.827
14	Str. Dblt?	0.864	531	5.111		
15	M. Dblt?	0.813	620	5.142	531	4.810
16	Wk. Dblt?	0.776	622	5.147		
17	Wk. Dblt?	0.720	711	5.142		
18	M. Dblt	0.671			711 640	4.790 4.839
19	V. Wk	0.645			642	4.827
20	Wk	0.627			731	4.816
			Average*	5.124 Kx.		4.818 Kx.

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*In both cases the first two reflections are not included in the average.

The overall decrease in volume of 10% observed by Trombe means that in his specimen 45% of the old structure was present.

In the new structure the 4f electron has probably moved up to hybridized 5d 6s orbitals to take part in bond formation. The cerium is then quadrivalent. The cell edge of 4.82 Kx. represents, as a first approximation, a single-bond radius of 1.56 Kx. This is in good agreement with the value 1.50 Kx. for quadrivalent cerium obtained from Pauling's paper (18).

LaBlanchetais (14) obtained 2.3 μ_B for the magnetic moment of the dense form and 2.55 μ_B for the quenched cerium. This corresponds to 15% quadrivalent cerium in her sample, if we take 0 and 2.56 μ_B as the magnetic moments of quadrivalent and tervalent cerium respectively.

Since this study was completed Lawson and Tang (19) have succeeded in obtaining the same dense form by applying a pressure of 15,000 atmospheres to the cerium. The lattice constant they obtained is 4.84 ± .03 Å.

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PART II

THE STRUCTURE OF UREA OXALATE

II THE STRUCTURE OF UREA OXALATE

Introduction

Urea oxalate, $2CO(NH_2)_2 \cdot (COOH)_2$, is an organic salt with ten hydrogen atoms. One may expect that in its structure many of the hydrogen atoms if not all will be used in forming hydrogen bonds. Since nitrogen and oxygen atoms would be involved a variety of such bonds are possible. Moreover, it is known that the carbonyl oxygen of urea has through resonance a negative formal charge (20). The role of this atom in the formation of the salt and in the structure is then of interest. In view of these considerations Professor J. H. Sturdivant suggested the investigation of the structure of this compound.

1. Historical

Groth (21) reported that urea oxalate crystallizes in the monoclinic prismatic class with $A_1 : A_2 : A_3 = 0.4106 : 1 : 0.9309$, and $\beta = 143^\circ 6'$. Lonsdale (22) found that the space group is $P\,2_1/c$, and that the size of the unit cell is $A_1 = 5.08$ Å., $A_2 = 12.42$ Å., $A_3 = 11.54$ Å., with $\beta = 142^\circ 56'$. She also found that there are two molecules per unit cell.*

According to Gaubert (23) the indices of refraction for the D lines of sodium are:

$$\alpha = 1.3885, \qquad \beta = 1.6116, \qquad \gamma = 1.6165$$

The acute bisectrix γ is perpendicular to (100), and the obtuse bisectrix γ is parallel to A_3. I have confirmed this optical orientation. The

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*The crystal axes I use are different from the ones in the literature, I have here and later converted the data reported by others into the values they would have with my axes. If the axes found in the literature are called $\underset{\sim}{a}$, $\underset{\sim}{b}$, and $\underset{\sim}{c}$, the transformation equations are $\underset{\sim}{A}_1 = \underset{\sim}{c}$, $\underset{\sim}{A}_2 = \underset{\sim}{b}$, and $\underset{\sim}{A}_3 = -\underset{\sim}{a} - 2\underset{\sim}{c}$. Thus the $(\bar{2}01)$ face in the notation of Groth and Lonsdale is the (100) face in my system.

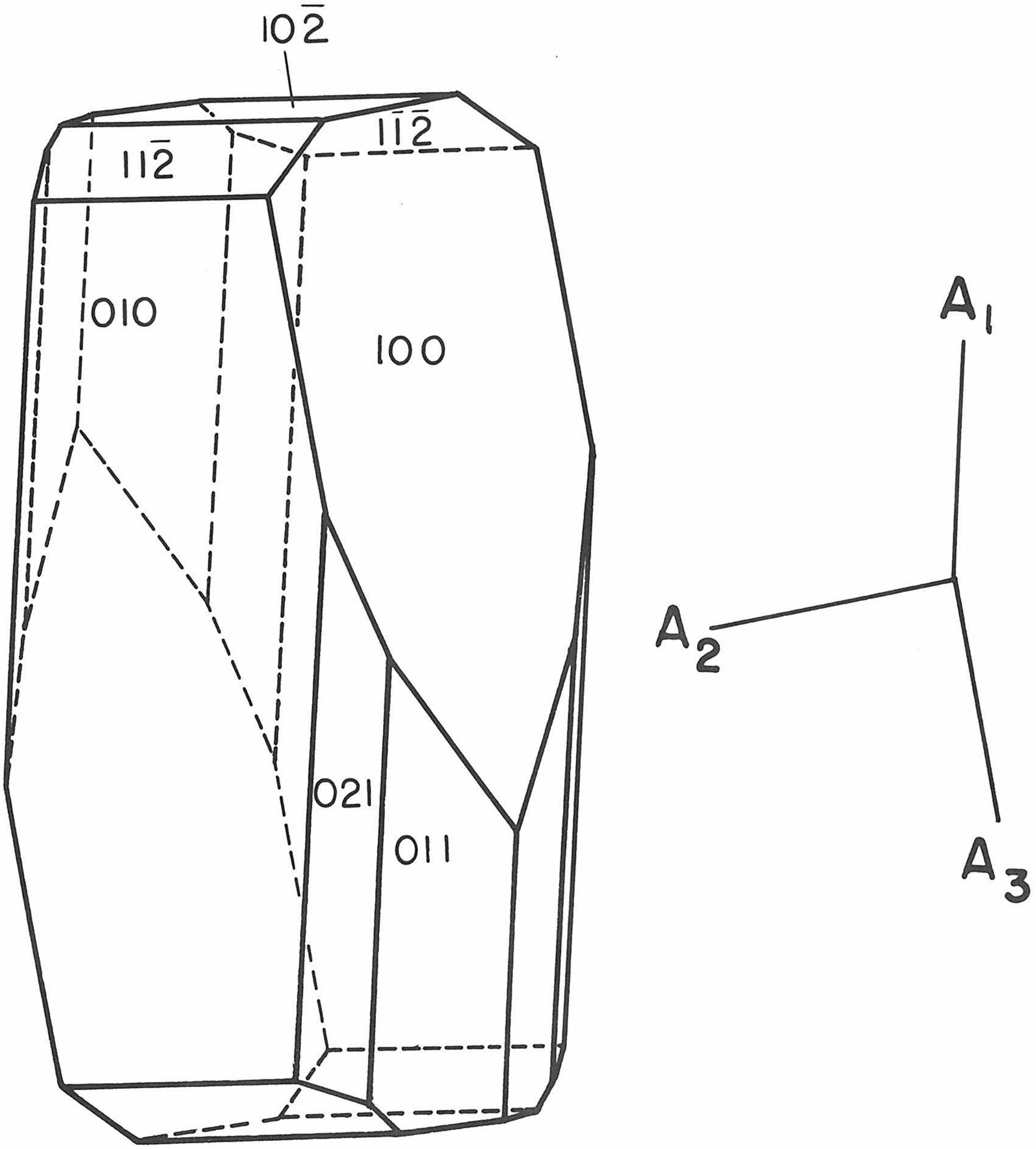

Figure 10

One typical habit of urea oxalate

orientation and the large negative birefringence of -0.228 indicate a layer structure parallel to (100).

Lonsdale (22) found the direction of maximum magnetic susceptibility to be normal to (100). She also reported that in X-ray diffraction photographs the 100 reflection was the most intense observed, and further that on suitably oriented Laue photographs the 100 reflection is accompanied by an elongated diffuse spot which is directed normal to this face. The size and direction of the diffuse spot along with other considerations led her also to predict a layer structure with the molecules lying parallel to (100) and linked together with hydrogen bonds.

2. Crystallography and Space Group

I obtained urea oxalate crystals by evaporating at room temperature a water solution of oxalic acid and urea in which the urea wa in 5% excess. The crystals I obtained had one of two habits. In the rarer habit, Figure 10, the crystal was elongated along A_1, the short axis, and bounded by $\{010\}$, $\{011\}$, and $\{021\}$, with the ends terminated by $\{102\}$, $\{112\}$, and $\{100\}$. These crystals were about one millimeter long.

In the more common habit laths grew parallel to (010) as long as one centimeter in the A_3 direction and two millimeters in the A_1 direction. The sides of the laths were bounded by $\{100\}$ and the ends terminated by $\{011\}$ and $\{021\}$. Twinning along (100) was very frequent.

The crystals cleaved and slipped very easily parallel to (100). Needles prepared by cleaving bent easily in the B_1 direction.

I determined the lattice constants with a camera which I had previously calibrated with sodium chloride. First I took well exposed rotation photographs about the three axes to establish the identity distances.

Then I took oscillation photographs of the orders of h00, 0k0 and 00ℓ ; and of the 404 and 2·0·10 reflections. To obtain reflections at large angles I used the $K\alpha$ radiations of iron and copper. The wavelengths used are given in Table 5.

Table 5

Wavelengths

	$K\alpha_1$	$K\alpha_2$	$K\alpha$
Fe	1.93579 Å.	1.93991 Å.	1.9373 Å
Cu	1.54050	1.54434	1.5418
Mo	0.70926	0.71354	0.7107

The calculation for each axis was made graphically (24) by plotting for example $A_1 \sin\beta$ from different orders and wavelengths against the Nelson and Riley function (25), $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$, and extrapolating to $\theta = 90^\circ$. After $A_1 \sin\beta$ and $A_3 \sin\beta$ were known, and hence the lengths of the reciprocal vectors B_1 and B_3, the value of $\cos\beta$ was twice determined by solving in the reciprocal lattice each of the triangles formed by the vectors $\underset{\sim}{h}_{40\bar{4}}$, $4\underset{\sim}{B}_1$, and $-4\underset{\sim}{B}_3$; and $\underset{\sim}{h}_{\bar{2}\cdot0\cdot10}$, $-2\underset{\sim}{B}_1$, and $10\underset{\sim}{B}_3$. The two values of $\cos\beta$ were then plotted against the Nelson and Riley function and the extrapolated value of $\cos\beta$ at $\theta = 90^\circ$ was taken as the true value. The cell dimensions I found are $\beta = 143^\circ 1'$, $A_1 = 5.128$ Å., $A_2 = 12.404$ Å., and $A_3 = 11.576$ Å., with a limit of error of .005 Å.

The density (22) of urea oxalate is 1.586 gm./cm.^{3} and the molecular weight is 210.15. These data give 2.01 formula weights per unit cell.

W Weissenberg photographs were taken about the three axes with copper radiation and again about the A_1 axis with molybdenum radiation. With some

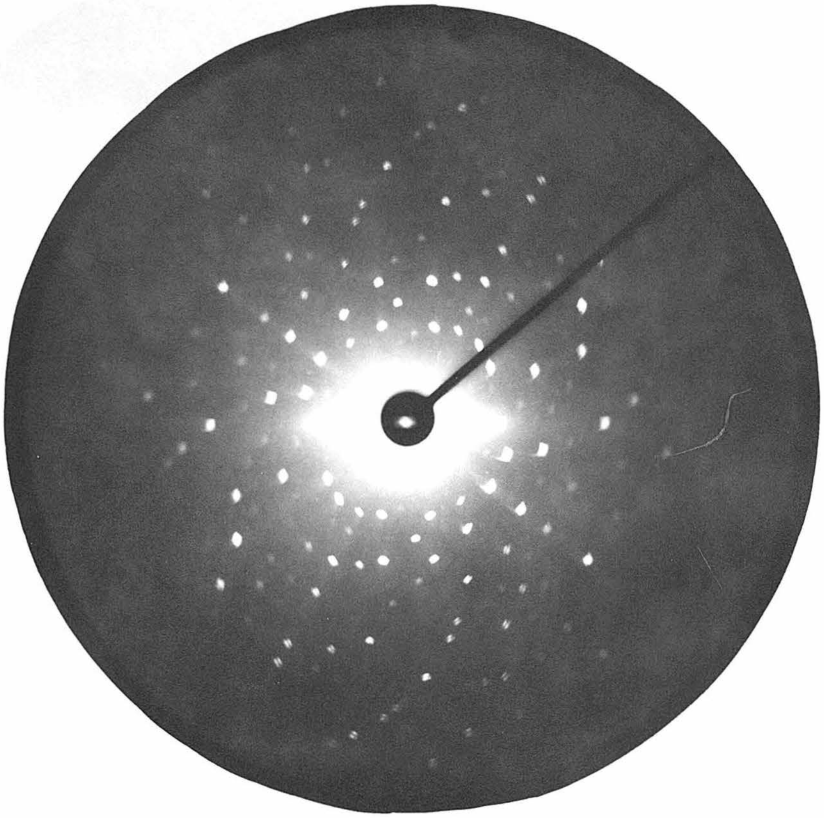

Figure 11

A Laue photograph of urea oxalate taken with the beam parallel to A_2. The radiation was from a tungsten target at 52 kv. peak.

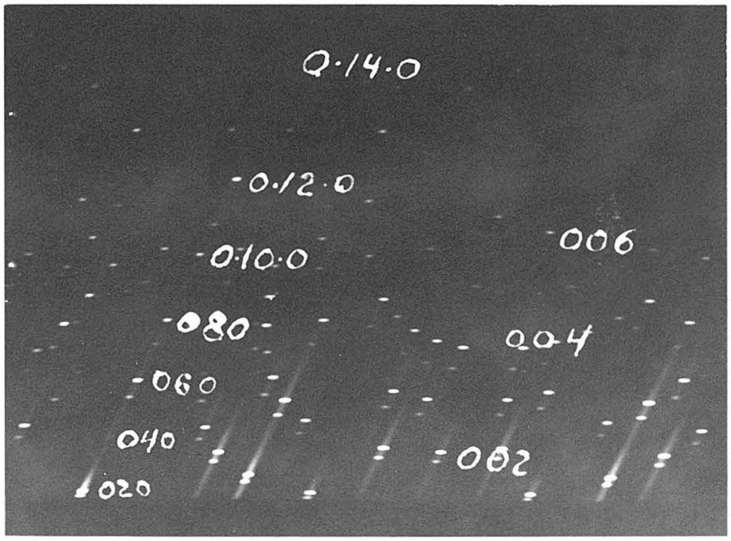

Figure 12

A zero-layer Weissenberg photograph of the [100] zone of urea oxalate. The photograph was taken with copper K radiation.

crystals a faint reflection at the position of 0·15·0 was noticed. On an overexposed diffraction photograph of such a crystal I found that although this reflection occurs at an angle where the α_1 and α_2 peaks of other maxima are distinctly separated there was only one spot and that very diffuse. I therefore concluded that this was not a Bragg but a diffuse reflection. Other than this I found for the first 20 orders that 0k0 was present only when k was even. I also found $h0\ell$ present only when ℓ was even. All other classes of reflections were observed. Pyroelectric tests with liquid air, which were controlled by tests on resorcinol, which is not centrosymmetric, gave no evidence that urea oxalate lacks a center of symmetry. Furthermore, all well-formed crystals appeared to have a center of symmetry, and the face development of some of them showed the symmetry 2/m. This symmetry was also shown by Laue photographs. In view of all these considerations the space group $P\ 2_1/c$ reported by Lonsdale was accepted.

3. The Determination of the Structure.

The space group $P\ 2_1/c$ has the following sets of special and general positions:

(a) (000) $(0\tfrac{1}{2}\tfrac{1}{2})$ (b) $(\tfrac{1}{2}00)$ $(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$

(c) $(00\tfrac{1}{2})$ $(0\tfrac{1}{2}0)$ (d) $(\tfrac{1}{2}0\tfrac{1}{2})$ $(\tfrac{1}{2}\tfrac{1}{2}0)$

(e) $\pm(x,y,z)$; $\pm\ (x,\tfrac{1}{2}-y,\ \tfrac{1}{2}+z)$.

The special positions are at centers of symmetry.

Since there are only two molecules per unit cell, their centers must occupy a set of special positions; consequently the molecules must have a center of symmetry. If we neglect the hydrogens, we need to locate seven atoms: $-COOH \cdot OC(NH_2)_2$. The determination of the structure is thus a 21-parameter problem.

We have seen how the optical and magnetic properties, the cleavage, and the size and direction of the diffuse spot associated with the 100 reflection indicate that all atoms lie in a plane parallel to (100). This is further supported by the observation that the first five orders of (100) show a normal decline. The fifth, sixth, seventh, and eighth orders, all which were brought into position to reflect with molybdenum K α radiation, were absent. I therefore proceeded with the assumption that the two molecules have their centers at (000) and $(0\frac{1}{2}\frac{1}{2})$ and that the atoms lie in the (100) plane.

To find the disposition of the atoms in this plane a two-dimensional Fourier projection along A_1 was decided upon. This projection is computed from the equation

$$\rho(0yz)\,A = 4\underset{k+\ell\ \text{even}}{\sum_{0}^{k}\sum_{0}^{\ell}} F_{0k\ell}\cos 2\pi ky\cdot\cos 2\pi\ell z \;-\; 4\underset{k+\ell\ \text{odd}}{\sum_{0}^{k}\sum_{0}^{\ell}} F_{0k\ell}\sin 2\pi Ky\cdot\sin 2\pi\ell z,$$

where $\rho(0yz)$ is the electron density per unit projected area and A is the projected area $A_2A_3\sin\beta$. For the coefficients $F_{0k\ell}$ one uses the experimentally observed structure factors $(F_{obs})_{0k\ell}$. The next step then was to measure F values.

A crystal was ground to a cylinder 0.3 mm. in diameter with its axis along A_1. A zero-layer Weissenberg photograph was taken with copper radiation and with four superimposed films in the camera. The intensities of the $0k\ell$ reflections were then estimated by the usual multiple film technique (26). It was assumed that the decrease in blackening of a given reflection between two successive films corresponded to a decrease in intensity by a factor of 3.7. The intensities were divided by the Lorentz and polarization factors, $\frac{1+\cos^2 2\theta}{\sin 2\theta}$, to obtain values of $(F_{obs})^2$. As described later the observed F's were subsequently modified by a factor which placed them on an absolute scale. No absorption or extinction corrections were made. The linear absorption coefficient times the radius for a 0.3 mm. cylinder is 0.225. The absorption therefore is low and uniform at all angles and can be included in the scale factor.

To obtain more structure factors another set of multiple film photographs were taken with a cylinder 0.33 mm. in diameter and molybdenum radiation. The films were interleaved with copper sheets 0.001 inch thick.

Only fourteen additional reflections were observed with molybdenum radiation. Many weak reflections that could still be seen on the photograph taken with copper were absent here. Of the additional reflections, many were so weak they could barely be seen. I found that their intensities could best be estimated by comparing them with other spots that were common to the two sets of photographs. The difference in the Lorentz factor in the two cases was taken into account.

It was next necessary to find a trial structure from which to calculate the signs of the observed F's. A Patterson projection along A_1 gave no information. I then took advantage of the fact that the structures of urea (27) and oxalic acid (28) are known.

Paper models of these molecules were arranged within the outlines of the unit (100) face. In this I was guided by the space group and the observation that the 0·12·0 and 0·11·4 reflections are usually strong. Two possible trial structures were found: one with the long axis of oxalic acid 28° from the A_2 axis, and the other with the oxalic acid making the same angle with A_3.

I then calculated the structure factors for each of the two positions. For the atomic scattering factors f_j I used the values for C, N, and O given in "The International Tables for the Determination of Crystal Structures". Now in the two orientations the carbon atoms of oxalic acid had different locations but the oxygens and the atoms of urea had nearly the same positions. As a result I found that between the two orientations the calculated F's might differ greatly, but that at low angles of reflection only a few of them had opposite signs. Neither set of calculated F's agreed very well with the observed one, but on the whole one could see that when the observed structure factors were high or low the calculated ones were likewise high or low. When I tried to improve the agreement by slightly shifting the atoms, I saw that here again the magnitudes of the calculated F's might change, but that very few of them changed their signs.

I therefore decided to make a preliminary Fourier projection. Even if the signs for the observed F's were obtained from the wrong trial structure, only a few of them could be wrong, and one might still expect the projection to give positive information.

I chose the orientation of the oxalic acid along A_2 as the trial structure from which to calculate the signs of the F's. Only the structure factors from reflections whose Bragg angle is less than 45° were used. Among these, those that agreed poorly with the calculated ones and those of whose signs I was otherwise uncertain were left out. Forty-nine terms remained with which to make the first Fourier projection.

The projection was calculated on an IBM machine at intervals in y and z of 1/60th of the cell edges (29).

The projection showed the position of six of the seven atoms in the asymmetric unit. The peak for the carbon in oxalic acid was absent. It was expected that it would show up when more terms were used in the Fourier series. Accordingly, from the position of the six peaks and the assumed position of this carbon atom the signs were calculated to a greater angular range of reflections. In this projection the peak for this atom was still absent, and in another one madewith still more terms the peaks I already had began to disappear.

I therefore began all over with the oxalic acid oriented along A_3 as the trial structure. Again the first projection was made with observed F's from planes whose angles of reflection were below 45°. It showed all seven peaks. From their positions the signs for additional structure factors were found and another projection was made. The peaks in this projection were well enough resolved to enable me to calculate the signs of all the structure factors obtained with copper radiation. At the same time I determined a tentative scale factor with which to put the observed F's on an absolute scale. This permitted me also to use the theoretical value of F_{000} in the next projection.

This projection was made with data from 102 reflections, all that I had from copper radiation. The peaks were round and well resolved. The signs of the structure factors calculated from their positions agreed with the signs used to make the projection. Thus the series had converged.

Nevertheless, it was decided to continue with another projection in which the fourteen additional structure factors obtained with molybdenum radiation were used.

This projection is shown in Figure 13. It is followed by the drawing Figure 14 which shows the projection of the atoms onto the (100) plane. The hydroxy oxygen is O_I.

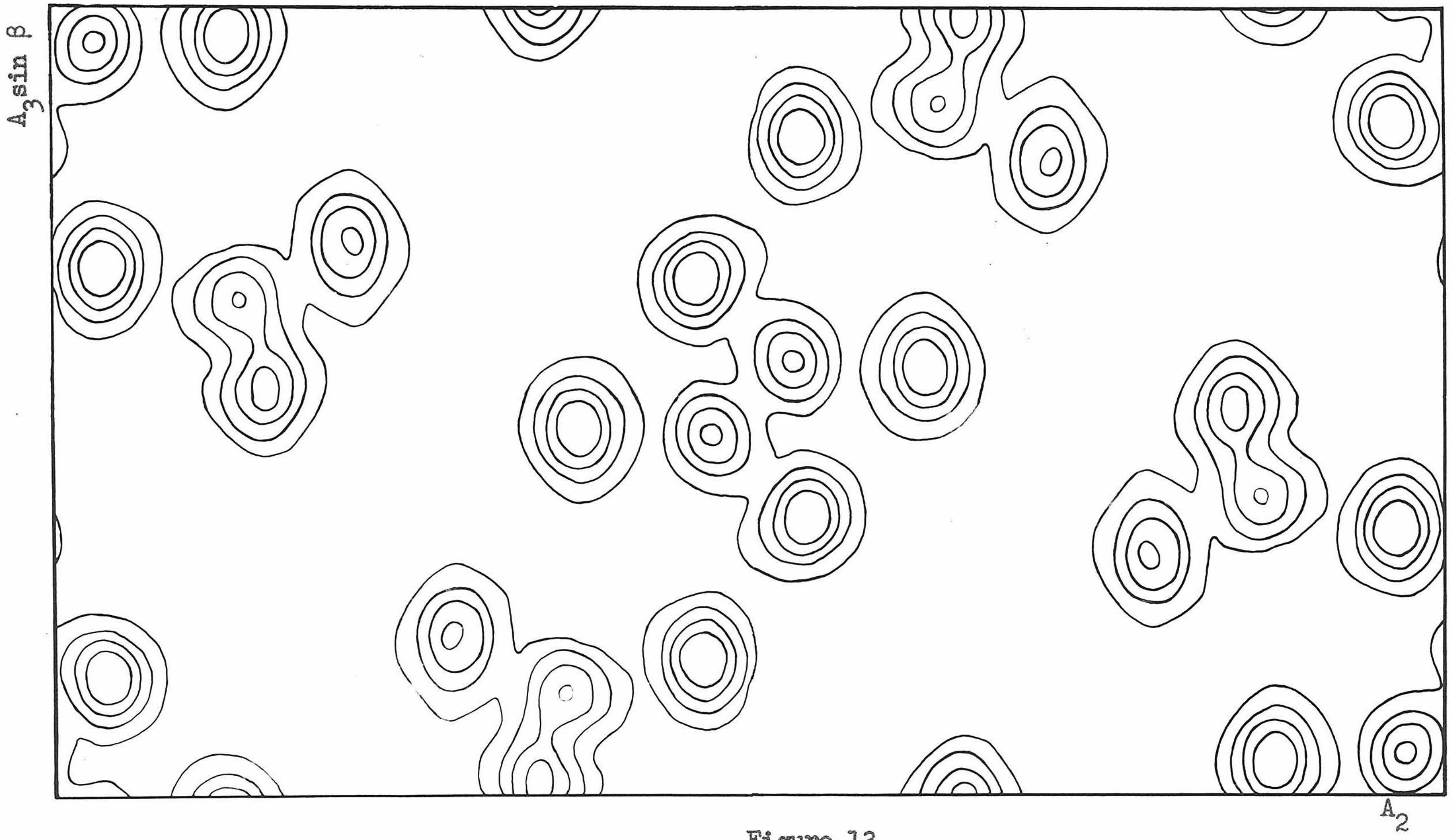

Figure 13

Urea oxalate. The final Fourier projection along A_1 onto the plane normal to A_1. The contour lines are at equal intervals, but the zero line has been omitted.

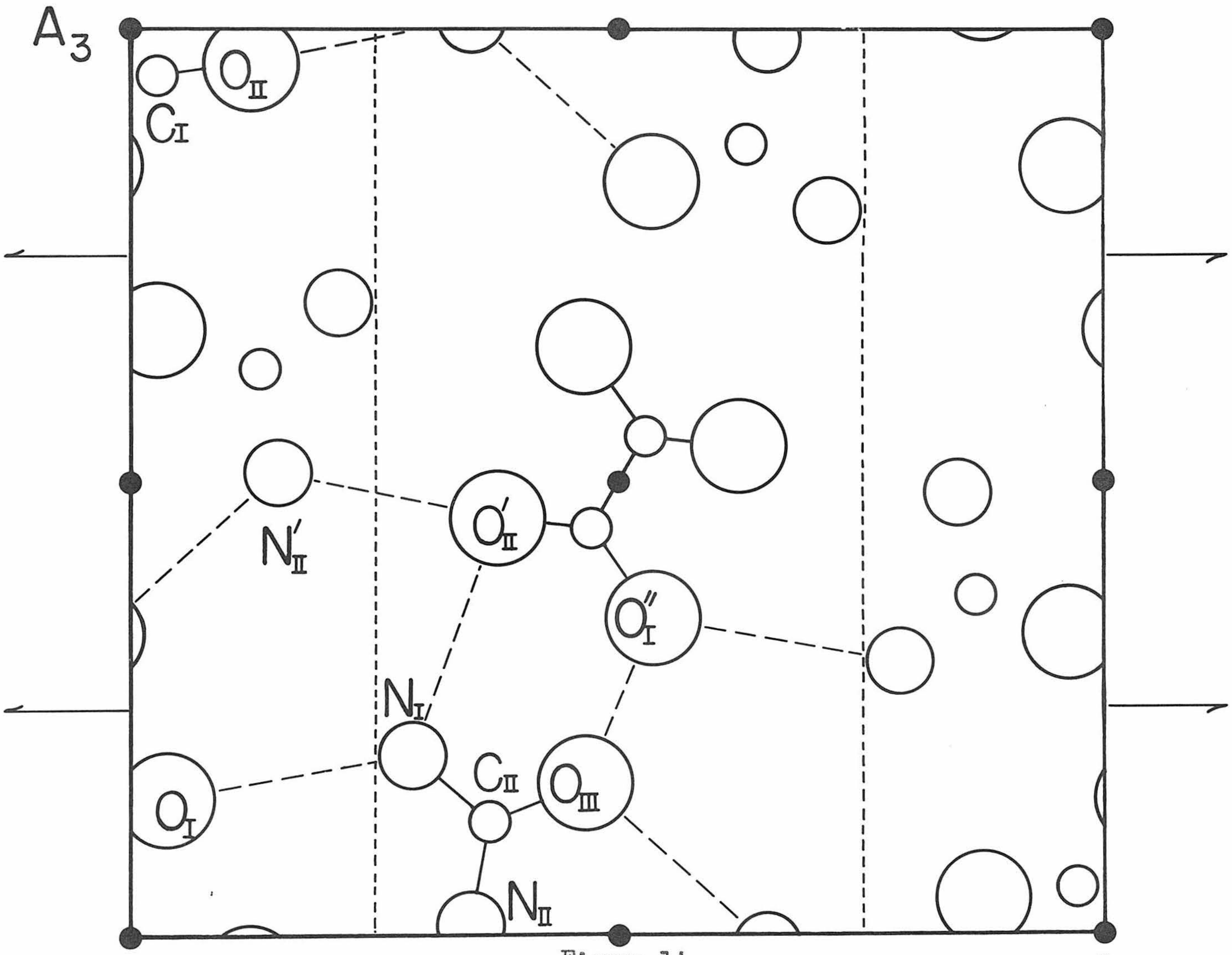

Figure 14

The structure of urea oxalate projected along A_1 onto (100). The filled circles are centers of symmetry. The dotted lines are glide planes, and the dashed lines are projected directions of hydrogen bonds. The atom O_I is the hydroxy oxygen of oxalic acid.

The Fourier projection has no false peaks nor sinks. The peaks are not quite so round as those in the projection made with copper data only. Twelve of the fourteen additional structure factors which had been introduced were from planes whose k indices ranged from 16 to 20 and ℓ indices from 0 to 3. They sharpened the peaks more in the A_2 direction than along A_3 and thus left them slightly elliptical.

I now determined the final values of the temperature factor and the scale factor to put the data on an absolute basis. Letting

$$H = \frac{\sin \theta}{2 \lambda}$$

I used the equation

$$k\, F_{obs} = e^{-4BH^2} F_{calc}.$$

This upon rearranging and taking logarithms becomes

$$\ln F_{obs}/F_{calc} = -4BH^2 - \ln k.$$

One could then get ln k and B from the intercept and slope of the straight line obtained in plotting $\ln F_{obs}/F_{calc}$ against $4H^2$. Actually I solved for them analytically by the method of least squares. For B I got 1.6 Å^2. Since the structure is a planar one it is likely that the thermal vibrations are anisotropic. Therefore, this value of B is probably correct only for the [100] zone.

Table 7 lists the values of F_{obs} and F_{calc} for this zone. The temperature correction is included in each F_{calc}. Except for (020) the agreement is very good. I believe the intensity of the reflection from this plane was low because of secondary extinction. If this and absent reflections are excluded

$$\frac{\sum \left| |F_{obs}| - |F_{calc}| \right|}{\sum |F_{obs}|} = 0.133.$$

When only the data from copper radiation are used the fraction is 0.126. I believe the latter figure is more representative of my work, because the molybdenum reflections were weak and hard to estimate.

The carbonyl oxygen of urea was distinguished from the nitrogen atoms by the heights of the peaks in the Fourier projection. This is shown in Table 6.

Table 6

Electron Densities at the Centers of the Fourier Peaks

Atom	Electrons/Å^2
C_I	10.0
C_{II}	9.7
N_I	10.0
N_{II}	10.7
O_I	12.3
O_{II}	11.8
O_{III}	12.3

We see that the atom which is identified as O_{III} has one of the highest densities in the projection. All nitrogen atoms have definitely lower densities than the oxygen atoms. The identity of the atom at O_{III} can also be deduced from the structure.

Up to now I had assumed that all atoms lie in the (100) plane and that all x parameters were therefore zero. This assumption was now examined more critically. The structure factor for hk0 reflections when k is odd is

$$F_{hk0} = -4\sum_j f_j \sin 2\pi hx \cdot \sin 2\pi ky.$$

This equation shows that if x were zero for all atoms then the entire class of hk0 reflections with k odd would vanish. Weissenberg photographs showed that this was not the case, and I therefore proceeded to find the x coordinates.

Figure 13 shows that a Fourier projection along A_2 or A_3 would not give resolved peaks. Nevertheless, in the hope of getting some information I made a projection along A_3. It gave back no more information than was used to make it, and so was not considered further.

I was more successful when I first estimated the positions of the atoms and then shifted them so as to bring the structure factors for the hk0 reflections into agreement. I followed this by making a Fourier projection along the [101] zone.* This zone makes only a 22° angle with the (100) face; therefore the peaks for C_{II} and N_{II} were not resolved, and the position of C_I was uncertain. However, the peaks for N_I and the three oxygen atoms were quite distinct, and by comparing this projection with that along A_1 I was able to get the x parameters of these atoms. The x coordinates of the N_{II} and the two carbon atoms I then reestimated from the molecular structures and the structure factors.

In fractions of the cell edges the positions of the seven atoms in the asymmetric unit are:

Atom	x	y	z
C_I	.018	.027	.949
C_{II}	.020	.368	.127
N_I	.010	.288	.199
N_{II}	.010	.349	.012
O_I	.006	.038	.150
O_{II}	.085	.125	.961
O_{III}	.038	.465	.168

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*A projection along this direction was suggested to me by Dr. Philip Vaughan. I was assisted in making it by Prof. Lynne L. Merritt, Jr.

I believe the y and z coordinates are correct within .02 Å. and the x coordinates within .06 Å. The refinement of the x coordinates is the object of a continuing investigation.

4. Discussion.

Some features of the structure are already well established. Those which are subject to change upon further refinement of the parameters I shall indicate during the discussion.

The structure is a layer one with the atoms almost lying in a plane which is parallel to (100). The layers are 3.085 Å. apart. The lower of two successive layers is translated in the A_3 direction by 0.35 A_3 or 4.11 Å. The layers are held together by van der Waals forces.

Within a layer the molecules are held together by hydrogen bonds, and all hydrogen atoms are used in bond formation. There is no distinct urea oxalate molecule. Rather, the structure is a vast network of urea and oxalic acid molecules.

The planes of the oxalic acid molecule and of the urea molecule are slightly tipped with respect to each other and to the (100) face. The plane of the oxalic acid at the origin of coordinates, Figure 14, makes an angle of 9° with (100) and its normal makes an angle of 82° with minus A_2. Of the orientation of the plane of the urea molecule I am more uncertain. With the present set of parameters the urea molecule that is labeled in the figure makes an angle of 2° with (100) and the normal makes an angle of 88° with minus A_2.

In oxalic acid the distances are C-C = 1.49, C_I-O_I = 1.32, C_I-O_{II} =1.24 Å.; and the O-C-O angle is 122°. Although the parameters need more refinement, the present values of the distances agree well with those found for N-acetylglycine by Carpenter and Donohue (30). They got 1.19 and 1.31 Å. for the C-O distances and 124° for the O-C-O angle. Their determination of the configuration of the carboxyl group is, I believe, the most accurate that has yet been made. In urea oxalate the two different C-O distances show that there is no oxalate ion present.

Within the urea molecule the distances are C_{II}-N_I = 1.32, C_{II}-N_{II} = 1.31, and C_{II}-O_{III} = 1.27 Å. The N-C-N angle is 121°. In the structure of urea itself the C-N distances were reported (27) as 1.37 Å. and the C-O distance as 1.25 Å. The N-C-N angle was given as 110°.

The lengths of the hydrogen bonds are:

N_I-H··O_I	3.15 Å.
N_I-H··O_{II}	2.94
N_{II}-H··O_{II}	2.93
N_{II}-H··O_{III}	2.98
O_I-H··O_{III}	2.47

The O_I-H··O_{III} distance of 2.47 Å. is shorter than any that have been reported. Unfortunately, the direction of this bond is almost along A_3, which makes its length very sensitive to the x coordinates of the atoms. It may be that after more refined analysis this distance will have to be revised upwards, but from my experience with this structure I believe that it will never reach the value of 2.54 Å. found in potassium dihydrogen phosphate. The length of a similar bond in N-acetylglycine is 2.56 Å.

5. Future Work.

Although the structure of urea oxalate is now known, more exact values of the hydrogen bond distances are of equal interest. To determine them as well as they can be, three-dimensional analyses have been under-taken. The continued investigation may also yield a better determination of the configuration of oxalic acid. In spite of numerous papers the structure of oxalic acid has not yet been satisfactorily determined.

Toward making three-dimensional analyses photographs have been taken about the A_1 axis up to the third layer with copper K α, and up to the fifth layer with molybdenum K α radiation. Another set of Weissenberg photographs have been taken about the A_3 axis up to the seventh layer with copper K radiation. Nearly all the intensities of the maxima in the photographs about the A_1 axis have been estimated.

Table 7

Urea Oxalate. Calculated and Observed Structure Factors of $0k\ell$ Reflections

$0k\ell$	F_{calc}	F_{obs}	$0k\ell$	F_{calc}	F_{obs}
002	16.8	16.9	040	-1.50	3.4
004	-2.4	3.5	041	-12.9	14.2
006	21.7	15.7	042	-37.5	37.9
008	-2.2	<1.6	043	3.4	4.6
			044	-12.9	10.6
011	15.8	13.6	045	4.6	5.8
012	-24.9	25.7	046	2.4	2.3
013	16.0	13.5	047	1.1	1.5
014	21.8	20.5	048	-9.3	8.3
015	-6.6	4.7			
016	3.2	4.5	051	-7.6	7.7
017	-4.4	4.1	052	-21.4	21.7
			053	1.4	<1.5
020	40.0	26.1	054	18.2	19.3
021	32.4	35.0	055	-13.0	10.4
022	0.5	<1.0	056	-1.4	<1.0
023	17.8	18.0	057	4.4	1.7
024	-18.7	15.7	058	-4.3	1.9
025	10.6	8.8			
026	6.7	5.0	060	23.1	24.1
027	9.0	5.5	061	4.5	5.9
028	-2.4	2.6	062	11.1	11.5
			063	-18.2	17.9
031	28.4	28.3	064	2.7	2.4
032	-14.0	12.1	065	1.0	3.2
033	-3.1	2.2	066	5.2	4.2
034	15.2	15.0	067	4.4	4.3
035	2.2	<1.8			
036	16.8	14.3	071	-0.2	<1.5
037	4.4	3.9	072	-20.9	18.6
038	-3.4	1.9	073	-2.2	<1.8
			074	12.6	12.5
			075	5.2	5.4
			076	-0.4	<1.9
			077	-10.5	9.0

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*All data are on absolute scale.

0kℓ	F_{calc}	F_{obs}
080	13.4	17.0
081	-2.7	2.7
082	16.8	17.6
083	8.9	11.1
084	3.2	3.2
085	6.1	7.4
086	-1.3	<1.8
087	3.8	3.3
091	7.7	7.7
092	-12.3	14.0
093	15.6	14.6
094	13.7	14.5
095	2.5	2.6
096	13.4	10.5
0.10.0	-16.4	15.7
0.10.1	13.2	15.3
0.10.2	-5.9	7.0
0.10.3	7.9	9.2
0.10.4	3.2	3.4
0.10.5	5.9	4.8
0.10.6	-7.3	6.6
0.11.1	0.1	<2.0
0.11.2	-5.7	7.1
0.11.3	-6.2	7.3
0.11.4	16.8	16.1
0.11.5	2.3	2.7
0.11.6	6.3	7.0
0.12.0	-26.9	25.6
0.12.1	-1.0	<1.9
0.12.2	3.6	2.2
0.12.3	1.0	7.5
0.12.4	6.3	2.1
0.12.5	3.1	2.7

0kℓ	F_{calc}	F_{obs}
0.13.1	-10.5	15.0
0.13.2	5.5	6.3
0.13.3	-8.3	10.3
0.13.4	-1.8	1.4
0.14.0	-3.0	3.9
0.14.1	-2.2	2.8
0.14.2	0.8	<1.5
0.14.3	-1.4	1.8
0.14.4	5.1	5.6
0.15.1	-2.7	1.8

Additional reflections obtained with Mo Kα

0.1.9	-5.9	3.5
0.2.9	3.6	3.3
0.12.6	-3.7	5.2
0.16.0	-8.4	9.4
0.16.1	4.3	3.5
0.16.2	2.2	3.3
0.17.1	3.0	3.4
0.17.2	3.5	3.7
0.18.0	-6.2	7.2
0.18.3	4.3	3.9
0.19.1	-4.2	3.7
0.19.2	1.3	3.7
0.19.3	-4.0	3.8
0.20.0	-3.7	5.5
0		

Table 8

Absolute Value of Observed Structure Factors for hk0 Reflections.

Copper K α Radiation

hk0	F_{obs}	hk0	F_{obs}
020	28.7	160	16.8
040	3.1	260	8.0
060	25.7	360	3.6
080	16.4		
0.10.0	13.7	170	0
0.12.0	25.3	270	0
0.14.0	3.1	370	0
100	81.0	180	10.1
200	39.3	280	5.3
300	12.6	380	1.9
110	13.1	190	6.3
210	9.8	290	8.0
310	4.3	390	4.7
120	24.2	1.10.0	10.9
220	10.9	2.10.0	7.6
320	4.3	3.10.0	2.8
130	12.2	1.11.0	4.2
230	9.3	2.11.0	4.6
330	4.2		
		1.12.0	20.9
140	3.6	2.12.0	10.9
240	3.1		
340	1.5	1.13.0	1.9
		2.13.0	2.0
150	2.1		
250	0	1.14.0	2.7
350	0		

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PROPOSITIONS

1. The cobalt carbide, Co_2C, discovered by Hofer and Peebles (1) has an orthorhombic unit cell with a = 8.66 Å, b = 4.66 Å., and c = 4.84 Å. There are eight formula weights per unit cell.

2. The A or high-temperature modification of cerium sesquioxide, Ce_2O_3, can be formed at 500°C. and not, as believed (2), (3) only above 1000°C.

3. The van Arkel method (4) is the most promising one of preparing europium metal for X-ray diffraction studies.

4. It would be worth while to determine the structure of urea nitrate. One can expect to find an even shorter O-H·O distance than was found in urea oxalate.

5. The assignment of three different atomic heat capacities to nitrogen by Satch and Sagobe (5) is based upon unsound reasoning and upon neglect of the contribution of hydrogen bonds to the energy of a structure.

6. The continuous series of solid solutions formed by nickel and copper are frequently cited as proof of the validity of the rules governing the formation of solid solutions in metals (6), (7). By the same rules one can expect cobalt and copper to form a like series of solid solutions. By all methods that have been tried only a limited solubility in the solid as well as the liquid state has been found (8), (9), (10), (11). It is proposed that the preparation of solid solutions of cobalt and copper be attempted by the van Arkel method.

7. In the Fourier projections of the structure of $AlCl_3$ made by Ketelaar, MacGillavry, and Renes (12) the "ghost" peaks indicate either a disorder in the positions of the Al atoms among the octahedral holes or

that the identity distances have been incorrectly determined. Contrary to what the authors report the peaks are not false and a result of the use of twinned crystals in the structure determination.

8. Quadrivalent cerium metal, which does not have a 4f electron, should also show changes in the M and N X-ray spectra (13) as well as in the magnetic susceptibility and electrical resistivity.

9. The dipole moments calculated for diethyl sulfite, triethyl phosphate, and tetraethyl silicate by Svirbely and Lander (14) do not agree with their models. A recalculation of the dipole moments from their models is given below

	Calculated S and L $\times 10^{18}$	Recalculated $\times 10^{18}$
Diethyl sulfite	3.09	3.13
Triethyl phosphate	3.03	2.52
Tetraethyl silicate	1.78	2.07

10. Bancroft (15) reported that the sulfite-sulfate cell is a semi-reversible one. The oxidation of the sulfite proceeds reversibly, but the reduction of the sulfate is irreversible. He reported that the potential of the cell can be computed from the equation

$$E = \frac{RT}{nF} \ln P \times P_{SO_3}$$

in spite of the fact that he also observed that it showed a strong dependence on the hydrogen ion concentration. He found the electrode potential to be independent of the sulfate concentration.

10 cont'd.

I propose that the cell is really a reversible one and that the reaction at the electrode is

$$2H_2SO_3 = S_2O_6^{=} + 4H^{+} + 2e^{-}$$

and that this is followed by the chemical reaction

$$S_2O_6^{=} + H_2O = H_2SO_3 + SO_4^{=} \quad (16)$$

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