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Radiation Laboratory

Contract No. W-7405-eng-48

THE CRYSTAL STRUCTURE OF UBi

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November 15, 1949

Berkeley, California

The Crystal Structure of UBi

Introduction

The existence of the compound UBi was demonstrated by Ahmann and Baldwin[1]

(1) D. H. Ahmann and R. R. Baldwin, CT-2961, November 12, 1945.

who made use of cooling curves, microscopic examination, and chemical analysis. Their x-ray results failed because of the pyrophoric nature of this material. We have prepared samples suitable for x-ray investigation and have shown that the compound has the sodium chloride structure.

samples for X-ray analysis were made in an effort to remove excessive contamination. In consideration of the relatively large volume of the preparation with respect to the exposed surface area of the crucible it was assumed that contamination of the alloys was small.

The highly pyrophoric character of the alloys required that all post-preparative handling be done in a dry-box[3] under inert atmosphere.

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(3) The dry box used is described by L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, Declassified Atomic Energy Commission Paper AECD-2242, October 15, 1945.

Preparation of Powder Specimens for X-Ray Study.

The first work was on an alloy of the atom ratio U/Bi = 1/2. The drilled or filed samples, powdered in propane atmosphere, in a stainless steel mortar to pass a 140 mesh screen, were sealed in pyrex capillaries which had been dried at 100°C for a day and left in the propane atmosphere for another day to allow the contained air to be replaced by propane. All inert gases in this work were dried through P_2O_5 before use. Four samples taken from four different levels from top to bottom all showed, on X-ray analysis, the composition to be principally UO_2 and Bi.

More careful specimen preparation was attempted by working in a high purity argon atmosphere. The dry-box was slowly and alternately swept with volumes of helium and argon from top and bottom inlets, respectively, in a manner to displace the dry-box contents with as little mixing as possible. Finally several volumes of argon were passed through with thorough mixing by

in a vacuum line and being evacuated at about 6×10^{-4} mm. of Hg for 4 hours. Argon was then admitted to the vacuum line to fill the capillaries and their container at 1 atmosphere, after which the container was removed from the vacuum line, covered, and placed in the dry box. The dry box atmosphere was then treated as above described. This somewhat tedious method was quite successful in eliminating oxidation.

Diffraction Results

Powder specimens of the compositions listed in Table I were studied by X-ray diffraction using Cu Kα X-rays filtered through nickel. Three new phases are designated "A", "B", and "C". A fourth phase, strong in samples of composition UBi and absent in all others, is attributed to UBi. Its pattern corresponds to a simple cubic lattice with a = 3.182 Å.

This very small cube is large enough for only one atom. Because of the closely 1:1 atom ratio of the compound, the somewhat different metallic radii of bismuth and uranium (1.52 and 1.42 Å respectively[4]) and their quite different

(4) L. Pauling, J. Am. Chem. Soc., 69, 542 (1947): values for single bond radii.

valence behavior, it is most reasonable to interpret the diffraction pattern as due to a sodium chloride structure with a = 6.364 Å. In this case, the observed lines correspond to the reflections with even indices which should be strong. Calculation shows that the reflections with odd indices, which are due to the difference in scattering power of uranium and bismuth, are too weak to be observed. Planes with mixed indices are absent because of the face-centered structure.

The intensities of the lines due to UBi were estimated by visual comparison with a set of standard marks made with variable exposure times. Intensities were calculated for the sodium chloride structure by the equation:

$$I = p \; F_{hkl}^{\;2} \; \frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta} \; 6.9 \times 10^{-7}$$

in which p is the multiplicity factor, F_{hkl} is the structure factor, and θ is the Bragg angle. The numerical factor normalizes the value to the arbitrary scale of the observed intensities, with which they are compared in Table II. The planes with mixed indices, which should all be absent, are omitted from the table. The agreement is as good as the accuracy of the intensity estimates.

The observed lattic constant, 6.364 ± 0.004 Å corresponds to a density of 11.52 ±.02 g. cm^{-3}.

The lines corresponding to phase "B" and listed in Table III were indexed on a body-centered tetragonal lattice with a = 3.95 ± 0.01Å and c = 4.22 ± 0.01 Å. Such a cell has room for only two uranium or bismuth atoms. Intensities calculated for two uranium atoms at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ are listed in Table III. They are normalized by the factor 5×10^{-6}. The observed intensities, judged by eye, are poor because they are in most cases near the limit of sensitivity of the film. The agreement is good considering these errors and the neglect of light atoms, absorption, and temperature factor. The density calculated from this cell for two uranium atoms and a few oxygens is of the order of 13. This is intermediate between the values 14.2 and 10.96 for UO and UO_2 respectively[5]. All known higher oxides of uranium are even less dense. Thus

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[5] R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald, "The Structures of the Carbides, Nitrides and Oxides of Uranium", J. Am. Chem. Soc., 70, 99 (1948).

Table III

Diffraction Data for Phase "B"

tetragonal	$\sin^2\theta$		intensities		
hkl	obs.[a]	calc.[c]	obs.[a]	obs.[b]	calc.
101	0.0711	0.0715	10	10	24
110	.0768	.0762	5[d]	3	12
002	.1340	.1336	3	3	3
200	.1527	.1524	3	4	4
112	.2096	.2098	6	5	5
211	.2239	.2239	8	7[d]	10
202	.2860	.2860	3	3[d]	3
220		.3048	<3	<3	1
103	.3385	.3387	3	-d	2
301	.3778	{.3763	5	3	4
310		.3810}			
222		.4384	<3	3	2
213	.4902	.4911	4	3	3
312	.5152	.5146	3	3	3
321		.5287	-d	3	3
004		.5344	-d	3	0.4
400	.6108	{.6096	3	<3	2
114		.6106}			
303		.6435	-d	<3	1
411		{.6811			
330	.6828	.6858	4	<3	3
204		.6868}			

[a]in pattern mixed with UBi

[b]in pattern mixed with Bi

[c]for a = 3.95 and c = 4.22 Å

[d]uncertain because of near coincidence with another line

Table IV

Diffraction Data for Phase "A"

intensity	$\sin^2\theta$ (Cu Kα)	remarks
W	0.0722	Phase B
S	.0779	Partly Phase B
S	.0852	
W	.1285	
S	.1630	
M	.1801	
M	.1934	
M-	.2113	Phase B?
M	.2250	Phase B?
M	.2350	
M+	.2422	
M	.2585	
M	.2856	Phase B?
S	.3132	
W	.3387	
M	.3762	Phase B?
M-	.4012	

Weaker lines, not listed, are also present.

W = weak

M = moderate

S = strong

Table V (continued)

Diffraction Data for Phase "C"

intensity	$\sin^2\theta$ (Cu Kα)	remarks
M	.3080	
M	.3303	
M	.3366	