where we have used $2K \sin \theta \simeq x_0$ and assumed $x, y \ll x_0$.

By setting

$$d = \frac{C^2 x_0^2}{16 K^4}$$

equation (20) can be written

$$\frac{1-d}{d} \left(x - \frac{\Delta}{1-d} \right)^2 - y^2 - \frac{\Delta}{1-d} = 0 \qquad (21)$$

which is the equation of the scattering surface in a plane. The scattering surface is cylindrically symmetrical around the reciprocal-lattice vector τ, and by using a cylindrical coordinate system (z, r, θ), with the z axis directed along τ we finally obtain the following equation for the scattering surface in reciprocal space

$$\frac{1-d}{d} \left(z - \frac{\Delta}{1-d} \right)^2 - r^2 - \frac{\Delta^2}{1-d} = 0 . \qquad (22)$$

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Coherent-Scattering Amplitude of ^{243}Am and ^{244}Cm*

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Neutron diffraction experiments have been completed on ^{243}AmO$_2$ and ^{244}Cm$_2$O$_3$. The coherent-scattering amplitude of ^{243}Am, relative to a value of 0.58×10^{-12} for oxygen, is 0.76 (1) $\times 10^{-12}$ cm. The value for curium is $\sim 0.7 \times 10^{-12}$ cm, which cannot be determined accurately in this experiment because both C-type (cubic, $a = 11.0$ Å) and A-type (hexagonal, isostructural with La$_2$O$_3$) Cm$_2$O$_3$ are present in the sample. Some of the difficulties in performing neutron diffraction experiments on these radioactive isotopes, which exhibit self-heating and spontaneous fission, are discussed briefly.

Introduction

Interest in the transuranium elements and their compounds has been almost totally confined, in the past, to nuclear physicists and chemists. Certainly, the structural chemistry of actinide compounds has been pursued vigorously, often on microgram quantities, since the

early days of the Manhattan Project (Seaborg, 1958). The increasing availability of transuranium isotopes has meant, however, that experimentalists can now think in terms of gram rather than microgram quantities, and, over the last few years at Argonne National Laboratory (ANL) the electronic structure of a number of actinide compounds has been investigated with a variety of experimental techniques. Neutron diffraction plays an important role in these studies for two major reasons. First, the ordered arrangement of magnetic moments (many actinide compounds are magnetic at

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low temperature) can be determined by neutron diffraction. Second, the crystal structure can be determined unambiguously from neutron diffraction patterns because, unlike the case of X-ray diffraction, the scattering is not dominated by the heavier actinide atom (Lander & Mueller, 1971). We have recently completed the first neutron diffraction experiments on gram quantities of ^{243}Am and ^{244}Cm and, in view of the unusual aspects of these elements, our experiments will be reported in some detail.

Sample characteristics

Both isotopes were obtained in the oxide form and prepared at the Savannah River Plant by neutron irradiation of ^{239}Pu, which was obtained from the ORNL Isotope Division. Isotopic and chemical analyses were performed at the source and indicate a high purity. The isotopic mass analysis for Am was reported as 99·83% ^{243}Am and 0·17% ^{241}Am, and the only other appreciable nuclide reported is 0·47 wt.% ^{244}Cm. The elemental impurities in AmO$_2$ totaled 0·13 wt.%, which consisted of < 100 p.p.m. for each of the following: Li, Na, K, Si, Cr, Ni, Ca, Al, Sn, Cd, B, Ag, Cu, Mg, Mo, Mn, Co, Pb, Ta, and 350, 250, and 200 p.p.m. of Fe, Zn, and Zr, respectively. For the curium sample, the isotopic analysis of Cm$_2$O$_3$ (in November 1968) was as follows: 95·08% ^{244}Cm, 0·04% ^{242}Cm, 0·02% ^{243}Cm, 0·73% ^{245}Cm, 4·02% ^{246}Cm, 0·07% ^{247}Cm, and 0·04% ^{248}Cm. The date is important in the case of curium because the half-life of the 244 isotope is 18·1 years, and, in the five years since production, 17·5% of ^{244}Cm will have decayed to the daughter products of ^{243}Cm and ^{243}Am. The elemental impurities, apart from ^{243}Am, totaled 0·24 wt.%, which consisted of < 100 p.p.m. for each of the following: Li, Na, K, Si, Ni, Ca, Al, Sn, Cd, B, Ag, Cu, Mg, Mo, Mn, Co, Pb, Ta, and 925, 250, 250, and 200 p.p.m. of Fe, Zr, Zn, and Cr, respectively.

Americium and curium are extremely radioactive and emit α-particles and γ-radiation. The ^{244}Cm isotope also exhibits spontaneous fission (Herold, 1965) and this sample presented special difficulties because of its intense radioactivity and the rather large quantity (2·2 g) used in the experiment. The α decay (half-life $t_{1/2}$ = 18·1 year) produces $3·7 \times 10^{14}$ disintegrations/min in the sample, and the spontaneous fission ($t_{1/2}$ = $1·4 \times 10^7$ year) produces $\sim 1·5 \times 10^9$ n/min. The fission spectrum of ^{244}Cm is similar to that of the other more common isotopes (e.g., ^{235}U and ^{239}Pu) and exhibits a peak at ~ 1 MeV with a high-energy tail extending to energies greater than 5 MeV.

Experimental details

The oxide samples (0·83 g of AmO$_2$ and 2·2 g of Cm$_2$O$_3$) were contained in argon-filled 6 mm diameter vanadium capsules approximately 3 cm long. The samples were loaded into a variable-temperature Janis cryostat at

the ANL CP-5 Research Reactor. The radiation at the outer cryostat wall was ~ 1 R/h; the level dropped to ~ 2 mR/h at a distance of 3 m where the diffractometer controls are located. (Note that an accumulated dose of ~ 100 mR/week may constitute the maximum permissible exposure.) The fast-neutron flux from the sample was reduced by a factor of five when 10 cm paraffin was piled around the cryostat.

The self-heating caused by α-particles, γ-rays, and neutrons is another important, and often troublesome, property of radioactive samples. The self-heating for ^{243}Am is 5·93 mW/g, and for ^{244}Cm is 2·87 W/g, i.e. 6·3 W with 2·2 g. At room temperature in the glovebox facility, the temperature of the vanadium capsule containing the curium sample was 160°C, and the platinum resistor located 1 cm from the sample in the cryostat read 118°K when the sample chamber was coupled by helium exchange gas to a liquid nitrogen (78°K) reservoir. The center of the sample was certainly much warmer than 118°K.

The neutron-diffraction experiments were performed on a standard two-circle diffractometer with either a germanium or graphite monochromator. Soller slits were used before the detector, but not before the monochromator or sample.

Results

(A) AmO$_2$

X-ray powder patterns of AmO$_2$ indicated a face-centered cubic structure with a lattice parameter (Chikalla & Eyring, 1968) of 5·380(1) Å. No extra lines were observed. The accepted lattice parameter is 5·377 Å, although the value can be as high as 5·385 Å because of radiation damage after long storage.

The neutron diffraction patterns, taken with the sample at both room temperature and 80°K, established that the structure is the fluorite (F) type. No extra
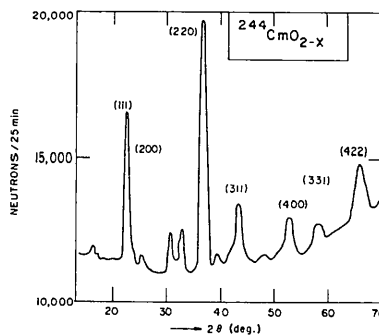

Fig. 1. Neutron diffraction pattern of ^{244}Cm$_2$O$_3$. The indexed lines are those of the fluorite (F) structure. Note that a constant background of 10 000 counts/25 min has been subtracted from the pattern. It is estimated that this is the contribution from the spontaneous fission within the ^{244}Cm isotrope.

lines were observed. The integrated intensities were reduced to structure factors, and the parameters were refined with a conventional least-squares routine. The observed and calculated intensities are given in Table 1. The coherent-scattering amplitude of $0.76(1) \times 10^{-12}$ cm is relative to that of oxygen (0.580×10^{-12} cm) and is derived assuming that the composition of the oxide is stoichiometric, $i.e.$, the O/Am ratio is 2·00. Chikalla & Eyring (1968) have reported that when the O/Am ratio is reduced slightly below 2·0 a two-phase region exists, in which dissociation occurs into the fluorite and large cubic (C-type) Am_2O_3 phases. The C-type structure, which is common to many rare-earth sesquioxides (Wyckoff, 1964), has a simple relationship to the F structure and has a cubic lattice parameter of ~ 11 Å, $i.e.$ almost exactly twice that of the fluorite structure. The C-type structure gives rise to additional

Table 1. *Observed and calculated neutron intensities for* $^{243}AmO_2$

The results of the least-squares refinement are S (scale factor) = 1·77 (2), B_{Am}(temperature factor) = 0·79 (6) Å², $B_O = 1.65$ (13) Å², $b_{Am} = 0.76$ (1) × 10⁻¹² cm, and residual = 1·5%. The fixed value of $b_O = 0.580 \times 10^{-12}$ cm has been used and an O/Am ratio of 2·00 assumed.

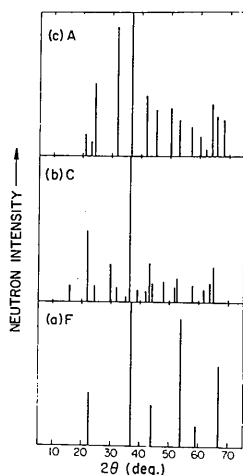| hkl	I_{obs}	I_{calc}
111	11·5 (3)	11·53
200	1·5 (2)	1·53
220	37·5 (4)	37·46
311	9·2 (4)	8·95
222	~0·7	0·44
400	8·3 (4)	8·33
331	4·8 (4)	4·96
420	~0·6	0·48
422	21·2 (7)	19·98

Fig. 2. Bar graphs of neutron diffraction patterns calculated for various phases of Cm_2O_3. (a) Fluorite (F-type) structure. (b) Large cubic bixbyite (C-type) structure. (c) Hexagonal La_2O_3 type (A-type) structure. See text and Fig. 1 for discussion.

peaks in the diffraction patterns and their absence in the neutron and X-ray patterns suggests that the AmO_2 sample used is stoichiometric.

(B) Cm_2O_3

X-ray diffraction patterns of the curium sample were inferior because of γ-radiation fogging and poor crystallinity. Despite the use of a number of filters in the X-ray camera, the high-angle lines ($d < 1.2$ Å) were never obtained satisfactorily. The low-angle lines indicated that the predominant structure is face-centered cubic, with a lattice parameter of 5·50 Å. The accepted value (Noé & Fuger, 1971, 1972) for CmO_2 is 5·359 Å, although, as with AmO_2, a higher value would be expected after long storage. The curium–oxygen system is structually rather complex, with the sesquioxide (Cm_2O_3) existing in the C, B, and A forms (Turcotte, Chikalla & Eyring, 1973). The C-type, which has been discussed, is the large cubic bixbyite structure, $a = 11.00$ Å. The B type is monoclinic, isostructural with Sm_2O_3, and has $a = 14.28$, $b = 3.652$, $c = 8.900$ Å, and $\beta = 100.31°$. The A type is the hexagonal rare-earth type, isostructural with La_2O_3, and has $a = 3.779$ and $c = 5.991$ Å. The X-ray lines indicated the presence of C-type Cm_2O_3, but the poor quality of the films and the absence of high-angle lines made a unique identification impossible.

The neutron diffraction pattern with the sample at 118°K is shown in Fig. 1. An important feature of this experiment is the high background caused by the spontaneous fission of the 244 isotope. The fission neutrons do not trigger the BF_3 detector with great efficiency (the ¹⁰B cross section for 1 MeV is ~300 mb, whereas for 0·1 eV it is 600 b), but it is impossible to prevent thermalization of many of the fission neutrons and these add, in this case, approximately 400 counts/min of constant background. This background has been *subtracted* in presenting Fig. 1. (At high angles, additional backscattering from our own and neighboring shielding enhances the background from the source.)

Unfortunately, a detailed analysis of the data shown in Fig. 1 is difficult because of both the complexity of the curium–oxygen phase diagram and the unknown coherent-scattering amplitude of curium. The X-ray patterns suggest that the sample is predominantly C-type Cm_2O_3, $i.e.$ O/Cm = 1·5. Least-squares analyses based on the C-type structure and using the intensities of Fig. 1 were not satisfactory (minimum residual ~ 11%). The most likely reason for the lack of agreement between calculated and observed intensities is that additional phases are present in the sample, particularly since the O/Cm ratio is not known accurately. By setting the positional parameters identical to those in the isostructural Pu_2O_3, the best fits were obtained with the scattering length of curium between 0·65 and 0·75 (× 10⁻¹² cm). To demonstrate qualitatively the calculation of intensities corresponding to Fig. 1, we present a series of bar graphs in Fig. 2. In the three,

$O/Cm = 1.5$, $b_{Cm} = 0.7 \times 10^{-12}$ cm, $b_O = 0.58 \times 10^{-12}$ cm, $B_{Cm} = 1.0$ Å^2, $B_O = 1.5$ Å^2, neutron wavelength is 1.22 Å, and all intensities are normalized to the strongest peak, which occurs at $2\theta = 37°$ in each structure.

Fig. 2(a) represents the diffraction pattern from a fluorite unit cell (F type) and is clearly too simple to represent the observed pattern given in Fig. 1. Fig. 2(b) represents the diffraction expected from the C-type structure and is in reasonable agreement with the observed intensities. The C-type structure, of all the modifications (A, B, and C) of the substoichiometric fluorite structure, has a weak diffraction peak at $2\theta = 15°$. The C-type structure also has two weak peaks at $2\theta = 30.5°$ and $2\theta = 33.0°$, which occur between the fluorite 200 and 220 lines. However, the C-type structure predicts that the peak at $2\theta = 30.5$ should be $2\frac{1}{2}$ times stronger than the peak at 33°. This ratio is not changed appreciably by varying the atomic parameters or O/Cm ratio. In our experiment (Fig. 1) these two peaks have equal intensity. Fig. 2(c) presents the pattern from the A-type La$_2$O$_3$ structure. The observed peak at $2\theta = 33°$, which is too strong to be accounted for by the C-type structure, arises from a small amount of the A-type structure, since the strongest peaks of the latter are at $2\theta = 37°$ (overlapping the strongest peak of the F and C structures) and $2\theta = 33°$. The monoclinic B-type structure has a complicated diffraction pattern (not shown), and we can exclude the possibility of appreciable amounts of this B-type structure.

Wallman (1964) and Noé, Fuger & Duyckaerts (1970) have reported that C-type Cm$_2$O$_3$ transforms spontaneously to the A-type hexagonal structure after several weeks, presumably as a result of radiation damage in the lattice. Our conclusions, at first glance, would appear to disagree with these findings, since, even after five years, our sample is predominantly ($\sim 80\%$) C-type Cm$_2$O$_3$. Noé, Fuger & Duyckaerts (1970) have also studied the $C \to A$ transformation as a function of temperature. At 300°C no transformation

occurs, whereas at 80°K the regular crystal lattice is so badly damaged by the self-irradiation and the lack of any thermal annealing that a semiamorphous material is produced. The self-heating of the sample used in our experiments was sufficient to produce a temperature of 160°C at the container wall, and estimates of the temperature at the center of the sample vary between 200 and 350°C, depending on the packing fraction and the size of the polycrystalline particles. In the neutron experiment, the sample was cooled for a period of five days, but the initial and final runs (Fig. 1 is the sum of four runs) were indistinguishable. We certainly have no evidence of an amorphous or metamict phase developing in the sample. An alternative, and in our view more likely, explanation for these apparent contradictory results rests on the fact that the oxygen content of our sample is unknown, but it is probably close to the most stable intermediate phase with a composition near CmO$_{1.71}$ (Turcotte, Chikalla & Eyring, 1973). For example, C-type Pu$_2$O$_3$ can exist with an O/Pu ratio between 1.5 and 1.75. The samples used by Wallman (1964) and by Noé, Fuger & Duyckaerts (1970) were certainly stoichiometric Cm$_2$O$_3$, but if our sample has a higher O/Cm ratio this might easily stabilize the lattice against the $C \to A$ transformation.

Conclusions

In Table 2 we present data on selected transuranium isotopes that are of interest to neutron diffractionists.

Our experiments on ^{243}Am have been successful. (1) The scattering length of 0.76 (1) $\times 10^{-12}$ cm has been determined accurately relative to an oxygen scattering length of 0.580×10^{-12} cm. (2) The neutron absorption with polycrystalline samples is small. For example, with a packing fraction of 0.5, which is average for an actinide polycrystalline sample, the value of μR is 0.40 for AmO$_2$. The transmission coefficient is therefore 0.51 and has little dependence on the dif-

Table 2. *Properties of transuranium isotopes*

Element	Isotope	Half-life α (yr)	Neutron (yr)	σ_{cap} (barns)	Energy = 0.0253 eV ($\lambda = 1.8$ Å) $\sigma_{fission}$ (barns)	b ($\times 10^{-12}$ cm)
Np	237	2.2×10^6	∞	166	0.02	1.055*†
Pu	238	86.4	4.9×10^{10}	590	17	?
	239	2.4×10^4	5.5×10^{15}	266	740	~ 0.8‡
	240	6.6×10^3	1.3×10^{11}	290	< 0.1	0.35§
	242	3.9×10^5	7.3×10^{10}	20	0	0.81§
Am	243	7.4×10^3	∞	105	0	0.76
Cm	244	18.1	1.4×10^7	10	1	~ 0.7
	245	8.3×10^3	∞	343	1727	?
	246	4.7×10^3	3×10^7	1.3	–	?
	247	1.6×10^7	∞	60	120	?
	248	3.5×10^5	4.6×10^7	4	0	?

* Cox & Frazer (1967). † Heaton, Mueller & Williams (1967). ‡ Neutron Diffraction Commission (1972). § Lander & Mueller (1971).

fraction angle. (3) The procedures we have developed for the encapsulation and irradiation of samples containing neptunium and plutonium appear to be adequate for ^{243}Am, although the latter is significantly more radioactive.

Although the experiments on ^{244}Cm have been interesting, the results were not as conclusive as those for AmO$_2$ because of the following reasons: (1) The scattering length is $\sim 0.7 \times 10^{-12}$ cm and the absorption is small, but a mixed-phase sample of Cm$_2$O$_3$ is clearly not the best choice for the determination of the scattering length. (2) The spontaneous fission from ^{244}Cm, although not prohibitive, does reduce significantly the signal-to-noise ratio. (3) The self-heating (6 W for our sample) and the high radiation level make our present technique inadequate, inasmuch as cooling the sample is beyond our cryogenic capabilities and the health hazard from the sample is appreciable.

More promising candidates are the 246, 247, and 248 isotopes of curium, all of which have significantly longer α and neutron half-lives (see Table 2). Unfortunately, only milligram quantities of these isotopes presently exist. Hopefully, the interest in curium, which has been reported as magnetic (Bansal, 1966) and is the 5f analogue of gadolinium with a half-filled f shell, will lead to a greater availability of these isotopes.

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