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Neutron diffraction study of $^{243}\text{AmO}_2$

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Résumé. — L'oxyde d'américium AmO_2 a été étudié par diffraction neutronique à différentes températures afin de vérifier l'apparition d'une phase antiferromagnétique en dessous de 8,5 K que des mesures de susceptibilité magnétique avaient prévue. Aucun ordre antiferromagnétique n'a été observé en accord avec des expériences Mössbauer. De plus, la longueur de Fermi de l'américium et les facteurs de température de l'américium et de l'oxygène ont été déterminés.

Abstract. — The actinide compound AmO_2 was studied by neutron diffraction at different temperatures in order to check the occurrence of antiferromagnetism below 8.5 K as predicted by magnetic susceptibility measurements. No antiferromagnetic order was observed in agreement with Mössbauer results. Furthermore, the coherent neutron scattering length of Am and the Debye-Waller factors for Am and O were determined.

1. Introduction. — Actinide dioxides (AnO_2 with $\text{An} \equiv \text{Th, Pa, U, Np, Am, Cm}$) form an interesting family characterized by the filling of the well localized 5f levels. UO_2 undergoes an antiferromagnetic transition at 31 K associated with a distortion of the oxygen sublattice [1]. NpO_2 undergoes a cooperative transition at 25 K observed by specific heat [2] and magnetic susceptibility [3] measurements. However, no magnetic moment has so far been detected by neutron diffraction [4, 5] (upper limit $0.5 \mu_B$). A moment of only $0.01 \mu_B$ can be associated with the magnetic hyperfine field observed by Mössbauer effect measurement [6]. In the case of AmO_2 , an antiferromagnetic transition was reported to occur at 8.5 K on the basis of susceptibility measurements [7] whereas no magnetic hyperfine field was detected by the Mössbauer effect [8]. In this paper we present the results of our investigation of this transition by neutron scattering measurements. Furthermore, the coherent neutron scattering length and the temperature factors for Am and O were obtained. The high radioactivity of the sample (150 rem/h at 1 cm) made the experiment particularly delicate.

2. Experimental details. — The purified $^{243}\text{AmO}_2$ [9] was refired at 900 °C under oxygen atmosphere. The isotopic composition of the actinide was 99.80 % ^{243}Am , 0.20 % ^{241}Am and trace amounts of Cm. Spark source mass spectrometry examination revealed the following impurities : 1 000 ppm Al, 300 ppm Cr, 700 ppm Cu, 300 ppm Fe, < 50 ppm Mn, 300 ppm Ni, < 100 ppm P, < 100 ppm Pb, $\lesssim$ 600 ppm Zn, 1 000 ppm ^{244}Cm .

The sample weighed 730 mg. Due to the high radioactivity and to the contamination hazard the sample was loaded into a double wall aluminium container welded by electron beam. Inside the first wall the sample was kept under helium atmosphere to insure a good thermal contact with the container (the self-heating of the sample was 5 mW). The cryostat used for the experiment was modified to allow detection of α -radiation during the experiment. The measurements were done at different temperatures, 293 K, 20 K and 6.5 K. Due to the self-heating 6.5 K was the lowest obtainable temperature. It was reached by pumping on the helium bath (helium temperature 1.5 K). The radiation level was 2 rem/h (γ) and 6 mrem/h (neutrons) at the outer wall of the

sample container. It dropped to 500 mrem/h (γ) at the outer wall of the cryostat.

Powder neutron diffraction data were obtained on the D2 diffractometer of the High Flux Reactor of the Institut Laue-Langevin (Grenoble). The neutron wavelength was 1.22 Å. The runs were done with 60' collimation in pile, 60' collimation between the monochromator and the sample and 10' collimation between the sample and the counter.

3. Results. — 3.1 LOW TEMPERATURE TRANSITION.

— In order to investigate the possible existence of an antiferromagnetic transition at 8.5 K [7] neutron diffraction patterns were recorded at both a higher temperature (20 K) and at a lower temperature (6.5 K). No variations were detected, within experimental uncertainties, in the neutron diffraction patterns at the two temperatures. In particular, figure 1 shows the low angle region of the neutron diffraction patterns where the (100) and (110) magnetic reflections should be observed at 6.5 K in the case of a type I antiferromagnetic ordering. Assuming this kind of magnetic ordering an upper limit of the ordered moment (μ_{ord}) can be obtained by comparing the minimum detectable (100) peak intensity I_{min} to the (111) peak intensity $I_{(111)}$. By taking I_{min} equal to the statistical error, as is usually done, one obtains $I_{\text{min}}/I_{(111)} = 1/200$ corresponding to $\mu_{\text{ord}} = 0.3 \mu_B$. However, we believe it is more realistic to take a value four times higher for I_{min} which corresponds to $\mu_{\text{ord}} = 0.6 \mu_B$.

Fig. 1. — Low angle neutron diffraction patterns of AmO_2 at temperature higher and lower than at 8.5 K at which antiferromagnetic ordering is supposed to occur.

3.2 NEUTRON COHERENT SCATTERING LENGTH AND TEMPERATURE FACTORS. — The neutron coherent scattering length of americium has only been determined once previously by Mueller *et al.* [10]. They found $b_{\text{Am}} = 0.76(1) \times 10^{-12}$ cm and temperature factors

$$B_{\text{Am}} = 0.79(6) \text{ \AA}^2 \quad \text{and} \quad B_{\text{O}} = 1.65(13) \text{ \AA}^2.$$

However, it is not clear from the publication if the temperature factors refer to 80 K or room temperature.

Our neutron diffraction data at 293 K, 20 K and 6.5 K were refined using a Busing-Levy Least Square Structure Factor Program in order to obtain b_{Am} , B_{Am} and B_{O} at the three temperatures. The results are shown in table I. In addition, a value for the lattice parameter equal to $5.380 \text{ \AA} \pm 0.002 \text{ \AA}$ at room temperature was obtained in agreement with previous values [10]. No temperature variation of this quantity was observed within the experimental errors. Table II presents the observed and calculated neutron intensity for the different Bragg reflections at one temperature, namely 20 K. The neutron coherent scattering length of oxygen was assumed to be $b_{\text{O}} = 0.580 \times 10^{-12}$ cm [11]. An absorption correction was applied to the observed intensities. The agreement between the observed and calculated intensities is expressed by the weighted residual R which takes the values $R = 1.5\%$ at 293 K, $R = 0.5\%$ at 20 K and $R = 1\%$ at 6.5 K.

The coherent neutron scattering length,

$$b_{\text{Am}} = 0.83(3) \times 10^{-12} \text{ cm},$$

was obtained assuming that the oxide was stoichiometric, i.e. O/Am ratio of 2. In fact, while a ratio

Table I. — Coherent neutron scattering lengths and temperature factors of AmO_2 .

Temperature	$b \times 10^{12}$ (cm)	B_{Am} ($\text{\AA}^2$)	B_{O} ($\text{\AA}^2$)
293 K	0.83 ± 0.04	0.64 ± 0.38	0.56 ± 0.27
20 K	0.83 ± 0.02	0.59 ± 0.17	0.42 ± 0.10
6.5 K	0.83 ± 0.02	0.50 ± 0.17	0.49 ± 0.13

Table II. — Observed and calculated intensities of AmO_2 Bragg reflections.

hkl	I_{obs}	I_{calc}
111	50 877	51 960
200	4 744	5 173
220	165 161	164 219
311	41 635	42 160
400	42 637	42 995
422	103 163	102 203
333,511	20 097	20 089

greater than 2 cannot be obtained with americium, a two phase region has been reported where the O/Am ratio is reduced slightly below 2 [12]. No extra peak was detected either by X-ray or neutron diffraction in our sample. This excludes the presence of a second phase within the detection limit. Moreover, the scattering length was also calculated by using only the odd Bragg peaks which have contribution from Am only and hence are independent of oxygen concentration. The scale factor used in this calculation was the same as that determined previously, thus b_{Am} is again scaled by b_o . The obtained value

$$b_{Am} = 0.835(30) \times 10^{-12} \text{ cm}$$

shows that deviation from stoichiometry is less than 0.5 % and has negligible influence on the given coherent scattering length.

4. Discussion. — The neutron investigation of the low temperature magnetic transition on AmO₂ shows that no antiferromagnetic order occurs below 8.5 K within the experimental limits indicated above. This confirms the results obtained by Mössbauer measurements. As a consequence of our results and according to the susceptibility measurements [7] which are unfortunately the only evidence up to now for a cooperative transition at 8.5 K, the transition in AmO₂ is apparently very similar to the transition in NpO₂.

It has been found in UO₂ that a distortion of the oxygen sublattice is associated with a first order magnetic transition [1]. In the case of NpO₂ and AmO₂ where no magnetic ordering is found, the transition might be only due to a lattice distortion associated with a cooperative Jahn-Teller transition.

At this point it is useful to recall the crystal field 5f ground states of the actinide dioxides.

UO ₂	: Γ_5 (triplet)	[1]
NpO ₂	: Γ_8 (quadruplet)	[13]
PuO ₂	: Γ_1 (singlet)	[13]
AmO ₂	: Γ_7 (doublet)	[7]
CmO ₂	: Γ_1 (singlet)	[13].

In PuO₂ and CmO₂, no transition is expected and in fact, none is found [14, 15]. In UO₂ the transition is magnetic and crystallographic. In NpO₂, the transition is apparently only crystallographic (there could be a magnetic ordering at very low temperature). In AmO₂, if the degeneracy of the Γ_7 doublet is lifted no magnetic ordering can occur (the first excited level Γ_8 is about 35 cm⁻¹ above the ground state [7]). Since NpO₂ and AmO₂ keep the fluorite structure, the only possible lattice distortion is the distortion of the oxygen sublattice, as in the case of UO₂. A single crystal diffraction study of NpO₂ is underway to try to detect such a distortion. A similar study would be very interesting in the case of AmO₂ as well as a confirmation of the 8.5 K transition.

The value of the coherent scattering length of ²⁴³Am, $b_{Am} = 0.83(2) \times 10^{-12}$ cm is slightly higher than the value found by Mueller *et al.* [9] but nevertheless the difference is less than 10 %. The temperature factors presented in this paper are $B_{Am} = 0.64$ and $B_o = 0.56$ at 293 K; they are much lower than the values given in ref. [9] ($B_{Am} = 0.79$; $B_o = 1.65$) and are comparable with values obtained for other actinide dioxides.

Neutron coherent scattering lengths of actinides have been determined up to curium, we thought it useful to collect them in table III.

Table III. — Coherent neutron scattering lengths of some actinides.

Isotope	$b(\times 10^{12})$ cm (¹)	Reference
²³² Th	1.000 (9)	WILLIS, B. T. M., <i>Proc. R. Soc. (London)</i> A 274 (1963) 122
²³¹ Pa	1.3 (2)	WEDGWOOD, F. A., BURLET, P., unpublished (1973) from PaO ₂
	0.91 (3)	WEDGWOOD, F. A., BURLET, P., unpublished (1973) from PaC
²³⁵ U	0.98 (6)	WILLIS, B. T. M., <i>Proc. R. Soc. (London)</i> A 274 (1963) 122
²³⁸ U	0.855 (6)	WILLIS, B. T. M., <i>Proc. R. Soc. (London)</i> A 274 (1963) 122
²³⁷ Np	1.05 (1)	HEATON, L., MUELLER, M. H., WILLIAMS, J. M., <i>J. Phys. Chem. Solids</i> 28 (1967) 1651
	1.054 (15)	COX, D. E., FRAZER, B. C., <i>J. Phys. Chem. Solids</i> 28 (1967) 1649
²⁴⁰ Pu	0.35 (1)	LANDER, G. H., MUELLER, M. H., <i>Acta Crystallogr.</i> B 27 (1971) 2284
²⁴² Pu	0.81 (1)	LANDER, G. H., MUELLER, M. H., <i>Acta Crystallogr.</i> B 27 (1971) 2284
²⁴³ Am	0.76 (1)	MUELLER, M. H., LANDER, G. H., REDDY, J. F., <i>Acta Crystallogr.</i> A 30 (1974) 667
	0.83 (2)	This paper
²⁴⁴ Cm	0.95 (3)	FOURNIER, J. M., BLAISE, A., MUELLER, W., SPIRLET, J. C., <i>Physica</i> 86-88B (1977) 30

(¹) With the assumption that $b_o = 0.580 \times 10^{-12}$ cm.

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