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Neutron diffraction study on $U_{0.5}Np_{0.5}O_2$ at low temperatures

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Résumé. — La solution solide $U_{0.5}Np_{0.5}O_2$ s'ordonne en dessous de 12 K et présente une structure magnétique différente de celle observée pour UO_2 . L'évolution de la largeur de la raie magnétique en fonction de la température pourrait suggérer un ordre magnétique à courte distance.

Abstract. — The results of a neutron diffraction study on $U_{0.5}Np_{0.5}O_2$ solid solution at low temperature are reported. Below $T = 12$ K the solid solution is magnetically ordered with a magnetic structure different from that of the UO_2 low temperature phase. The temperature dependence of the observed magnetic line width could suggest an eventual short range nature of the magnetic order. The neutron diffraction results are supported by Mössbauer spectroscopy measurements.

1. Introduction.

Elastic neutron diffraction experiments have been recently carried out [1, 2] on the first available NpO_2 single crystal in order to investigate the 25 K phase transition suggested by heat capacity [3] and magnetic susceptibility measurements [4, 5]. In reference [1] the state of art concerning the knowledge of this phenomenon before neutron measurements was briefly reviewed. By neutron diffraction, no magnetic ordering was detected and no evidence of a lattice distortion, either external or internal was observed. On the other hand, UO_2 undergoes a transition at 30.8 K associated to an antiferromagnetic ordering of type I and to a Jahn-Teller distortion [6]. So, in order to understand by an indirect way the nature of the NpO_2 25 K phase transition the magnetic properties of $U_{1-x}Np_xO_2$ ($0.15 < x < 0.75$) solid solution have been recently

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studied [7] by magnetic susceptibility and ^{237}Np Mössbauer measurements. It was found that the solid solution, at least for $x < 0.25$, undergoes two distinct magnetic transitions at different temperatures, the highest one presumably occurring on U site, the lower on Np sites. The collective Jahn-Teller mechanism and quadrupolar ordering found in UO_2 below $T_N = 30.8$ K [6, 8] and predicted in NpO_2 [9] was not observed in the solid solution by Mössbauer spectroscopy. Thus neutron diffraction experiment on $\text{U}_{0.5}\text{Np}_{0.5}\text{O}_2$ between 3 and 40 K have been undertaken to obtain information on the magnetic structure of the solid solution. The composition $x = 0.5$ was thought to be particularly significant since each type of site would have a first neighbouring shell in which the same or the other type of site would be present with equal probability if the two ions mix ideally without clustering effects.

2. Experimental details and results.

$\text{U}_{0.5}\text{Np}_{0.5}\text{O}_2$ fluorite solid solution was prepared by coprecipitation of NpO_2 in HNO_3 (8 N) and $\text{UO}_2(\text{NO}_3)_2$ by NH_4OH at $\text{pH} = 10.5$. The precipitate was then heated 3 hours at $1\,700$ °C in an argon (95 %)-hydrogen (5 %) atmosphere to avoid oxygen non-stoichiometry. Subsequent X-ray diffraction analysis do not revealed any broadening of the diffraction lines. Three grams were sealed in a double-Al container by electronic bombardment of the neutron experiment.

Neutron powder diffraction study was performed at the Institut Laue-Langevin (Grenoble, France) high flux reactor using D1B multidetector. Neutron wavelength used was $\lambda = 2.522$ Å; neutron diffraction patterns were recorded for the temperature range $3 \leq T \leq 37$ K.

The deduced lattice constant, $a = 5.4624 \pm 0.0003$ Å, agrees well with the values found for NpO_2 and UO_2 [1, 6].

No magnetic line previously observed in UO_2 was found at low temperature, as shown in figure 1. Nevertheless a single weak magnetic line, which appears in the same figure, was obtained; the higher Miller reflections are probably too small (due to the magnetic form factor) to be observed. The observed position of this magnetic line is temperature dependent, as it appears from figure 2, the Bragg angle decreasing when temperature decreases. Moreover the extrapolated value at $T = 0$ K of the line angular position ($2\theta = 23.20 \pm 0.07^\circ$) is quite near to the angular position $2\theta = 23.07^\circ$ of the $h = 1/2, k = 1/2, l = 1/2$ line referred to the nuclear unit cell. This result shows that the solid solution magnetic structure is different from the one previously found in UO_2 .

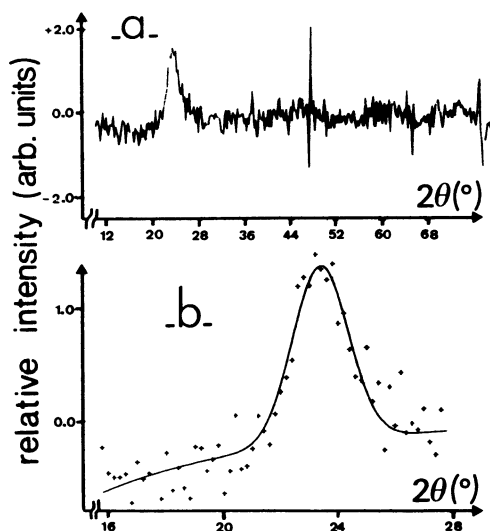


Fig. 1. — (a) Result of the subtraction between the neutron diffraction spectra obtained at $T = 3$ K and $T = 37$ K; (b) The magnetic line observed at $T = 3$ K.

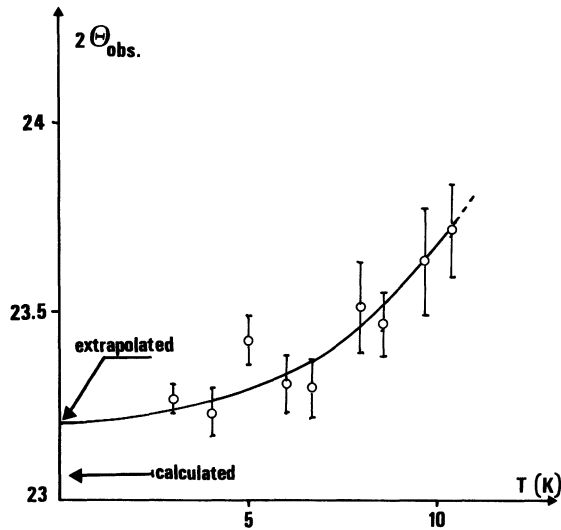


Fig. 2. — Observed position of the magnetic line vs. temperature. The $2\theta_B$ experimental value extrapolated to $T = 0$ K and the angular position of the $(1/2, 1/2, 1/2)$ line referred to the nuclear unit cell, are indicated by arrows.

The intensities of the $1\ 1\ 1$, $2\ 0\ 0$ and $2\ 2\ 0$ nuclear reflections are apparently not affected by the magnetic ordering. Figure 3 reports the magnetic line integrated intensity I_{int} as a function of temperature. Figure 4 presents the observed values of the full width at half maximum $\Gamma_{1/2}$ as a function of temperature. The value of $\text{tg } \theta / \text{tg } \theta_M$ (θ and θ_M being the Bragg angles of the magnetic line and of the monochromator respectively) is 0.51. Two remarks can be made :

a) the width of the magnetic line is quite large ($\Gamma_{1/2} > 1^\circ$) as compared to the experimental resolution ($\Gamma_{1/2} = 0.2^\circ$);

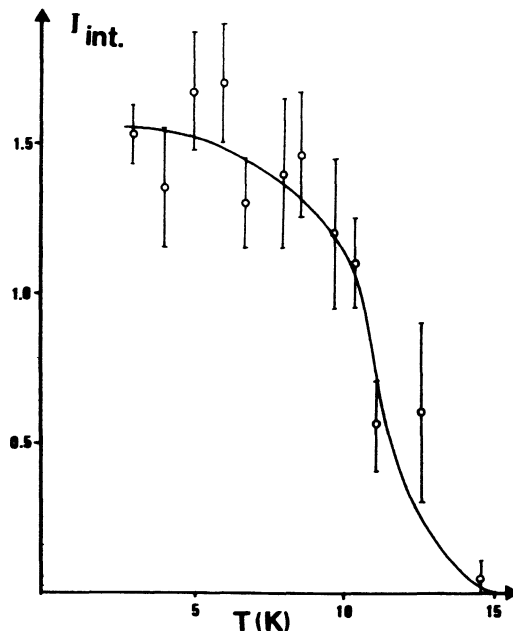


Fig. 3. — Magnetic line integrated intensity as a function of temperature.

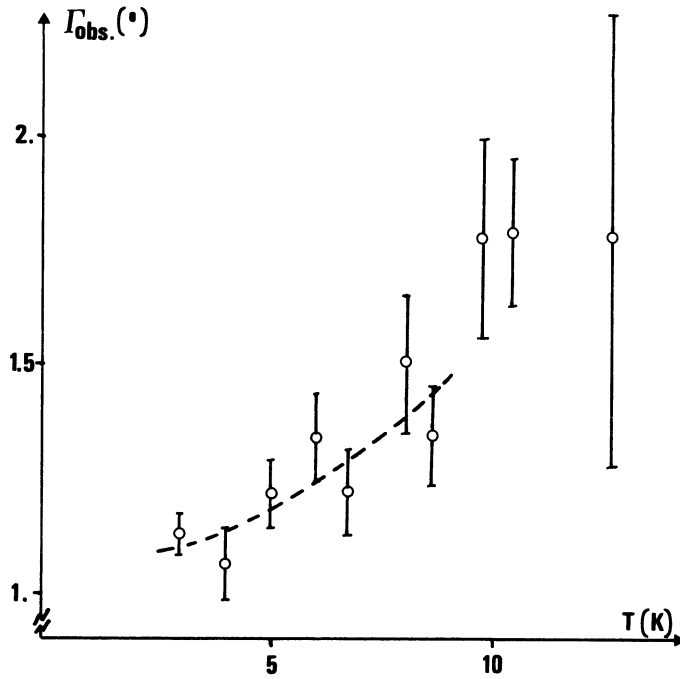


Fig. 4. — Experimental values of the full width at half maximum of the magnetic line vs. temperature.

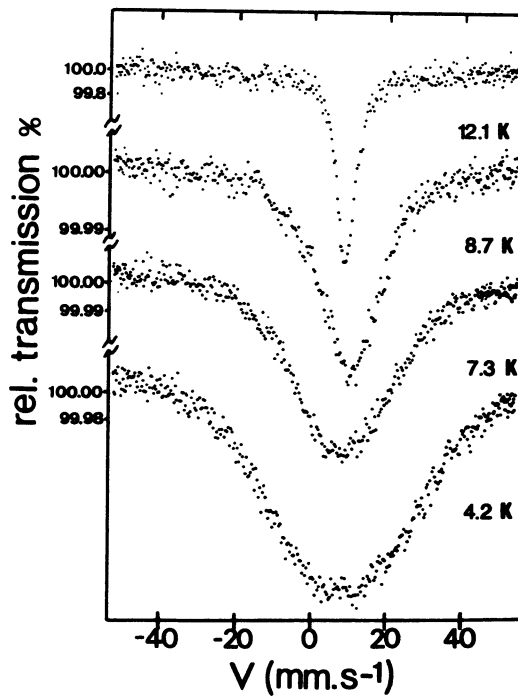


Fig. 5. — Typical ^{237}Np Mössbauer spectra obtained at various temperatures for the $\text{U}_{0.5}\text{Np}_{0.5}\text{O}_2$ solid solution.

b) the width is temperature dependent decreasing when the solid solution is being cooled.

One possible explanation of these two facts could be the occurrence of a short range of the magnetic order, with a correlation length increasing as the temperature decreases.

In fact in this assumption, the correlation length, very roughly evaluated by the Scherrer equation (see, for instance, Ref. [10]), would have an order of magnitude of 35 Å at $T \simeq 10$ K. As the temperature is decreased, the correlation length would slightly increase without any occurrence of long range order also at the lowest investigated temperature values; according to the previously mentioned very rough evaluation, the correlation length at $T = 3.0$ K would be 60 Å.

On the other hand, nuclear reflections not showing any broadening at all temperature investigated, clustering effects of the two ions should be excluded.

^{237}Np Mössbauer spectra were performed on the same powder sample (200 mg) at various temperatures from 4.2 to 15 K. Typical spectra are displayed on figure 5; they are virtually identical to those observed by some of us for all the other $U_{1-x}Np_xO_2$ solid solutions [7]. The isomer shifts coincide with that of pure NpO_2 and below $T_0 \sim 12$ K the magnetic broadening of the spectra is confirmed. Moreover the ordering temperature of the Np ions ($T_0 \sim 12$ K) observed by Mössbauer resonance agrees, inside the experimental uncertainties, with neutron data.

3. Conclusions.

The following informations have been obtained by the present experiment :

- a) Clustering effects of Np and U ions should be excluded.
- b) The solid solution $U_{0.5}Np_{0.5}O_2$ orders magnetically at low temperature. This fact confirms the recent work [7] by Mössbauer and magnetic susceptibility measurements.
- c) The magnetic structure of $U_{0.5}Np_{0.5}O_2$ is different from the magnetic structure of UO_2 . As a consequence, the partial replacement of U atoms by Np atoms in UO_2 does not imply a simple dilution effect as it was observed in the case of $U_{1-x}Th_xO_2$ [11]. Therefore, the observed results suggest a complex magnetic interaction, possibly coupled with partial ordering of the lattice.
- d) The observed temperature dependent large values of the full width at half maximum of the only one magnetic line in $U_{0.5}Np_{0.5}O_2$ could suggest an eventual short range nature of the magnetic order.
- e) The intensity of the observed magnetic reflection is quite low. At present, an evaluation of the magnetic moment is not possible without further information on the antiferromagnetic structure. On the other hand, the ordered moment value deduced from Mössbauer technique was $\sim 0.5 \mu_B$.

This work seems to open a small breach in the till now impenetrable wall surrounding the mysterious low temperature NpO_2 phase transition. By applying neutron diffraction and Mössbauer resonance to solid solutions having different compositions we will try to elucidate at first the nature of the magnetic order observed in $U_{0.5}Np_{0.5}O_2$ and then, perhaps, of the low temperature phase transition in pure neptunium dioxide.

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