Classification
Physics Abstracts
61.12

Recent results on the NpO_2 25 K transition by neutron diffraction

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(Reçu le 9 juin 1981, accepté le 9 juillet 1981)

Résumé. — Des expériences de diffraction élastique ont été effectuées sur les premiers cristaux disponibles de NpO_2 . Le but de ces expériences était d'explorer la transition préalablement observée à 25 K dans cet oxyde. Les principaux résultats de cette étude sont l'absence d'arrangement magnétique à basse température, la limite du moment ordonné détectable étant de $\mu_{\text{ord}} \leq 0,1 \mu_B$ par atome de neptunium, ainsi que l'absence de distorsion du réseau aussi bien externe qu'interne, le déplacement éventuel du sous-réseau oxygène dû à une distorsion interne devant être $\Delta_O \leq 0,010 \text{ \AA}$.

Abstract. — Elastic neutron diffraction experiments have been carried out on the first available NpO_2 single crystals. The aim of this experiment was to investigate the 25 K transition occurring in this oxide. As main results of this study no magnetic ordering was detected, the limit of detectability being $\mu_{\text{ord}} \leq 0.1 \mu_B$ per Np atom, and no evidence of a lattice distortion either external or internal was observed. The sensitivity for a possible detection of an oxygen displacement was $\Delta_O \leq 0.010 \text{ \AA}$.

1. Introduction. — The behaviour of NpO_2 has been extensively studied at low temperature by all the various techniques available but, till now, no satisfactory answer to the problem of the 25 K transition has been given. At first the heat capacity measurement [1] showed a λ peak at 25.3 K suggesting an antiferromagnetic transition. This result was confirmed by subsequent magnetic susceptibility measurements [2, 3] indicating a maximum in the $\chi(T)$ curve around 25 K whereas the effective paramagnetic moment at higher temperature ($\mu_{\text{eff}} = 2.95 \mu_B$) was consistent with the Np^{+4} ground state [4]. However two independent powder neutron diffraction studies [5, 6] failed to detect magnetic ordering giving an upper limit $\mu_{\text{ord}} \leq 0.4 \mu_B/\text{Np atom}$ (assuming a type I antiferromagnetic ordering). At the same time a Mössbauer effect study was carried out [7]; it revealed a very slight broadening of the linewidth below 22 K for two samples of different stoichiometry ($\text{NpO}_{1.92}$ and $\text{NpO}_{2.03}$). This broadening is consistent with an hyperfine field at the ^{237}Np nucleus of approximately 40 kOe corresponding to an esti-

mated moment of $0.01 \mu_B$, i.e. much less than 1 % of the paramagnetic moment.

Recently the Mössbauer investigation was repeated [8] both on powder and single crystals having the $\text{NpO}_{2.00}$ stoichiometry, the broadening found is comparable with the one reported for $\text{NpO}_{2.03}$ [7]. The magnetic susceptibility was also remeasured [9] on polycrystalline sample; the transition was found at 25.3 K with $\mu_{\text{eff}} = 3.6 \mu_B$ and $\theta_p = -170 \text{ K}$ but the shape of the $\chi(T)$ curve below the transition seems different from that of an antiferromagnet, the susceptibility becoming temperature independent. A polarized neutron diffraction study [10] confirmed the Np ions are tetravalent Np^{+4} . Thus, the absence of a sizeable moment on the Np ion is puzzling, since Np^{+4} ions are Kramers ions in the $5f^3$ configuration for which a singlet ground state is impossible.

An alternative explanation for the 25 K transition in stoichiometric NpO_2 is quadrupolar ordering. The absence of magnetic ordering may mean :

I) The transition is not associated with magnetic

ordering as in some 4 f-systems but in this case either the magnetic ordering must take place at a lower temperature or the susceptibility must diverge; since neither of these facts are observed down to 2 K this possibility is unlikely.

II) The Γ_8 ground state being split by the Jahn-Teller effect gives two Kramers doublets and the ground state doublet can have, accidentally, a very small magnetic moment: this has been theoretically proposed [9] and appears to be the only possible explanation.

In this paper we present the results of neutron diffraction experiments which have been carried out on single crystals of NpO_2 in order to investigate the 25 K first order transition.

2. Experimental details. — Some small NpO_2 single crystals (0.5 mm^3) which were prepared at the JRC Karlsruhe Establishment [10] were mounted on specially built aluminum capsules in order to carry out neutron diffraction experiment on a four circle diffractometer. Preliminary measurements were done at the FR2 reactor in Karlsruhe whereas the final experiments were performed on the D10 diffractometer at the High-flux Reactor of Institut Laue-Langevin in Grenoble.

NpO_2 crystallizes in the face centred cubic fluorite structure and has a lattice constant $a = 5.434 \text{ \AA}$ at room temperature. Despite the very small dimension of our crystals it was possible to collect reflections of the three types, namely:

i) high intensity reflections

$$(h + k + l = 4n) |F_0| = 4 |b_{\text{Np}} + 2b_{\text{O}}|,$$

ii) medium intensity reflections

$$(h + k + l = 2n + 1) |F_0| = 4 |b_{\text{Np}}|,$$

iii) low intensity reflections

$$(h + k + l = 4n + 2) |F_0| = 4 |b_{\text{Np}} - 2b_{\text{O}}|$$

where F_0 is the structure factor without consideration of the thermal vibrations, b_{Np} and b_{O} are the Np and oxygen coherent scattering length, respectively. A recent experiment performed on the same crystals [11] leads to the conclusion that the value of b_{Np} is $1.00 \times 10^{-12} \text{ cm}$ rather than $1.055 \times 10^{-12} \text{ cm}$ [5, 6] and that the crystal is stoichiometric ($b_{\text{O}} = 0.58 \times 10^{-12} \text{ cm}$).

The high intensity reflections were somewhat effected by extinction. Therefore the small size of the used crystals seems to be an optimum between the two appropriate requirements of sufficiently high reflection intensity and sufficiently low extinction.

3. Results. — **3.1 SEARCH FOR ANTIFERROMAGNETIC ORDER ON NpO_2 CRYSTALS.** — In order to investigate the possible appearance of an antiferromagnetic order below the 25 K transition temperature with a sensitivity higher than the ones obtained in referen-

ces [5] and [6] the use of a single crystal was coupled to the use of the most performing diffractometer existing at I.L.L. for this purpose, namely the above mentioned D10. However before doing that, a neutron powder experiment was carried out on the D1B diffractometer of I.L.L. confirming the absence of magnetic ordering of any type at low temperature within the limit of a slightly better sensitivity than [5] and [6]. Then the experiment was performed on the D10 diffractometer. At first the crystal was oriented by detecting the previously mentioned three types of nuclear Bragg reflections. Then the reflections (001) (403) (010) (221) and (003), whose eventual appearance would indicate an antiferromagnetic ordering, were investigated. All these reflections obey the rule (mixture of even and odd indices) characterizing reflections which should occur for an antiferromagnetic ordering of type I, as for UO_2 below the 30 K phase transition.

Actually no significant neutron intensity was observed for any of these investigated reflections. However it was possible to assess an upper limit of the ordered moment (μ_{ord}) by using a similar procedure as the one used in reference [12] in the case of AmO_2 . The minimum detectable peak intensity of a magnetic reflection, I_{min} , was compared to the peak intensity $I_{(111)}$ of the (111) nuclear reflection. By taking I_{min} equal to twice the statistical error of the background, one obtains $I_{\text{min}}/I_{(111)} = 1/2400$ corresponding to $\mu_{\text{ord}} \leq 0.1 \mu_{\text{B}}$. This limit appears to be four times smaller than the previous determination on powder samples achieved by neutron scattering.

3.2 SEARCH FOR JAHN-TELLER DISTORTION. — At first the appearance below 25 K of a Jahn-Teller distortion of the type already observed in UO_2 [13] was investigated. This distortion is obtained by combination of a $T_{2g}(Q^1)$ shear deformation with a T_{1g} pure rotation. If such distortion would occur, one should observe the appearance of superstructure reflections (hkl) with one odd and two even Miller indices. The search concerned the (643) reflection which was the observable reflection of this kind with the highest Miller indices. Indeed like the occurrence of magnetic structure is easily evidenced with low Miller indices reflection when the magnetic form factor is not much smaller than 1, the occurrence of a structural deformation will be easily seen with high Miller indices reflections. No appearance of neutron peak below 25 K was observed as is shown on figure 1. By taking the minimum observable intensity I_{min} , equal to twice the statistical error, a maximum value $d\sigma_{\text{D}}$ for the molar cross section for oxygen displacement $d\sigma_{\text{D}} = 1.6 \text{ mb/mole}$ was obtained. From this value an upper limit for the oxygen displacement associated with this kind of distortion $\Delta_{\text{O}} \leq 0.010 \text{ \AA}$ was evaluated.

Then the eventual appearance of a Jahn-Teller distortion of the type already observed in $\text{Zr}(\text{CaY})\text{O}_2$ [14] was investigated. This distortion would corres-

Fig. 1. — The total neutron intensity collected for the (643) and (651) forbidden reflections as a function of scattering angle at $T = 10$ K.

Fig. 2. — The integrated intensity of the strong (642) reflection as a function of temperature, the transition temperature being 25 K.

pond to a mode with $E_u + A_{2u}$ symmetry. For such a distortion (hkl) reflections with one even and two odd Miller indices should appear. The search concerned the (651) reflection. Again no significant peak was observed below 25 K (Fig. 1). By a similar procedure to the above mentioned for the other type of Jahn-Teller distortion, a value $d\sigma_D = 3.6$ mbarn/mole of the minimum detectable cross section and a value $\Delta_O \leq 0.012$ Å for the oxygen displacement associated with such a distortion were obtained.

Figure 2 reports the integrated intensity of the strong (642) nuclear reflection as a function of temperature. Across the 25 K transition no variation of intensity is visible. Therefore an eventual influence of a distortion on the crystal perfection at the transition temperature should be excluded. In fact an eventual variation of the crystal perfection would have influenced the extinction properties of the crystal and therefore the integrated intensity.

4. Discussion. — The neutron investigation of the low temperature phase transition of NpO_2 on a powder and single crystal showed that no antiferromagnetic order could be detected below 25 K within experimental limits. According to this limit an upper value for the ordered moment $\mu_{\text{ord}} \leq 0.1 \mu_B$ was obtained for type I antiferromagnetism which is sensibly lower than the previous upper value from

polarized neutrons diffraction measurements [11]. This upper limit appears compatible with the magnetic moment obtained from Mössbauer experiments [7, 8].

We first checked that there was no change in the cubic symmetry i.e. no *external* distortion, an *internal* distortion of the oxygen sublattice being then the only possibility. A search for the two possible kinds of distortion of the oxygen sublattice leads to an evaluation of an upper limit of the oxygen displacement $\Delta_O \approx 0.010$ Å. This value corresponds to the order of magnitude predicted by Erdős and Solt from model calculation [9]. Nevertheless the validity of this model cannot be confirmed or excluded by the presently obtainable sensitivities in the detection of such a Jahn-Teller distortion by neutron diffraction techniques.

The present results are the most precise which can be obtained at this time with such small crystals and it is not obvious that bigger ones will be ever grown. Thus, it is dubious that the more and more puzzling NpO_2 transition will be experimentally cleared up by diffraction experiments. However, it should be noted that a distortion of the UO_2 type involves a T.O. phonon which is Raman active [15]. Therefore, the existence of the distortion could be checked by inelastic scattering of light or of neutron using photographic techniques. Such experiments have been already planned.

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