

## Spin-relaxation phenomena of cubic $\Gamma_8$ in Mössbauer spectra of $^{237}\text{Np}$ in $\text{NpO}_{2+x}$

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Mössbauer studies of  $^{237}\text{Np}$  in  $\text{NpO}_{2+x}$  at temperatures 4.2 to 77 K were performed. The spectra show spin-relaxation phenomena which strongly depend on  $x$  and temperature. They are analyzed in terms of spin relaxation in a split cubic  $\Gamma_8^{(2)}$  quartet of  $\text{Np}^{4+}(^4I_{9/2})$ . It is concluded that the Orbach-Blume mechanism ( $1/\tau \propto T^5$ ) is the dominant spin-lattice-relaxation process.

Spin-relaxation phenomena in Mössbauer spectra of cubic paramagnetic systems are very intriguing and have recently caught much attention.<sup>1</sup> Of particular interest are those within a  $\Gamma_8$  state which were little studied to date. These phenomena are studied here using crystals of the nonstoichiometric tetravalent oxides  $\text{MO}_{2+x}$  ( $M = \text{Np}$ ). These crystals, of the simple cubic  $\text{CaF}_2$  structure, exhibit unusual magnetic phenomena when  $M = \text{U}$ .<sup>2</sup> For some time it was believed that also  $\text{NpO}_2$  orders magnetically at low temperatures.<sup>3</sup> Our present Mössbauer studies show that  $\text{NpO}_{2+x}$  ( $x = 0.10, 0.15, 0.23$ ) are paramagnetic down to 4.2 K. The changes in the observed spectra at low temperatures are the result of paramagnetic relaxation phenomena in a  $\Gamma_8^{(2)}$  cubic ground state of  $\text{Np}^{4+}(^4I_{9/2})$ . The extra oxygen added to  $\text{NpO}_2$  produce an axial crystalline field which affects the  $\text{Np}^{4+}$  ground state, splitting the cubic  $\Gamma_8^{(2)}$  into two Kramers's doublets. This leads to a great decrease in the spin-spin relaxation rates. The analysis of the relaxation rates for the  $\text{NpO}_{2+x}$  system shows that the spin lattice Orbach-Blume relaxation mechanism<sup>4</sup> becomes the dominant relaxation process. It is the first time that this mechanism is observed for an actinide and first time to be measured by the Mössbauer effect.

The hyperstoichiometric  $\text{NpO}_{2+x}$  phases were obtained by decomposition of  $\text{NpO}_2(\text{OH})_2$  prepared as follows: A nitric acid solution  $10^{-2}M$  of  $\text{Np}^{6+}$  has been brought slowly from pH 6 to pH 8 by an addition of a solution of tetramethylammonium hydroxide. The precipitate was decomposed under controlled heating (100–300 °C) and vacuum conditions to the aimed  $x$  value of  $\text{NpO}_{2+x}$ . Verification of the  $x$  value was performed by using the method proposed by Nens *et al.*<sup>5</sup> The crystal structure was studied by a Philips PW 1365/60 x-ray diffractometer attached to

a glove box. The x-ray powder diffraction measurements proved that crystals of single-phase fluorite structure, isostructural with  $\text{UO}_2$ , were obtained. Slight broadening of the x-ray diffraction lines indicated probably the presence of local distortions from the perfect fluorite structure. The unit-cell size obtained was  $5.4384(6) \text{ \AA}$  for  $\text{NpO}_{2.23}$  in comparison to  $5.4434(6) \text{ \AA}$  for pure  $\text{NpO}_2$ .

The Mössbauer studies of the 59.6-keV transition of  $^{237}\text{Np}$  were performed using a conventional constant acceleration drive system. The absorbers were kept in a plastic oven inside a helium cryostat. The Mössbauer source was  $^{241}\text{Am}$  metal. The observed Mössbauer spectra of  $^{237}\text{Np}$  in  $\text{NpO}_{2+x}$  show the following major features: At temperatures above 25 K a single relatively narrow, temperature-independent, absorption line was observed. As the temperature is decreased below 25 K a significant line broadening occurs. The spectra also contain a line of variable intensity (sample dependent,  $\sim 3\%$  for the  $x = 0.23$  sample) at an isomer shift which corresponds to  $\text{Np}^{5+}$ . The spectra for  $\text{NpO}_{2.23}$  are shown in Fig. 1. At 4.2 K the spectra extend to widths of up to 38 mm/sec but by no way do they correspond to magnetic order. It seems quite clear that all the broadening phenomena observed are due to paramagnetic spin relaxation. It is thus of interest to understand how the added oxygen changes the properties of the Np ions and the nature of spin-relaxation mechanisms.

$\text{Np}^{4+}(5f^3, ^4I_{9/2})$  in the cubic environment of  $\text{NpO}_2$  has a  $\Gamma_8^{(2)}$  ground state.<sup>6,7</sup> In this case, spin-spin relaxation rates are high and explain the relatively narrow Mössbauer absorption lines observed.<sup>3</sup> In  $\text{NpO}_{2+x}$ , as oxygen is added, local axial distortions are produced. These distortions are observable directly by the x-ray studies mentioned before. The

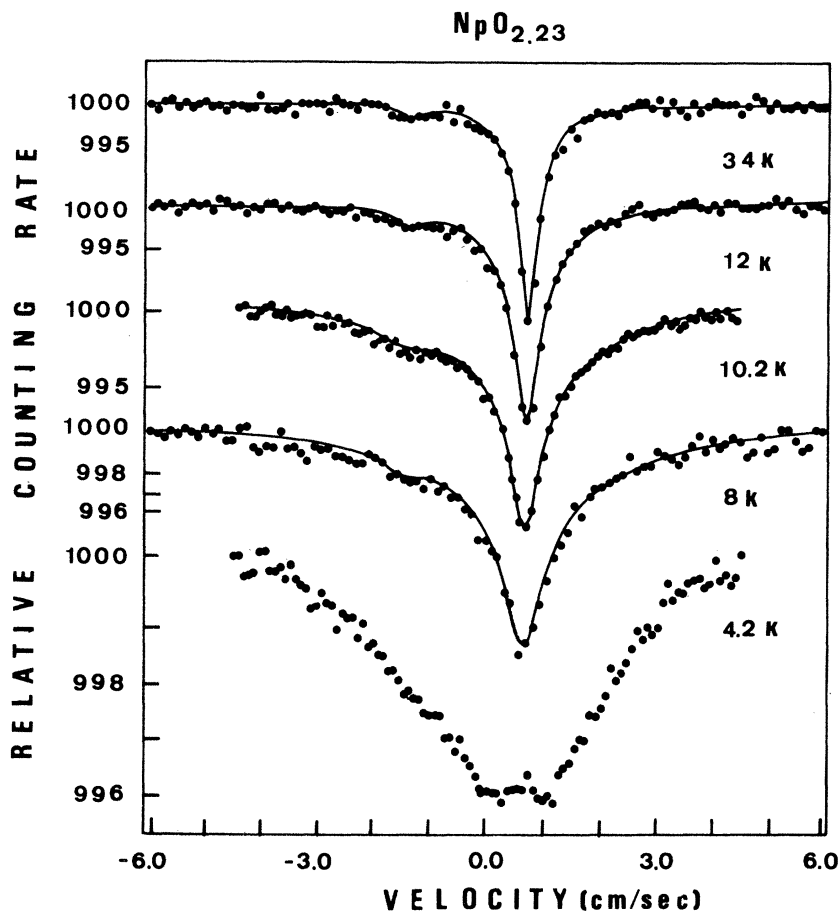


FIG. 1. Mössbauer spectra of  $\text{NpO}_{2.23}$ . Solid curves are least-squares fitted using rate equation relaxation theory.

distortion splits the quartet into two doublets, one of them may become of extreme anisotropy<sup>6,7</sup> leading probably to lower spin-spin relaxation rates.<sup>8</sup> Having these considerations in mind we tried to analyze the Mössbauer spectra in a quantitative manner to yield the temperature dependence of the spin-relaxation rates.

The analysis of a  $^{237}\text{Np}$  Mössbauer spectrum ( $\frac{5}{2} \rightarrow \frac{5}{2}$  transition) for an ionic  $\Gamma_8$  state under relaxation conditions is in principle, possible, using the methods of Clauser and Blume and Shenoy and Dunlap.<sup>9</sup> However, it involves diagonalization of matrices of order  $576 \times 576$ . Under the conditions of fast relaxation and in particular in  $\text{NpO}_{2+x}$  where the  $\Gamma_8^{(2)}$  ground state is split into two Kramers's doublets, one of them possibly of extreme anisotropy, one may estimate the spin-relaxation rate either from the observed linewidth or using simple relaxation theory, applicable in effective field cases.<sup>10</sup>

In any theory of relaxation phenomena in Mössbauer spectra, at high-spin-relaxation rates, in paramagnetic systems, a single absorption line should be observed (assuming no quadrupole splitting), with

a linewidth at half-height given by

$$\Gamma = \Gamma_0 + 4\pi\tau\bar{\nu}^2. \quad (1)$$

Here  $\Gamma_0$  is the linewidth in the limit of  $\tau = 0$  and  $\bar{\nu}^2$  is the average of the square of the magnetic splittings,  $\nu = (g_e m_e - g_0 m_0)H$ . In our case of the slightly split  $\Gamma_8$ ,  $\bar{\nu}^2$  is temperature independent and thus if one plots the temperature dependence of  $\Gamma - \Gamma_0$  one obtains the temperature dependence of  $\tau$ . Such an analysis shows that one can fit the temperature dependence of  $1/\tau$  by a formula of the form

$$1/\tau = A + BT^n, \quad (2)$$

where  $n = 5$ . Here  $A = 1/\tau_{ss}$  represents the spin-spin relaxation rate and the second term represents the spin-lattice-relaxation rate ( $1/\tau_{sl}$ ). The experimental results for  $\Gamma - \Gamma_0$  as a function of  $x$  and  $T$  are given in Table I. In Fig. 2 we plot  $1/(\Gamma - \Gamma_0)$  as a function of  $T^n$  yielding linear dependence for  $n = 5$ . In Fig. 2 we also include the experimental results of Dunlap *et al.*<sup>3</sup> which also follow formula (2). Such a temperature dependence of  $1/\tau_{sl}$  corresponds to the Orbach-Blume spin-lattice-relaxation mechanism.<sup>4</sup>

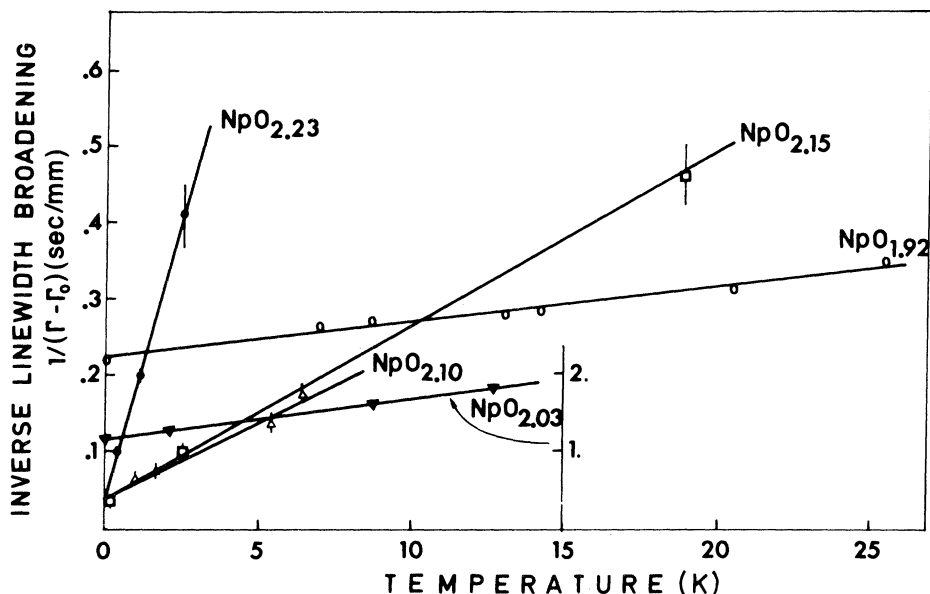


FIG. 2. Temperature dependence of the inverse of the Mössbauer absorption linewidth broadening. The solid lines describe the linear dependence of  $T^5$ . The dashed curves for  $\text{NpO}_{1.92}$  and  $\text{NpO}_{2.03}$  were obtained from the solid curves representing  $\Gamma$  in Fig. 1 of Ref. 3;  $\Gamma_0$  was chosen to be the high-temperature limit of  $\Gamma$ , 2.4 and 2.0 mm/sec, respectively.

This mechanism is applicable to a fourfold multiplet, two Kramers's doublets of an energy difference small in comparison to temperature; this is exactly the case of our  $\Gamma_8^{(2)}$  state. If we choose as the wave functions for the two doublets those which correspond to  $V_6=0$  (Refs. 6 and 7) we obtain for  $\bar{\nu}^2$  the value

TABLE I. Temperature dependence of the  $^{237}\text{Np}$  Mössbauer absorption linewidth broadening in  $\text{NpO}_{2+x}$ .  $\Gamma_0=4.8$  mm/sec is the linewidth at temperatures above 25 K. The relatively large value of  $\Gamma_0$  is probably due to local quadrupole interactions present in  $\text{NpO}_{2+x}$ .

Fraction $x$	Temperature (K)	$\Gamma - \Gamma_0$ (mm/sec)
0.10	10.0(5)	15.5(3)
	11.0(5)	13.8(3)
	14.0(5)	7.2(3)
	14.5(5)	5.5(3)
	25(1)	0.0(3)
	35(1)	0.0(3)
	51(1)	0.0(3)
0.15	7.2(5)	28(2)
	12.0(5)	10.4(3)
	18.0(5)	2.2(3)
	35(1)	0.0(3)
	51(1)	0.0(3)
0.23	8.0(5)	10.1(3)
	10.2(5)	5.0(3)
	12.0(5)	2.4(3)
	34(1)	0.0(3)

$9 \times 10^{18} \text{ sec}^{-2}$  and  $1/\tau = (0.9 \times 10^{11} + 4.5 \times 10^5 T^5) \text{ sec}^{-1}$  for  $x=0.1$ ,  $1/\tau = (0.9 \times 10^{11} + 5.1 \times 10^5 T^5) \text{ sec}^{-1}$  for  $x=0.15$ , and  $1/\tau = (0.9 \times 10^{11} + 3.4 \times 10^6 T^5) \text{ sec}^{-1}$  for  $x=0.23$  (Fig. 2). Because of the uncertainty in the real value of  $\bar{\nu}^2$ , the absolute values for  $1/\tau$  may be in error of up to an order of magnitude.<sup>11</sup> But even then these are extremely short spin-lattice relaxation times. These extremely short values for  $\tau_{sl}$  are consistent with the spin-relaxation-rate estimates for the  $\Gamma_8$  state of  $\text{Dy}^{3+}$  in  $\text{CaF}_2$ .<sup>7</sup> These are shorter than any spin-lattice relaxation rates ever measured in this range of temperatures (7 to 18 K).

Under the same assumptions we used in calculating  $\tau$  one can use the rate equation method<sup>10</sup> to calculate the full Mössbauer spectra. One observes in Fig. 1 that very good agreement can be obtained in the spectra down to 8 K, yet not in the 4.2-K spectrum, where a detailed relaxation-theory treatment is needed.

As final conclusion we can say that although adding oxygen to  $\text{NpO}_2$  does not destroy the gross cubic  $\text{CaF}_2$  structure, the local crystalline field at the Np site has an axial component which leads to the phenomena observed in the present Mössbauer study. It seems that this is one of the rare cases in which the Orbach-Blume relaxation mechanism is observed and measured quantitatively to yield extremely short relaxation times. It is the first time this mechanism is observed in actinides and the first time observed and measured by the Mössbauer effect.

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