



**HAL**  
open science

## Mössbauer studies of neptunium fluorozirconate glass

J. Jove, J. Gal, W. Potzel, G. Kalvius, J. Spirlet, M. Pages

► **To cite this version:**

J. Jove, J. Gal, W. Potzel, G. Kalvius, J. Spirlet, et al.. Mössbauer studies of neptunium fluorozirconate glass. *Journal de Physique Colloques*, 1979, 40 (C4), pp.C4-190-C4-191. 10.1051/jphyscol:1979460 . jpa-00218856

**HAL Id: jpa-00218856**

**<https://hal.science/jpa-00218856>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Mössbauer studies of neptunium fluorozirconate glass

J. Jove (\*), J. Gal (\*), W. Potzel (\*\*), G. M. Kalvius (\*\*), J. C. Spirlet (\*\*\*) and M. Pages (\*)

(\*) Laboratoire Curie, 11, rue Pierre-et-Marie-Curie, F75231 Paris Cedex 05, France

(\*\*) Physik Department, Technische Universität München, D8046 Garching, Germany

(\*\*\*) Institut Européen des Transuraniens, D75 Karlsruhe, Germany

**Résumé.** — Un nouveau composé vitreux, le fluorozirconate de neptunium ( $\text{NpBa}_6\text{Zr}_{12}\text{F}_x$ ) a été préparé et les spectres Mössbauer ont été mesurés à 4,2 K et 77 K. On observe deux raies de résonance. L'une est attribuée à des ions  $\text{Np}^{4+}$  se trouvant en position normale pour le neptunium dans ce composé. On suppose que la seconde raie provient d'ions Np qui occupent des sites de  $\text{Ba}^{2+}$ . Le déplacement isomérique de cette dernière raie suggère une configuration  $5f^1 6d^1$ .  $\text{Np}^{4+}$  présente des effets de relaxation paramagnétique.

**Abstract.** — A new neptunium fluorozirconate glass ( $\text{NpBa}_6\text{Zr}_{12}\text{F}_x$ ) has been prepared and its Mössbauer spectrum was measured at 4.2 K and 77 K. Two resonance lines were observed. One is assigned to the  $\text{Np}^{4+}$  ions occupying the normal Np sites in the compound. The other is thought to arise from Np which has replaced some of the  $\text{Ba}^{2+}$  ions. The isomer shift of those ions suggests a configuration near  $5f^1 6d^1$ . The  $\text{Np}^{4+}$  ions exhibit paramagnetic relaxation.

The measurement of hyperfine interactions by Mössbauer spectroscopy is a sensitive tool for the determination of electronic properties of actinide materials [1]. In particular, neptunium and its compounds were studied thoroughly. From the isomer shift one deduces the charge state of the neptunium ion and other properties of the chemical bond. Magnetic hyperfine splittings have largely been interpreted in terms of the counterplay between localized and itinerant magnetism which is a unique feature of the light 5f elements. Quadrupolar interactions give information on local site symmetry (crystal structure) and also on the covalency of the chemical bond [2].

In this note we report the successful preparation together with first Mössbauer measurements of a vitreous neptunium compound. In particular isomer shift data will be discussed. Non-crystalline Np materials have previously not been investigated by Mössbauer spectroscopy except for some studies using frozen solutions of  $^{241}\text{Am}$  compounds as sources for the neptunium resonance [3]. A neptunium fluorozirconate glass was prepared on the basis of the phase diagram [4] for U and Th glasses. The pertinent parameters were extrapolated to the Np case. The reaction was performed in a Ni crucible and resulted in a glass which was hardly transparent to light and exhibited a violet to black colour. Its nominal composition is  $\text{NpBa}_6\text{Zr}_{12}\text{F}_x$ ,  $x \approx 60$ . X-ray measurements proved the compound to be amorphous. Transmission Mössbauer spectra of the 60 keV resonance in  $^{237}\text{Np}$  were obtained using a standard electromechanical unit coupled to a fast

nuclear counting system [5]. The source was 300 mCi of  $^{241}\text{Am}$  metal [6] deposited onto a Ta foil. Its temperature remained at 4.2 K while the absorber could be brought from 4.2 K to 77 K. Since the glass sample ( $\sim 500 \text{ mg/cm}^2$ ) contains the Np in rather high dilution and since its Debye temperature is comparatively low, the strong source and the fast counting system are essential to obtain spectra of sufficient quality at temperatures above 4.2 K.

Figure 1 shows the spectrum at 4.2 K. It mainly consists of two resonances: a broad line centred around  $(-4.0 \pm 1.0) \text{ mm/s}$  and a sharp line located at  $(+41.0 \pm 0.2) \text{ mm/s}$ . All shifts are given relative to the absorption line of  $\text{NpAl}_2$  at 77 K ( $+13.8 \text{ mm/s}$  vs. Am metal). In figure 2 isomer shifts of some neptunium compounds are depicted [1]. The

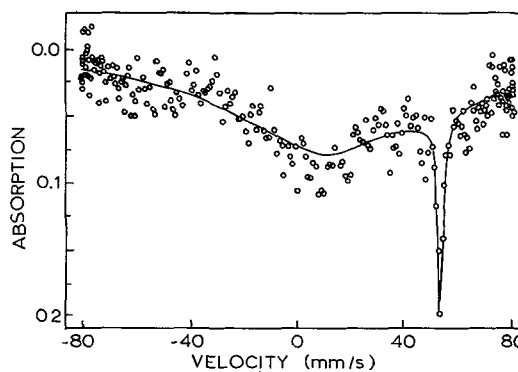


Fig. 1. — Mössbauer spectrum of the neptunium fluorozirconate glass taken with a source of Am metal. Source and absorber are at 4.2 K. Total count rate per velocity point is  $2 \times 10^8$ . The solid line is a simple fit with two Lorentzian lines.

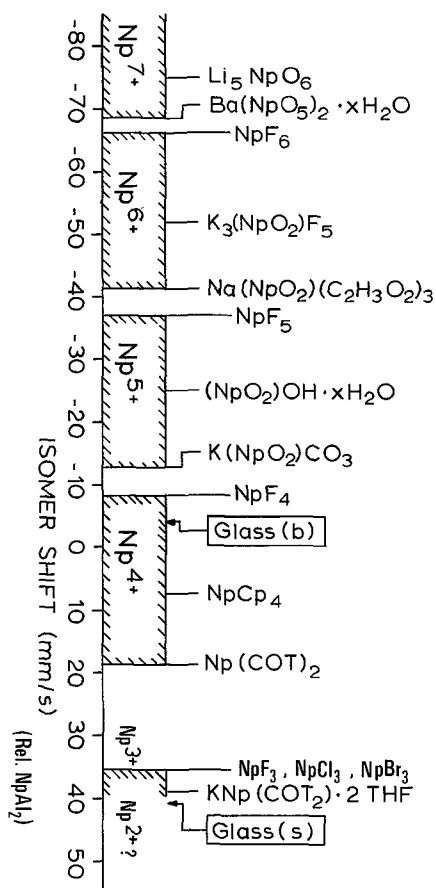


Fig. 2. — Diagram of isomer shifts of neptunium compounds. Zero shift corresponds to a  $\text{NpAl}_2$  absorber.

positions of the broad (b) and the sharp (s) resonance line of the fluorozirconate glass are also given. There exists a characteristic range of isomer shifts for each of the known charge states of Np. The most ionic compounds (e.g. the fluorides  $\text{NpF}_x$  with  $x = 3, 4, 5, 6$ ) have the most negative shift. Increasing covalency moves the resonance to more positive velocities. The broad line of the fluorozirconate glass poses no difficulty. It represents weakly covalent  $\text{Np}^{4+}$  species. Their presence is expected

since in analogous Th glasses, it is known that the actinide ion (Th) has the tetravalent charge state [4]. The isomer shift of the sharp line is unusual since it is more positive than the shifts of even the most covalent  $\text{Np}^{3+}$  compounds measured to date [7]. A rough correlation of isomer shifts with electron configuration has been attempted [8] on the basis of Dirac-Fock and relativistically corrected Hartree-Fock self-consistent field calculations for free ions. Clearly, the validity of such results in chemical compounds is questionable [9], but they will provide insight into general trends. The nominal configuration of  $\text{Np}^{3+}$  is  $5f^4$ . The addition of a  $5f$  electron (i.e.  $\text{Np}^{2+}$ - $5f^5$ ) would shift the resonance into the vicinity of  $+70$  mm/s. The addition of a  $6d$  electron (i.e.  $5f^4 6d^1$ ) causes only about one fourth as large a shift [8] and the resonance will occur between  $+40$  and  $+45$  mm/s which agrees well with the position of the sharp line. The free atom configuration of Np is  $5f^4 6d^1 7s^2$ . A configuration near  $5f^4 6d^1$  may be considered nominally a divalent neptunium, but could be interpreted as well as a highly covalent  $\text{Np}^{3+}$ . The stability of a  $6d$  occupancy in Np ions in solids is still an open question. Furthermore, the interpretation of isomer shifts in terms of mixed electron configuration is not always unique. The presence of  $6p$  and  $7s$  densities may alter the picture. We tentatively assign the sharp line as to come from additional Np ions which have replaced some of the  $\text{Ba}^{2+}$  ions in the glass. The large width of the  $\text{Np}^{4+}$  resonance is due to paramagnetic relaxation [10]. Indeed, the spectrum taken at 77 K shows a significant reduction in width. A more detailed analysis together with measurements on new samples is forthcoming. Preliminary data obtained with a glass sample prepared under other conditions (Pt crucible) shows the absence of the resonance at  $+41$  mm/s. In addition, optical absorption and fluorescence studies are planned to further elucidate the question of a  $5d$  occupancy.

**Acknowledgments.** — We are grateful to Pr. C. K. Jørgensen for his helpful comments.

#### References

- [1] DUNLAP, B. D. and KALVIUS, G. M. in *The Actinides: Electronic Structure and Related Properties*, A. J. Freeman and J. B. Darby, Jr. (Academic Press) 1974, p. 237ff.
- [2] DUNLAP, B. D., *J. Physique Colloq.* **37** (1976) C6-307.
- [3] GAL, J., HADARI, Z., YANIR, E., BAUMINGER, E. R. and OFER, S., *J. Inorg. Nucl. Chem.* **32** (1970) 2509.
- [4] POULAIN, M., CHANTHANASINH, M. and LUCAS, J., *Mat. Res. Bull.* **12** (1977) 151 and LUCAS, J., private communication.
- [5] KALVIUS, G. M., POTZEL, W., KOCH, W., FORSTER, A., ASCH, L., WAGNER, F. E. and HALDER, N., *AIP Conf. Proc.* **38** (1977) 93.
- [6] SPIRLET, J. C. and MÜLLER, W., *J. Less-Common Metals* **31** (1973) 35.
- [7] KARRAKER, D. G. and STONE, J. A., *J. Inorg. Nucl. Chem.* **39** (1977) 2215.
- [8] DUNLAP, B. B., SHENOY, G. K., KALVIUS, G. M., COHEN, D. and MANN, J. B., in *Hyperfine Interactions in Excited Nuclei*, G. Goldring and R. Kalish, eds. (Gordon and Breach) p. 709.
- [9] KALVIUS, G. M., *ibid.*, p. 523.
- [10] SHENOY, G. K. and DUNLAP, B. D., *Phys. Rev. B* **13** (1976) 1353.