Journal of Alloys and Compounds 271–273 (1998) 872–875

# Effects of self-radiation damage on electronic properties of $^{244}Cm^{3+}$ in an orthophosphate crystal of $YPO_4$

G.K. Liu[a,*], S.T. Li[a], J.V. Beitz[a], M. Abraham[b]

[a]*Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*
[b]*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

## Abstract

The electronic energy level structure of the α-emitting isotope $^{244}Cm^{3+}$ ($t_{1/2}$=18.1 years) doped into single crystals of $YPO_4$ has been studied using site-selected laser spectroscopic methods. Electronic transitions between the nominal $^8S_{7/2}$ ground state and the $^6D_{7/2}$ state of $Cm^{3+}$ were utilized to characterize the effects of α-decay-induced structural damage. The total splitting of the four doublets in the ground multiplet is 12.5 $cm^{-1}$, and that of the excited multiplet is 611 $cm^{-1}$. Due to radiation damage accumulated in 17 years since the crystals were grown, the inhomogeneous line width of the $^8S_{7/2} \leftrightarrow {}^6D_{7/2}$ transitions is broader than 50 $cm^{-1}$ as measured without site selection. The line width of resonant fluorescence line narrowing (RFLN) is less than 1 $cm^{-1}$ at 4 K. A total of 12 satellite lines were observed symmetrically spacing about the RFLN line. The position, width, and intensity of these satellite lines have been analyzed to gain information on the electronic and structural properties of the actinide ions in the disordered lattice of $Cm^{3+}$:$YPO_4$. © 1998 Elsevier Science S.A.

*Keywords:* Radiation damage; Inhomogeneous line broadening; Orthophosphates

## 1. Introduction

Inhomogeneous line broadening is ubiquitous in solid-state spectroscopy. For lanthanide and actinide ions in crystals, line broadening of optical transitions between crystal-field states of different electronic multiplets within a 4f or 5f electronic configuration arises from static crystalline defects. The inhomogeneous line width of a purely electronic f–f transition is typically about 1 $cm^{-1}$ in single crystals and broader than 100 $cm^{-1}$ in glasses. Generally, inhomogeneous line broadening is considered a nuisance, since it obscures the observation of detailed energy level structure or homogeneous line widths. However, studies of inhomogeneous line broadening, in principle, can provide us with information about the nature and distribution of defects in crystals [1,2]. In this paper, we will address a special case of inhomogeneous line broadening, namely that induced by self-radiation damage on crystalline structure.

Self-radiation damage-induced spectral line broadening is a major factor that can prevent detailed optical, EPR, or NMR spectroscopic studies of short-lived actinide isotopes in solids. For $^{244}Cm^{3+}$ ions diluted into single crystals of $LuPO_4$ and $YPO_4$, EPR and optical absorption measurements were previously conducted soon after the crystals were grown [3,4]. EPR measurements of the energy splitting and the effective $g$ factor for the $^8S_{7/2}$ ground state of $Cm^{3+}$ ions in damaged crystals were possible, because the crystal field interaction and the inhomogeneous line broadening are extremely weak in this nominal S state. The optical spectra obtained were of rather poor quality, because radiation damage produced significant broadening of optical transitions within a few days after the crystals were grown. For this reason, a less radioactive isotope, $^{248}Cm$ with a $4.7\times10^5$-year half-life, was later doped into $LuPO_4$ crystals, and high-resolution optical spectra then were obtained [5–7].

It is now possible with site-resolved high-resolution and nonlinear laser spectroscopy methods to largely eliminate the effects of inhomogeneous line broadening, and enable the crystal-field energy level structure, as well as the hyperfine and superhyperfine energy level structures, to be measured with kHz resolution. Fluorescence line-narrowing experiments have recently been performed on the homogeneous line broadening for $^{248}Cm^{3+}$ in a heavy

---

*Corresponding author. Tel.: +1 630 2524630; fax: +1 252 4225; e-mail: gliu@anlchm.chm.anl.gov

PII: S0925-8388(98)00237-0

metal fluoride (ZBLAN) glass [8] as a function of temperature, as well as the ground-state splitting of $^{245}Cm^{3+}$ that was present as a decay product of $^{249}Cf^{3+}$ in single crystals of $LaCl_3$ [9]. We have now studied the spectroscopic properties of $^{244}Cm^{3+}$ in $YPO_4$ and $LuPO_4$. In the present work, our interest is focused on inhomogeneous line broadening as a consequence of radiation damage. The characteristics of α-decay-induced crystalline damage in a 17-year-old single crystal of $YPO_4$ containing $^{244}Cm^{3+}$ ions have been elucidated by means of spectroscopic analyses.

## 2. Experimental details

Single crystals of $YPO_4$ doped with $^{244}Cm^{3+}$ ions were grown in 1980 using a high-temperature flux technique described previously [3]. The initial concentration of the Cm isotopes was ~1% by weight. The orthophosphate crystals of $YPO_4$ have a body-centered tetragonal zircon-type structure [4]. An actinide ion substituting for an $Y^{3+}$ site has $D_{2d}$ site symmetry. Since $^{244}Cm$ is an α particle emitter with a relatively short life time ($t_{1/2}=18.1$ years) and rarely fissions (spontaneous fission half-life, $1.34\times10^7$ years), significant α-decay-induced radiation damage has accumulated in the ensuing 17 years. Transmission electron microscopy images of $^{244}Cm^{3+}$ in a $LuPO_4$ crystal, also grown in 1980, have shown that the crystalline lattice now is partially amorphous and has numerous nanometer scale cavities that have formed as a result of α-decay damage [10].

An argon ion laser pumped tunable CW dye laser with a band width of 0.07 $cm^{-1}$ was the excitation source for recording fluorescence line narrowing (FLN) and excitation spectra. A monochromater with a spectral band pass of 0.3 $cm^{-1}$ was used to select the fluorescence energy of the emission from the $^6D_{7/2}$ state. The time-gated fluorescence emission was detected by a cooled photomultiplier connected to a lock-in amplifier. For FLN measurements, two acousto–optic modulators were used in series to convert the CW laser beam into a pulse train. A mechanical chopper synchronized with the modulators was set in front of the monochromater to block residual laser light while passing $Cm^{3+}$ fluorescence. With this time-resolved pump-then-detect method, scattered laser light was discriminated against by more than a factor of $10^{-6}$ when recording fluorescence.

Initial studies used a pulsed 355-nm laser as the excitation source. The observed line width of the $^6D_{7/2}$ fluorescence emission was broader than 50 $cm^{-1}$ at temperatures below 10 K. When excitation of $Cm^{3+}$ ions was induced by the modulated CW laser to the upper levels of the $^6D_{7/2}$ multiplet, and subsequent fluorescence emission from the lowest doublet at 16 570 $cm^{-1}$ was monitored, the emission spectrum became narrower and its line center shifted as a function of excitation energy as shown by Fig. 1a,b. As shown in Fig. 1c, dramatic line narrowing was achieved only when the emitting state (the lowest doublet of the $^6D_{7/2}$ multiplet centered at 16 570 $cm^{-1}$) was directly excited. In addition to the RFLN line, satellite lines on both sides of the resonant line were observed. The satellite lines are attributed to the emission to the other three doublets of the ground multiplet of the $Cm^{3+}$ ions that coincidentally (accidentally) have the same excitation energy, and to the emission of $Cm^{3+}$ ions that have different excitation energies, but were excited from different ground-state doublets of $Cm^{3+}$ ions. This enables the observation of a maximum of 12 satellite lines that are symmetrically spaced about the resonant line. In a single crystal of $LuPO_4$ doped with $^{244}Cm^{3+}$ ions, a RFLN spectrum including 12 sharp satellite lines was indeed obtained [11]. In $^{244}Cm^{3+}$:$YPO_4$, the satellite lines were not completely resolved because of severe radiation damage. The solid lines in Fig. 1c are a nonlinear least-square best fit to the experimental spectrum. The ground-state energy levels of $Cm^{3+}$ that result from this fitting are listed

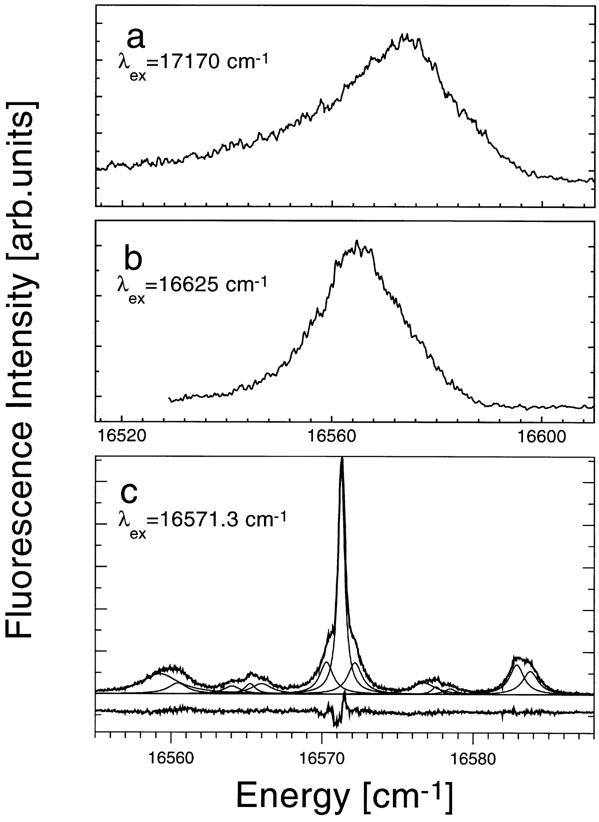

Fig. 1. Fluorescence emission spectra of $Cm^{3+}$:$YPO_4$ at 4 K for the laser excitation energy, $\lambda_{ex}$, noted. The excitation was to: (a) the top doublet, (b) the second doublet, and (c) the lowest (resonant) doublet of the $^6D_{7/2}$ excited state. Spectrum (c) is plotted in a different scale from 16 555 to 16 588 $cm^{-1}$. The smooth solid curves in (c) are the result of nonlinear least-squares fitting to the RFLN spectrum, which consists of a resonant line in the center and 12 satellite lines on two sides. The residual curve for the fitting is shown at the bottom of (c).

Table 1
Measured crystal-field energy levels of $Cm^{3+}$ in $YPO_4$ at 4 K

| Leading free-ion state (S L J) | Leading component of crystal-field state (M) | Observed level in $YPO_4$ ($cm^{-1}$)[a] |
|---|---|---|
| $^8S_{7/2}$ | 7/2 | 0.0 |
| | 5/2 | 5.3 |
| | 3/2 | 11.6 |
| | 1/2 | 12.5 |
| $^6D_{7/2}$ | 7/2 | 16 570 |
| | 5/2 | 16 628 |
| | 5/2 | 16 950 |
| | 1/2 | 17 181 |

[a] Values for the $^8S_{7/2}$ multiplet are based on a nonlinear least-squares fit to the observed data shown in Fig. 1c, and that for the $^6D_{7/2}$ multiplet are measured centers of inhomogeneous lines in an excitation spectrum.

in Table 1. Also in Table 1, the energy levels observed for the four crystal-field doublets of the excited $^6D_{7/2}$ multiplet are listed.

We have further observed that the FLN spectrum, consisting of a resonant line and a maximum of 12 satellite lines, varied dramatically as the laser excitation energy varied across the inhomogeneously broadened line center. The satellite lines became broader until they were indistinguishable as the excitation energy was tuned to higher or lower energies about the line centered at 16 570 $cm^{-1}$, whose inhomogeneously broadened width is 50 $cm^{-1}$.

## 3. Discussion

Inhomogeneous line broadening of optical transitions is induced by random shifts of crystal-field energy levels due to crystalline defects or localized electronic disordering, such as charge imbalance. In the $Cm^{3+}$:$YPO_4$ crystal we studied, self-radiation damage is the dominant source of line broadening. For the $^8S_{7/2}$ ground state to the $^6D_{7/2}$ excited-state transitions, the line broadening is mainly due to the crystal-field energy level shifts in the excited state. In the nominal $^8S_{7/2}$ state, the total crystal-field splitting is only 12.5 $cm^{-1}$, because the interaction matrices involving the $^8S_{7/2}$ free-ion state vanish in the ground multiplet. The observed splitting is due, in part, to higher order coupling mechanisms that induce mixing of the excited-state wave functions into the ground multiplet [9,12]. Other mechanisms, including relativistic effects, also give a considerable contribution [13]. For the excited state, the non-vanished crystal-field interaction is the leading mechanism for free-ion energy level splitting of the $^6D_{7/2}$ state, as well as for inhomogeneous line broadening. A total splitting of 611 $cm^{-1}$ was observed for the $^6D_{7/2}$ multiplet. Accordingly, the inhomogeneous line broadening of the $^8S_{7/2}\leftrightarrow{}^6D_{7/2}$ transitions is dominated by the crystal-field energy level variation in the excited state. The effect of radiation damage-induced structural changes on the electronic energy level structure of $Cm^{3+}$ is not significant in its ground state. This conclusion is supported by the observation of as many as 12 symmetrically spaced satellite lines in resonant excitation and fluorescence line-narrowing spectra as the laser wavelength was varied across the center of the inhomogeneously broadened line. This special electronic property of $Cm^{3+}$ allows us to use the inhomogeneous line width of the $^8S_{7/2}\leftrightarrow{}^6D_{7/2}$ transitions to characterize the crystal-field energy level variation and thereby link the energy level variation to the crystalline damage.

As shown in Fig. 1, sharp lines were observed only in the resonant fluorescence line-narrowing spectrum. Laser excitation of $Cm^{3+}$ into any of the crystal-field doublets or vibronic states above the lowest crystal-field doublet centered at 16 571.3 $cm^{-1}$ did not result in narrow emission lines, although the shape and location of the line center varied for different excitation energies (see Fig. 1a,b). Since phonon-induced broadening at temperatures below 4 K should be much less than the observed line width, and the laser band width is also negligible, the excitation energy-dependent emission spectra shown in Fig. 1 suggest that the damage induced variation in the crystal-field energy levels of the $^6D_{7/2}$ state is not correlated between different crystal-field doublets. Selected by a narrow-band laser, a set of $Cm^{3+}$, ions that accidentally have the same excitation energy between the ground state and one of the four crystal-field doublets of the $^6D_{7/2}$ excited multiplet, may have different energies for transitions into other states. This suggests that a set of $Cm^{3+}$ ions that have different solid-state environments may accidentally have the same transition energy in the upper states of the $^6D_{7/2}$ multiplet. This accidental degeneracy is removed as the ions nonradiatively relax into the lower emitting doublet. Thus, the previously excited $Cm^{3+}$ ions in the emitting state have energy levels spread around 16 570 $cm^{-1}$. The broad emission spectrum represents the energy level differences in the excited state. Since the line width and center of the non-resonant FLN spectrum varies as a function of the excitation energy, there is a certain degree of correlation between different doublets within the same multiplet. The character of inhomogeneous line broadening reflects a complex ion–lattice interaction in this damaged crystal [1,2].

In the FLN spectrum shown in Fig. 1c, $Cm^{3+}$ ions of the same energy level structure emit resonantly, of course, at the same energy (16 571.3 $cm^{-1}$) and at another three different energies, respectively, to the ground-state doublets other than that from which the excitation was induced. Therefore, a total of four emission lines are expected to be observed. Because the inhomogeneous line width is broader than the total splitting of the ground state due to the much larger crystal-field interaction in the $^6D_{7/2}$ excited state, simultaneous excitation of $Cm^{3+}$ ions of different excitation energies (due to different local environments) is possible at a given laser energy. To be excited with the same laser energy, a set of $Cm^{3+}$ ion must be initially in different doublets in the ground state that are populated at liquid helium temperature. Therefore, a given laser energy can select four different $Cm^{3+}$ groups with excitation energy differences that are determined by ground state splitting. Subsequently, each of the four groups could produce four emission lines with the central RFLN line in four-fold degeneracy (its intensity is about four times that of satellite lines). Therefore, when the laser energy was varied in the range of 16 570±25 $cm^{-1}$, and at a temperature at which all four levels of the ground state are populated, a maximum of 12 satellite lines would be observed symmetrically spaced about the resonant line. The satellite lines correspond to emission from $Cm^{3+}$ ions in four different energy levels (in the same excited state) to the four crystal-field doublets of the ground state that approximately have the same energies for all of the $Cm^{3+}$ ions. In order to be excited by the same laser energy and contribute to the FLN spectrum, the maximum difference in excitation energy for $Cm^{3+}$ ions in different local environments must not exceed the total splitting of the ground state. Thus, one group of $Cm^{3+}$ ions is excited from the lowest doublet of the ground state, another group is excited from the second doublet of the ground state, and so on. Given the non-correlated nature of inhomogeneous broadening, there is no guarantee that one set of $Cm^{3+}$ ions excited from a specific ground-state doublet has the same local environment. It is clear that the $Cm^{3+}$ ions excited from different ground doublets should have different local environments.

The spectroscopic properties of $^{244}Cm^{3+}$ ions in the 17-year-old $YPO_4$ crystal are different from those of trivalent $^{248}Cm$ ($t_{1/2}=4.7\times10^5$ years) in similar crystals, in which the inhomogeneous line broadening of optical transitions is less than the ground state splitting (fewer number of satellite lines are observable in an FLN spectrum) [5–7], and from that of $^{248}Cm^{3+}$ ions in glasses [8] in which inhomogeneous line broadening is much larger than 100 $cm^{-1}$ (no sharp satellite lines were observable). This suggests that the degree of disorder induced by α-decay damage is much larger than that induced by crystalline defects formed in the crystal growth, and less than that induced in a glass matrix. The same conclusion was obtained from studies of similar materials with electron microscope imaging techniques [10]. Although, after 17 years of α-decay damage, the surrounding lattices for most of the existing $^{244}Cm^{3+}$ ions may have undergone significant displacements and distortion, the nearest neighboring coordination and charge density may have been left without severe damage. Because the electrostatic interaction between the f elements and the lattice field is distance dependent, long-range lattice damage only perturbs electrostatic interactions to a certain degree which induces modest variations in the electronic energy level structure of a 5f electron state.

Based on the above arguments, the width of our nonresonant FLN spectra of $^{244}Cm^{3+}$ ions in $YPO_4$ represents the excited-state energy level variation. This allows us to introduce a line-broadening parameter to quantitatively evaluate the degree of crystalline damage. Consider the ratio of energy level variation induced by radiation damage versus the total crystal-field splitting of the $J=7/2$ excited multiplet. This ratio is about ~0.08 for the sample we studied. In comparison, this value should approach 1 for f element ions in glasses, because the crystal-field energy levels are not distinguishable for most multiplets in such hosts. For f element ions in single crystals, this ratio is generally less than 0.01. When such ions are radioactive and radiation damage accumulates, the inhomogeneous line broadening parameter is expected to become larger.

## Acknowledgements

Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, US Department of Energy under contract number W-31-109-ENG-38.

## References

[1] B.B. Laird, J.L. Skinner, J. Chem. Phys. 90 (1990) 3880.
[2] G.K. Liu, Jin Huang, J.V. Beitz, Phys. Rev. B 48 (1993) 13351.
[3] M.M. Abraham, L.A. Boatner, Phys. Rev. B 26 (1982) 1434.
[4] M.M. Abraham, L.A. Boatner, C.B. Finch, W.K. Kot, J.G. Conway, G.V. Shalimoff, N.M. Edelstein, Phys. Rev. B 35 (1987) 3057.
[5] W.K. Kot, N.M. Edelstein, M.M. Abraham, L.A. Boatner, Phys. Rev. B 48 (1993) 12704.
[6] J. Sytsma, K.M. Murdoch, N.M. Edelstein, L.A. Boatner, M.M. Abraham, Phys. Rev. B 52 (1995) 12668.
[7] K.M. Murdoch, N.M. Edelstein, L.A. Boatner, M.M. Abraham, J. Chem. Phys. 105 (1996) 2539.
[8] R.T. Brundage, R.L. Powell, J.V. Beitz, G.K. Liu, J. Lumin. 69 (1996) 121.
[9] G.K. Liu, J.V. Beitz, J. Huang, J. Chem. Phys. 99 (1993) 3304.
[10] G.K. Liu, J.S. Luo, S.T. Li, C.-K. Loong, M.M. Abraham, J.V. Beitz, J.K. Bates, L.A. Boatner, in: Scientific Basis for Nuclear Waste Management, vol. 21 (in press).
[11] G.K. Liu, S.T. Li (in press).
[12] B.G. Wybourne, Phys. Rev. 148 (1966) 317.
[13] D.J. Newman, Adv. Phys. 20 (1971) 197.