Effects of self-radiation damage on electronic properties of $^{244}$Cm$^{3+}$ in an orthophosphate crystal of YPO$_4$

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Electronic energy level structure of alpha-emitting isotope $^{244}$Cm$^{3+}$ ($t_{1/2}=18.1$ y) 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 alpha-decay induced structural damage. The total splitting of the four crystal field 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 metamict phases of Cm$^{3+}$:YPO$_4$. 

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Introduction

Inhomogeneous line broadening is ubiquitous in solid state spectroscopy. For lanthanide (4f) and actinide (5f) ions in crystals, line broadening of optical transitions between crystal-field states of different electronic multiplets within an f-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 previously were conducted soon after the crystals were grown [3,4]. EPR measurements of the crystal field 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 is 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 4.7x10$^5$ year
half-life, was later doped into LuPO₄ crystals, and high resolution optical spectra then were obtained [5,6,7].

It is now possible with site-resolved high resolution and nonlinear laser spectroscopy methods to largely eliminate the effects homogeneous line broadening and enable the crystal-field energy level structure, as well as hyperfine and superhyperfine energy level structure, to be measured with kHz resolution. Fluorescence line narrowing experiments recently measured homogeneous line broadening for ²⁴⁸Cm³⁺ in a heavy metal fluoride (ZBLAN) glass[8] as a function of temperature and the ground state splitting of ²⁴⁵Cm³⁺ that was present as a decay product of ²⁴⁹Cf³⁺ in single crystal of LaCl₃ [9]. We have recently studied the spectroscopic properties of ²⁴⁴Cm³⁺ in YPO₄ and LuPO₄. In the present work, our interest is focused on the inhomogeneous line broadening as a consequence of radiation damage. The characteristics of alpha-decay induced crystalline damage in a 17-year old single crystal of YPO₄ containing ²⁴⁴Cm³⁺ ions have been elucidated by means of spectroscopic analyses.

**Experimental details**

Single crystals of YPO₄ doped with ²⁴⁴Cm³⁺ ions were grown in 1980 using a high-temperature flux technique described previously [3]. The initial concentration of Cm isotopes was ~1% by weight. The orthophosphate crystals of YPO₄ have a body-centered tetragonal zircon-type structure [4]. An actinide ion substituting for an Y³⁺ site has D₂d site symmetry. Because ²⁴⁴Cm is an alpha particle emitter with a relatively short life time (t₁/₂=18.1 y) and rarely fissions (spontaneous fission half-life: 1.34×10⁷ y), significant
alpha-decay induced radiation damage has accumulated since the crystals were grown 17 years ago. Transmission electron microscopy images of $^{244}$Cm$^{3+}$ in LuPO$_4$ grown at the same time have shown that the crystalline lattice now is partially amorphous and has numerous nanometer scale cavities that have formed as a result of alpha 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 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. This inhomogeneous line broadening is comparable to that for actinide ions in glasses and about a hundred times broader than the typical ones for actinide ions in single crystals. This result thus suggests that, after 17 years of self-radiation damage, the crystalline lattice surrounding the remaining $^{244}$Cm$^{3+}$ ions has undergone extensive metamictization.
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 16570 cm$^{-1}$ was monitored, the emission spectrum became narrower and its line center shifted as a function of excitation energy as shown by Figs. 1a and 1b. 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 16570 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 3 doublets of the ground multiplet of the Cm$^{3+}$ ions that 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 [12]. In $^{244}$Cm$^{3+}$:YP$_2$O$_5$, the satellite lines were not completely resolved because of severer radiation damage. The solid lines in Fig.1c are nonlinear least square best fit to the experimental spectrum. The ground state energy levels of Cm$^{3+}$ that result from this fitting are listed in Table I. Also in Table I, the energy levels observed for the 4 crystal field doublets of the excited $^6D_{7/2}$ multiplet are listed.

For Cm$^{3+}$ ions in a crystalline lattice without structure damage or defects, a total of only 4 lines in a fluorescence spectrum would be expected to result from emission to the 4 crystal field doublets of the ground multiplet. Moreover, the line shape and positions of those lines would be independent of the initially excited, higher lying energy level. The more complicated fluorescence spectra shown in Fig. 1 tell us that the energy level
variation of Cm$^{3+}$ in the sample we studied is on the order of 50 cm$^{-1}$ and is not correlated
between the crystal field states investigated. A set of Cm$^{3+}$ ions may accidentally have the

<table>
<thead>
<tr>
<th>Leading Free-Ion State (S L J)</th>
<th>Component of Crystal-Field State (M)</th>
<th>Observed Level in YPO$_4$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^8S_{7/2} )</td>
<td>7/2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>12.5</td>
</tr>
<tr>
<td>( ^6D_{7/2} )</td>
<td>7/2</td>
<td>16570</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>16628</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>16950</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>17181</td>
</tr>
</tbody>
</table>

\( ^8S_{7/2} \) 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.
same energy in one crystal field state, but the energies of the same set of ions have different
ergies in other states. The crystal field splitting in the ground multiplet is less than the
inhomogeneous line broadening of the $^8S_{7/2} \leftrightarrow ^6D_{7/2}$ transitions. This means that the 50
$\text{cm}^{-1}$ inhomogeneous line width is dominantly due to the energy level variation in the
lowest crystal field doublet of the $^6D_{7/2}$ excited state. This special electronic property of
Cm$^{3+}$ ion enables the observation of sharp satellite lines in FLN spectrum.

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 16570 $\text{cm}^{-1}$ whose inhomogeneously broadened width is 50 $\text{cm}^{-1}$.

Discussion

Inhomogeneous line broadening of optical transitions is induced by random shifts
of crystal-field energy levels due to crystalline defects or localized electronic disordereding
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 $\text{cm}^{-1}$,
because the interaction matrixes involving the $^8S_{7/2}$ free-ion state vanish in the ground
multiplet. The observed splitting is due to higher order coupling mechanisms that induce
mixture of the excited state wave functions into the ground multiplet [9,12]. For the excited state, the non-vanished crystal field coupling of the \( ^6D_{7/2} \) state is the leading mechanism for free-ion energy level splitting 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 \( \text{Cm}^{3+} \) 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 \( \text{Cm}^{3+} \) 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 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 \( \text{Cm}^{3+} \) into any of the crystal field doublets or vibronic states above the lowest crystal field doublet centered at 16570 cm\(^{-1} \) did not result in narrow emission lines, although the shape and location of the line center varied for different excitation energies (see Figs. 1a and 1b). 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 structure 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 16570 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 (16571.2 cm$^{-1}$) and at other 3 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 at the same laser energy, Cm$^{3+}$ ions must be from different doublets in the ground state and be 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 4 folds of degeneracy (its intensity is about 4 times of that of satellite lines). Therefore, when the laser energy was varied in the range of 16570 ±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 in symmetrically spaced about the resonant line. The satellite lines correspond to emission from Cm³⁺ ions in 4 different energy levels (in the same excited state) to the 4 crystal field doublets of the ground state that approximately have the same energies for all of the Cm³⁺ ions. In order to be excited by the same laser energy and contribute to the FLN spectrum, the maximum difference in excitation energy for Cm³⁺ ions in different local environments must not exceed the total splitting of the ground state. Thus, one group of Cm³⁺ ions is excited from the top level of the ground state, another group is excited from the lowest level of the ground state, and so on. Given the non-correlated nature of inhomogeneous broadening, there is no guaranty that one set of Cm³⁺ ions excited from a specific ground state doublet has the same local environment. It is clear that the Cm³⁺ ions excited from different ground doublets should have different local environments. Although the energy level variation in the ⁸S₇/₂ ground state is small in comparison with that in the excited state, the different line widths for symmetrically located satellite lines on opposite sides of the resonant line, as shown in Fig. 1c, are attributed to residual effects of inhomogeneous line broadening.

The spectroscopic properties of ²⁴⁴Cm³⁺ ions in the 17-year old YPO₄ crystal are different either from those of trivalent ²⁴⁸Cm (t¹/₂ = 4.7×10⁵ y) in the similar crystals in which the inhomogeneous line broadening of optical transitions is less than the ground state splitting thus fewer number of satellite lines are observable in an FLN spectrum [5-7],
or that of $^{248}$Cm$^{3+}$ ions in glasses [8] in which inhomogeneous line broadening is much larger than 100 cm$^{-1}$ and no sharp satellite lines were observable. This suggests that the degree of disorder induced by alpha decay damage is much larger than that induced by crystalline defects formed in crystal growth and less than that 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 alpha-decay damage, the surrounding lattices for most of the existing $^{244}$Cm$^{3+}$ ions may have undergone significant displacements and distortion, the nearest neighboring bonding and coordination 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. It was observed that the alpha decay induced structural damage is not uniform. More severe damage immediately surrounding Cm$^{3+}$ ions was evident in FLN spectra as the excitation energies were moved further away from the center of the inhomogeneous line profile. In this case, the RFLN spectrum showed no sharp satellite lines but only a broad wing on each side of the resonant line. This is the behavior observed in RFLN spectra of $^{248}$Cm$^{3+}$ in a ZBLAN glass [8].

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 to 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.

Acknowledgments

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Fig. 1  Fluorescence emission spectra of Cm$^{3+}$:YPO$_4$ at 4 K for the laser excitation energy, $\lambda_{\text{ex}}$, noted. The excitation was to a) the top doublet, b) the second doublet, and c) the lowest (resonant) doublet of the $^6\text{D}_{7/2}$ excited state. Spectrum c) is plotted in a different scale from 16555 cm$^{-1}$ to 16588 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 in two sides. The residual curve for the fitting is shown at the bottom of c).
a
\[ \lambda_{\text{ex}} = 17170 \text{ cm}^{-1} \]

b
\[ \lambda_{\text{ex}} = 16625 \text{ cm}^{-1} \]

c
\[ \lambda_{\text{ex}} = 16571.3 \text{ cm}^{-1} \]