Journal of Alloys and Compounds, 213/214 (1994) 207–211
JALCOM 4033

Linear and non-linear spectroscopy of tetravalent actinide ions in CeF_4

G.K. Liu, G. Jursich*, J. Huang**, James V. Beitz and C.W. Williams
Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 (USA)

Abstract

This paper reports laser spectroscopy studies on the tetravalent actinide ions Bk^{4+} and Cf^{4+} doped into CeF_4. Fluorescence line narrowing (FLN) and spectral hole burning were applied to unravel the complex 5f state spectra that arise from inhomogeneous line broadening and the presence of two intrinsic metal ion sites. When a persistent spectral hole was burned in an inhomogeneously broadened zero phonon line of 1 at.% Cf^{4+} in CeF_4, satellite spectral holes were also observed in other inhomogeneously broadened lines of Cf^{4+}. In the FLN spectra of 0.1 at.% Bk^{4+} in CeF_4, a linear relationship was observed between the excitation-laser photon energy and the energies of the Bk^{4+} emission lines. These experimental results can be understood in terms of one limit of a general model of inhomogeneous broadening, namely the limit in which there is a one-to-one correspondence between the optical transition energy and local structure in a disordered system.

1. Introduction

Because the unfilled 4f electron shell is screened from the crystal field by the outer 5s and 5p electrons, the f–f electron transitions of lanthanide ions in solids are sharp and give rise to characteristic optical spectra. By exploiting non-linear methods, such as spectral hole burning (SHB), fluorescence line narrowing (FLN) and time-domain transient spectroscopic techniques, it is possible to eliminate the effect of strain-induced inhomogeneous broadening, and provide a spectral resolution of megahertz in optical spectroscopy [1]. This has stimulated many studies on fundamental lanthanide ion properties, including energy transfer, optical dephasing, hyperfine and superhyperfine interactions, and the effects of fluctuating local environments.

The 5f electrons of actinide ions have similar spectroscopic and dynamic properties to the 4f electrons in lanthanide ions. Laser spectroscopic studies of actinide ions in solids [2–5] are providing new information that was not accessible using conventional light sources. Because of the greater radial extent of 5f electron wave functions, with respect to those of the shielding 6s and 6p shells, the coupling of actinide 5f electrons to the ligand field in solid phases is expected to be stronger than that found for 4f electrons in comparable lanthanide systems. Consequently, laser spectroscopy work on actinides provides unique opportunities for the study of ion–environment interactions.

The FLN and SHB techniques are particularly useful for investigating the nature of inhomogeneous line broadening. In a disordered system, such as a doped crystal, individual dopant ions typically have different transition energies within the inhomogeneously broadened line of a given electronic transition, because of inhomogeneity in the local environment. It may happen that ions of different local environments are accidentally degenerate (*i.e.* absorb at the same wavelength) for a given optical transition. The probability of such accidental degeneracy persisting over a range of optical transitions is extremely small, particularly if the transitions involve crystal field levels arising from different free ion states.

We use the term correlation to denote the observation of a linear relationship between the laser excitation wavelength and the wavelength of fluorescence-line-narrowed optical transitions. FLN – and related SHB studies – of such energy correlations have been reported for a number of systems [6–8]. Both correlated and uncorrelated inhomogeneous broadening have been proposed to explain the experimental observations. Recently, Laird and Skinner [9] developed a general statistical theory to describe the microscopic nature of inhomogeneous broadening in a disordered system. We have extended their model to facilitate comparison with experimental observations. Furthermore, we recently

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*Present address: American Air Liquide, Chicago Research Center, 5230 S. East Avenue, Countryside, IL 60525, USA.

**Present address: Department of Physics and Astronomy, University of Wisconsin at Eau Claire, Eau Claire, WI 54702, USA.

SSDI 0925-8388(94)04033-Z

used the extended model in a detailed analysis of the excitation line narrowing spectra of Cf^{4+} doped into CeF_4 [5]. Based on the 5f electron states investigated, we observed some correlation in studies within inhomogeneously line-broadened transitions in this system.

Persistent SHB in actinide compounds was first observed in Cm^{4+} doped into CeF_4 [2], based on photo-induced distorted site ions. In this mechanism, non-radiative relaxation of excited Cm^{4+} results in changes in the photo-excited ion's local environment, as evidenced by a change in the ion's 5f state energy level structure. In the present work, we have carried out SHB studies on Cf^{4+} in CeF_4, and these support the theoretical analysis we reported previously [5]. In addition, we report measurements and analysis of FLN spectra of Bk^{4+} in CeF_4.

2. Experimental details

Samples were prepared by coprecipitation of trivalent actinide ions and Ce^{3+} as fluorides from aqueous solutions. The precipitate was heated in HF gas to generate anhydrous trifluorides, and then in excess F_2 gas to produce the tetrafluoride phase of interest. The resulting powders were sealed off in fused silica tubes containing He gas, to ensure good thermal contact. The host material, *i.e.* CeF_4, is isostructural with UF_4 [10]. In these compounds, the metal ion sits on either of two sites – one of C_2 symmetry and the other of C_1 symmetry. There are 12 metal ion sites in one unit cell; eight metal ion sites are of C_1 symmetry and four are of C_2 symmetry. Each metal ion is surrounded by eight fluorine ions arranged in a slightly distorted antiprism configuration. Substitution for Ce^{4+} places the actinide ions on sites of C_1 or C_2 symmetry and non-equivalent local environments. Consequently, differences in the local environment and energy level structure are expected for the 4+ actinide ions on the two crystallographically distinct sites. The isotopes used to prepare the doped samples were ^{249}Bk and ^{249}Cf.

The excitation source was a pulsed, tunable dye laser, equipped with a pressure-scanned etalon and grating, pumped by a *Q*-switched Nd:YAG laser. The bandwidth of the dye laser was 0.03 cm^{-1} with an etalon in the dye laser oscillator cavity, and 0.4 cm^{-1} without an etalon in the cavity. The laser pulse duration was approximately 5 ns and the pulse rate was 10 Hz. Fluorescence from the sample in a variable temperature cryostat was selected using long-pass filters and a 1 m monochromator, and detected using a cooled photomultiplier. Boxcar detectors connected to a computer were used to acquire emission and excitation spectra, which were normalized to the dye laser energy using a pyroelectric detector. The optogalvanic effect and an etalon fringe pattern were used to calibrate the excitation spectra and to measure the laser bandwidth. The emission spectrum of a neon lamp was recorded to calibrate the actinide fluorescence spectra.

3. Results and discussion

3.1. FLN spectra of Bk^{4+} in CeF_4

We have studied two emitting states of 0.1 at.% Bk^{4+} in CeF_4. The 16 375 cm^{-1} emitting state corresponds to the lowest energy component of $^6D_{7/2}$, *i.e.* the first excited $J=7/2$ multiplet; the state at 20 360 cm^{-1} corresponds to the lowest energy component of $^6P_{5/2}$, *i.e.* the first excited $J=5/2$ multiplet. Our FLN measurements centered on the fluorescence lines arising from the 16 375 cm^{-1} emitting state to the four components of the $^8S_{7/2}$ ground multiplet. The observed line shape and center positions in these fluorescence spectra were functions of the excitation laser wavelength. The widths of the fluorescence line from the two emitting states were 8–12 cm^{-1} when using laser excitation energies above 20 360 cm^{-1} (*i.e.* in spectral regions dominated by vibronic transitions). When excitation was into the zero phonon states of the $J=5/2$ and 7/2 multiplets, the fluorescence lines became much narrower and the line center positions shifted with changes in the excitation laser wavelength. This effect had been observed previously in this system [11] but was not understood in detail.

Figure 1 shows the non-resonant fluorescence line narrowing spectrum of Bk^{4+} on the C_1 site. The assignment of the site-selective spectra was made with

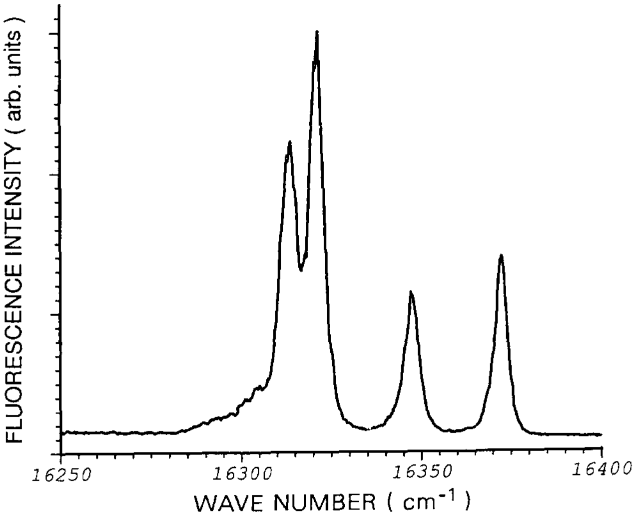

Fig. 1. Non-resonant fluorescence line narrowing spectrum of 0.1% Bk^{4+} ions in CeF_4 at 4.2 K. The laser excitation was to the $J=5/2$ excited state at 20 359 cm^{-1}. The four lines represent the transitions from the $J=7/2$ emitting state to the crystal field levels of the ground multiplet.

the assumption that the difference in excitation intensities is consistent with the different numbers of the two sites in each unit cell. The $J=7/2$ spectrum was recorded using 20 359 cm^{-1} excitation. The four lines in the spectrum are transitions from the lowest component of the $J=7/2$ emitting state to the four crystal field levels of the $J=7/2$ ground multiplet. The observed line widths (about 4.5 cm^{-1}) are limited by the monochromator resolution.

Resonant FLN spectra were obtained for Bk^{4+} ions on both C_1 and C_2 sites. The relationship between the excitation energy and the emission energies was obtained by scanning the laser from -27 to $+22$ cm^{-1} with respect to the center of the 16 367 cm^{-1} Bk^{4+} absorption line. The Bk^{4+} fluorescence emission spectrum was recorded at each excitation wavelength. As shown in Fig. 2, a linear relationship was observed between the laser excitation energy offset ΔE from line center and the corresponding shift ΔF in line center position of each of the four Bk^{4+} emission lines. The full squares in Fig. 2 correspond to the resonant FLN line, while the full lines are linear least-squares fits to the experimental data. Table 1 lists the slopes for the resonant FLN line data and for the three non-resonant transitions corresponding to higher-lying components of the $J=7/2$ ground state.

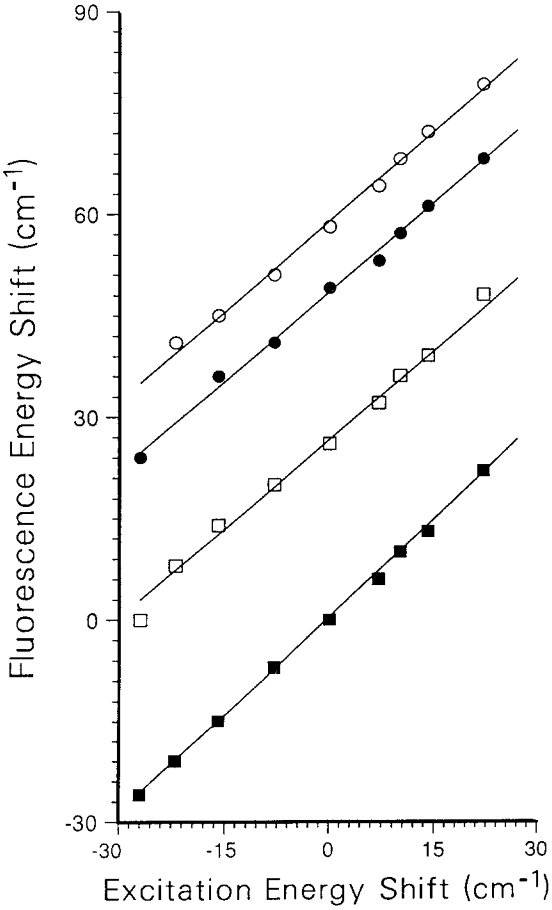

Fig. 2. Relationship between excitation energy and emission energy of the $^8S_{7/2}$ and $^6D_{7/2}$ transitions. The excitation energy offset $\Delta E=0$ corresponds to the center of the inhomogeneous line at 16 367 cm^{-1}. A value of $\Delta E=0$ corresponds to emission energies of 16 367 cm^{-1} (■), 16 393 cm^{-1} (□), 16 416 cm^{-1} (●) and 16 425 cm^{-1+} (○). All the data were recorded at 4.2 K.

Based on our previous analysis [5], the data for the resonant FLN line alone do not provide sufficient information to determine the nature of the inhomogeneous broadening. However, the linear relationship between ΔE and ΔF for each of the three non-resonant FLN bands is definitive evidence of a correlation between the energy states from which the emission occurred. The differing slopes provide evidence as to the variation in the energy distribution of Bk^{4+} ion in different crystal field states.

3.2. SHB spectrum of Cf^{4+} in CeF_4

SHB was observed below 60 K for Cf^{4+} on both of the C_1 and C_2 sites in 1 at.% Cf^{4+} in CeF_4. As was the case in our previous study of SHB in 5f transitions of Cm^{4+} in CeF_4 [2], the holes burned in zero phonon lines of Cf^{4+} persisted for hours. The efficiency of the hole burning process and the width of the resulting holes were temperature dependent.

The hole burning spectrum of Cf^{4+} on the C_2 site at 12 K is shown in Fig. 3. The broken curve is the inhomogeneously broadened excitation profile of the $^7F_6$-to-$^5G_4$ transition before hole burning. The hole was burned during 3 min of laser irradiation (1800 laser pulses) at a peak intensity of 80 MW cm^{-2} per pulse at 20 293 cm^{-1}, *i.e.* the center of the inhomogeneously broadened line for the lowest component in the $^5G_6$ multiplet. The resulting deep hole was probed by reducing the laser power and scanning the laser wavelength. In addition to the primary hole at 20 293 cm^{-1}, satellite spectral holes were observed in higher-lying bands (see Fig. 3). When the laser was tuned to burn a hole in a higher-lying component of the $^5G_4$ state, a satellite hole was then observed at 20 293 cm^{-1}.

TABLE 1. Energies of the crystal field components of the $^8S_{7/2}$ ground state of the C_1 site Bk^{4+} in CeF_4 and $\Delta F/\Delta E$, *i.e.* the observed dependence of shifts in the line center position of a $^6D_{7/2}$-to-$^8S_{7/2}$ transition on shifts in laser excitation energy measured with respect to the line center of the emitting level of $^6D_{7/2}$ (uncertainties shown in parentheses)

$^8S_{7/2}$ component (cm^{-1})	$\Delta F/\Delta E$
0	0.97(0.05)
26(1)	0.87(0.05)
49(1)	0.89(0.05)
58(1)	0.89(0.05)

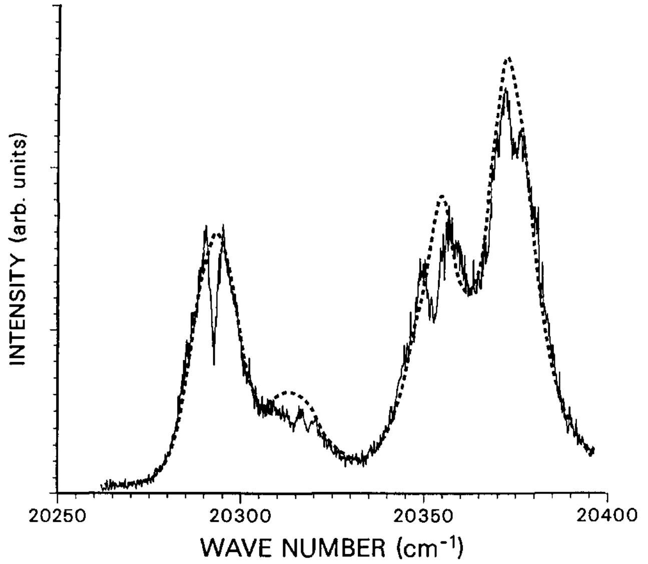

Fig. 3. SHB spectrum of 1% Cf^{4+} in CeF_4 at 12 K obtained at 20 293 cm^{-1} excitation. The spectrum monitored using 15 596 cm^{-1} emission is for Cf^{4+} on the C_2 site. The broken curve shows the excitation profile without hole burning. The full curve shows the primary hole burned at 20 293 cm^{-1} and satellite holes at higher energies.

The presence of satellite holes in the SHB spectrum provides evidence of an energy correlation between different electronic states perturbed by structural disorder in this system. The ions that absorb the same energy (20 293 cm^{-1}) to the lowest state of the $^5G_6$ multiplet have the same transition energies as those for the investigated higher-lying components of the multiplet. This suggests that the energies between different states are correlated, since the probabilities of the accidental degeneracy for three or more states are extremely small. The satellite holes also provide evidence that the excitation spectrum is inhomogeneously broadened for the transitions from the ground state to the crystal field energy levels above the lowest component of the excited $^5G_4$ multiplet.

This result is completely in agreement with the excitation line narrowing (ELN) spectra of this system [5]. Broad bands above 20 400 cm^{-1} were observed and are attributed to a mixture of purely electronic and vibronic transitions. Under our experimental conditions, no spectral holes could be burned in the bands of the $^5G_4$ multiplet above 20 400 cm^{-1}.

The hole burning effect in this system is attributed to photo-induced site distortion. This non-photochemical mechanism is discussed in ref. 2. After initial excitation into the $^5G_4$ state, a Cf^{4+} ion relaxes radiatively and non-radiatively. Non-radiative relaxation can transfer a portion of the excitation energy into lattice potential energy, apparently through vibronic coupling. When this occurs, a rearrangement of the local structure may follow, before the ion finally relaxes into the ground state. The photo-induced site distortion in this system is stable at temperatures below 80 K but at higher temperatures is reversed by thermal activation.

An important aspect of SHB is the hole width. In principle, the width of the hole is twice the homogeneous line width for that transition, provided the bandwidth of the burning laser is much narrower than the hole [1]. At 4 K, the hole burned at 20 293 cm^{-1} was (0.8 ± 0.2) cm^{-1} wide when using a laser bandwidth of 0.03 cm^{-1}. Therefore, the homogeneous line width for this crystal field component of the $^7F_6$-to-$^5G_4$ transition is about 0.4 cm^{-1} at 4 K. The homogeneous line width became 0.7 cm^{-1} at 12 K. A hole was also burned for the $^7F_6$-to-$^5G_6$ transition at 15 597 cm^{-1}, while fluorescence from $^5G_6$-to-$^7F_5$ was monitored. The observed hole width was 2.5 cm^{-1} at 12 K. Because this hole was too broad to be probed using the dye laser in its narrow bandwidth mode (etalon plus pressure scanning), the dye laser without an etalon was used, which resulted in a probe laser bandwidth of 0.4 cm^{-1}. Thus, the line width for the $^5G_6$-to-$^7F_5$ transition was obtained from the convolution of the homogeneous line width and the laser bandwidth. This gave a value of 0.85 cm^{-1} for the homogeneous line width, assuming that the line shapes are Lorentzian. Since the burning–probing cycle took 5–8 min in our experiments, any spectral diffusion resulting from fluctuations in the local environment on that time-scale contributes to the observed hole width.

4. Conclusions

The FLN and SHB methods have been used to investigate the energy level structure of two actinide systems in which optical transitions are very broad because of inhomogeneous broadening. The results have provided evidence of an energy correlation between the different electronic states of Bk^{4+} in CeF_4 and Cf^{4+} in CeF_4. The observation of primary and satellite spectral holes in different 5f electron transitions provides evidence that ions which have the same transition energy between two states have identical transition energies to the other investigated states. Our FLN experiments on selected Bk^{4+} bands showed that the shift in the fluorescence line center position from a lower-lying emitting state is linearly related to the shift in laser wavelength that populated a higher-lying state or the emitting state directly. This one-to-one correspondence between the energy levels of different states provides evidence, in agreement with one limit of the theory of Laird and Skinner [9], that transplutonium ions excited by a narrow band laser have similar local environments in these disordered materials.

The FLN and SHB techniques applied in the present work are particularly useful for probing structural defects of a disordered system in which optical transitions are inhomogeneously broadened. For a system in which the inhomogeneous line broadening is correlated, the FLN method provides a direct measure of the energy level shift of impurity ions as a function of defect perturbation, thus enabling the variation in local structure to be probed.

Acknowledgments

This work was performed under the auspices of the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-ENG-38. The Bk and Cf isotopes used in this work were supplied by the transplutonium element production facilities at Oak Ridge National Laboratory.

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