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Laser Induced Fluorescence of $^{249}Bk^{4+}$ in CeF_4*

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We report the first observation of fluorescence from the $5f^7$ ion Bk^{4+}. Fluorescence measurements were used to establish the total ground state splitting of this ion and to probe the higher lying electronic states in the Bk^{4+} $5f^7$ configuration. In CeF_4, which is isostructural with the actinide tetrafluorides [1], the metal atom is 8-fold coordinate with the adjacent fluorine atoms arranged to give a distorted square antiprismatic structure. There are two distinct low-symmetry actinide sites within the unit cell in this class of compounds. Non-equivalent sites have the potential of making spectral interpretation difficult owing to the multiplicity of spectral lines that can arise. The crystal-field analysis is also complex because of the low symmetry involved.

Two Bk^{4+} fluorescence bands were detected. One band observed at 16 375 cm^{-1} is assigned as a transition from an excited $J = 7/2$ state to the ground $J = 7/2$ state. The other band observed at 20 360 cm^{-1} is assigned to a transition from a $J = 5/2$ state to the ground state. From laser excitation spectra taken with sample temperature near 4 K, a rather simple $5f^7$ energy level structure has been deduced which is consistent with the assumption of a single average D_{4d} site symmetry.

In the Russell–Saunders coupling scheme, the lowest free-ion level of the $5f^7$ configuration is formally $^8S_{7/2}$ and thus remains degenerate in any crystal field. However in the present case, there is sufficient mixing of higher lying states with other L–S character into the ground state to substantially reduce the extent of the ^8S-character. From the fluorescence spectra recorded in this study, the total ground state crystal-field splitting of Bk^{4+}:CeF_4 is determined to be 58 cm^{-1}. This is much larger than that observed in the isoelectronic actinide Cm^{3+} in other halide crystal hosts [2, 3].

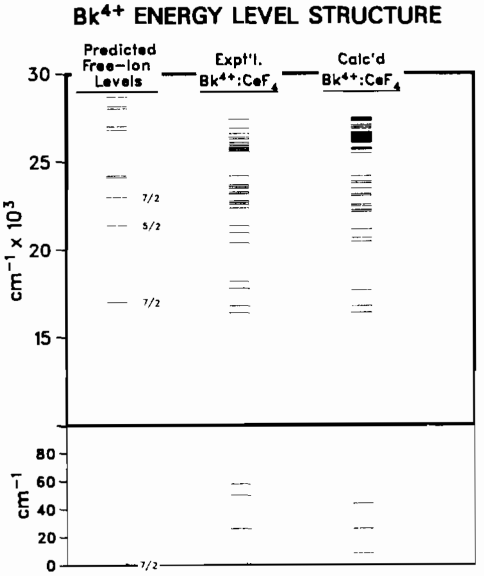
Experimental

A tunable dye laser (NRG PTL-2000) pumped by a N_2 laser (Molectron UV-14) was used as the excitation source. The output of the dye laser consisted of ~8 nsec pulses at a 20 Hz repetition rate with a pulse energy varying from 1–40 μJ depending on the particular dye used.

The sample consisted of polycrystalline CeF_4 doped with a 1% mol fraction of Bk^{4+}. A variable temperature dewar (Oxford CF204) was used to maintain sample temperature ~4–296 K. Excitation spectra were recorded by scanning the dye laser while monitoring the intensity of the 16 375 cm^{-1} emission band. Fluorescence spectra were recorded by tuning the dye laser to specific absorption peak and dispersing the fluorescence through a 1 m monochromator (Engis Model 1000).

Results and Discussion

Figure 1 presents an energy level diagram which summarizes observed peak positions in the excitation and fluorescence spectra taken with the sample near 4 K, together with a preliminary D_{4d} crystal-field fit to the data. Some weaker broad peaks which are attributed to phonon sidebands are not shown. The vibronic nature of some of these bands was demonstrated by comparing excitation and fluorescence spectra. Excitation spectra taken at room temperature agree well with the room temperature absorp-



Crystal Field Calculation: D_{4d} site symmetry

Free Ion		Crystal Field
$F^2 = 56088$	$\alpha = 24.7$	$B_{20} = -107$
$F^4 = 46713$	$\beta = -660$	$B_{40} = -6898$
$F^6 = 32203$	$\gamma = 1256$	$B_{60} = 2084$
	$\zeta = 3251$	

Fig. 1. Energy level diagram of Bk^{4+}. All parameters listed are in units of cm^{-1}.

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tion spectrum of BkF_4 [4] provided one subtracts out the large sloping baseline.

The 20 360 cm^{-1} fluorescence band consists of three resolved spectral lines each with a linewidth of ~15 cm^{-1}. The total lifetime of each component is ~0.5 μsec. In a 4–75 K temperature range this fluorescence appears the same, except for a slight broadening of peaks and a shorter lifetime. Since the 5 K excitation spectrum of this region shows only one peak, the three observed spectral lines seen in this fluorescence band result from the splitting of the ground state rather than from more than one fluorescing level. From the peak positions of the fluorescence lines, the lowest three energy levels are deduced as 0, 26 ± 2, 55 ± 2 cm^{-1}. As additional confirmation of this ground state splitting, excitation spectra in the 20 360 cm^{-1} region were taken in a temperature range of 4–77 K, and at higher temperatures two additional lines appeared at the lower energy side of the 20 360 cm^{-1} peak. These additional 'hot' bands result from thermal population of higher lying components of the ground state. Energy differences of these 'hot' bands agree well with those observed in this fluorescence band.

The 16 375 cm^{-1} fluorescence band is more complex to analyse. Although the total lifetime of each component is ~250 μsec, the relative intensity and halfwidth of each component depends on which transition is being excited. The energy differences between the three peaks at the high energy side of this band match those on the 20 360 cm^{-1} fluorescence band and are the result of the ground state splitting. Additional structure at the lower energy end of this band is believed to be due to Bk^{4+} ions in an altered site environment. In the excitation spectrum, this additional structure shows up as a shoulder on the single peak observed at 16 375 cm^{-1}.

The 16 375 cm^{-1} fluorescence band appears with the narrowest linewidths when it is excited directly rather than exciting a higher lying state and relying on relaxation (primarily non-radiative decay) to populate the fluorescing level. In this case the 16 375 cm^{-1} fluorescence band appears as four lines with the peak position of the highest energy component being equal to the excitation energy 16 375 ± 2 cm^{-1}, and the remaining lines centered at 16 349, 16 325 and 16 318 cm^{-1}. From the energy differences of these lines, the ground state splitting is determined to be 0, 27, 51 and 58 cm^{-1} with an uncertainty of ~2 cm^{-1}. Taking linewidth considerations into account, this ground state splitting result is consistent with that observed in the 20 360 cm^{-1} fluorescence band.

To summarize, fluorescence from Bk^{4+}:CeF_4 has been observed for the first time and is used to probe f electronic structure of this $5f^7$ ion and the complete ground state splitting has been determined.

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