ANL/PP--70969

DE92 003547

Energy Up-Conversion and Trapping: Dynamics of 5f States of Bk^{4+} in CeF_4

G. K. Liu and James V. Beitz

Argonne National Laboratory, Argonne, IL 60439, USA

Energy transfer mechanisms of excited 5f states of Bk^{4+} (0.05 atom%) in CeF_4 containing circa 0.95 atom% Cf^{4+} have been investigated at 4 K. The observed anti-Stokes fluorescence arises from both up-conversion and two-photon excitation. Nonexponential decays of Stokes fluorescence are ascribed to both excitation-excitation annihilation and site-dependent trapping processes and, therefore, are not describable by the Inokuti-Hirayama or exciton annihilation models. Based on the Forster-Dexter energy transfer theory, a new model is developed to fit the observed fluorescence decay data.

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Most spectroscopic studies of actinide (5f) ions have focused on determination of electronic energy level structure. The dynamic nature of 5f states is largely unexplored. Based on the greater radial extent of 5f electron wave functions, with respect to those of the shielding 6s and 6p shells, the mobility of excited 5f states of actinide ions in compounds is expected to be intermediate between that of excited 4f states of lanthanide ions and 3d states of transition-metal ions.[1,2] Excited-state dynamics and energy transfer of transuranium ion Cm^{4+} in CeF_4 have been reported recently.[3] Energy transfer among the excited Cm^{4+} ions was evidenced by nonexponential fluorescence decays which depended on excitation intensity and frequency. In addition to up conversion, cross relaxation and excitation transfer to traps were also shown to be important in that system. The derived energy-transfer rates for 5f states of Cm^{4+} via cross relaxation and up conversion were two orders of magnitude higher, at equal ion densities, than those of trivalent lanthanide-ion 4f states and approach those of transition-metal ion 3d states.

In this Letter, we report the first study on dynamics of the excited 5f states of the transuranium ion Bk^{4+}, using CeF_4 as a host. The sample studied was one in which two Bk^{4+} fluorescing states, one at 16375 cm^{-1} and the other at 20360 cm^{-1}, previously had been observed in emission terminating on components of the $^8S_{7/2}$ ground state[4]. The 16375 cm^{-1} emitting state corresponds to the lowest energy component of the first exited $J=7/2$ multiplet while the 20360 cm^{-1} state is the lowest energy component of the first excited $J=5/2$ multiplet.[4] The $^{249}Bk^{4+}$:CeF_4 sample, when originally prepared, contained 1 atom% Bk (i.e., $Bk_{0.01}Ce_{0.99}F_4$), but, due to beta decay of ^{249}Bk, the Bk content was 0.05 atom% at the time of the present work (with 0.95 atom% of decay daughter ^{249}Cf).

Lifetime measurements were carried out using laser-induced fluorescence for the two emitting states of Bk^{4+}. Following excitation at 28195 cm^{-1}, the observed decay of the emitting state at 20360 cm^{-1} was predominantly exponential with a lifetime of 0.7 μs [see Fig. 1(b)]. The exponential character of the decay of 20360 cm^{-1} state provides evidence that radiative emission of photons and nonradiative emission of phonons are the predominate deexcitation processes influencing its dynamics. In contrast, the decay of 16375 cm^{-1} state was always nonexponential at short times following pulsed (5 ns) laser excitation. At long times, the decay of the 16375 cm^{-1} state was found to be exponential with a lifetime of 550 μs.

Emission from the 20360 cm^{-1} state was also observed when the laser wavelength was tuned from 16375 to 17775 cm^{-1} to pump Bk^{4+} ions into the components of the first excited (J=7/2) multiplet [see Fig. 1(a)]. The observed anti-Stokes fluorescence exhibited very different dynamics than that observed from the same emitting state when using 28195 cm^{-1} excitation. The time evolution of the anti-Stokes fluorescence exhibited a fast initial decay followed by a nonexponential slower decay on a longer time scale. The dominant fast initial decay appears exponential with a decay time of circa 0.7 μs, similar to that observed following excitation at 28195 cm^{-1}.

A number of processes can lead to the observed anti-Stokes fluorescence: (a) step-wise excitation and direct two-photon absorption,[3,5] (b) up-conversion due to energy transfer among the excited Bk^{4+} ions,[5-8] and (c) cooperative emission or up-conversion of coupled ion pairs.[8-10] Process (c) can be ruled out because of the lack of additional spectral lines due to ion pairs. As monitored by anti-Stokes fluorescence, the excitation profile of the 17775 cm^{-1} band (the highest component of the first excited multiplet) is identical to that found when monitoring Stokes fluorescence from the 16375 cm^{-1} emitting state. Only process (b) provides a rationale for the observed long time nonexponential decay of the 20360 cm^{-1} state following excitation of Bk^{4+} bands in the range from 16375 to 17775 cm^{-1}. An up-conversion process involving the long-lived 16375 cm^{-1} state evidently feeds the 20360 cm^{-1} state, resulting in anti-Stokes fluorescence whose dynamics thereby becomes coupled to that of the 16375 cm^{-1} state. The observed rise time of emission from the 20360 cm^{-1} state, using 17775 cm^{-1} or 28195 cm^{-1} excitation, is comparable to the laser pulse width which provides evidence that process (a) feeds the 20360 cm^{-1} state only during or shortly after the laser pulse and so has no effect on the longer time, nonexponential, decay of 20360 cm^{-1} state.[3,11] Over the range of excitation wavelengths investigated, the nonexponential decay of the 20360 cm^{-1} state occurs only on excitation of components of the lower lying, first excited (J=7/2) multiplet.

We attribute the observed anti-Stokes emission from the 20360 cm^{-1} state to contributions from processes (a) and (b), i.e. two-photon excitation followed by rapid nonradiative decay to the 20360 cm^{-1} state and energy transfer involving the 16375 cm^{-1} state of Bk^{4+} that results in up-conversion over a much longer time scale [see Fig. 1(c)]. Identification of the processes giving rise to anti-Stokes fluorescence is possible due, in part, to the large difference in lifetimes of the 16375 cm^{-1} and 20360 cm^{-1} emitting states of Bk^{4+} in the absence of up-conversion. The high density of 5f energy states of Bk^{4+} from 30000 to 40000 cm^{-1} suggests that two photon excitation and up-conversion processes might be efficient.[2-4]

The importance of up-conversion processes in this system has also been confirmed by observation of excitation-intensity dependent Stokes fluorescence decays using 17775 cm^{-1} excitation. The initial decay rate of the 16375 cm^{-1} state is higher using 28 MW/cm^2 excitation intensity [see Fig. 2(a)] than at 1 MW/cm^2 excitation intensity, an intensity at which the anti-Stokes fluorescence was not observable [see Fig. 2(b)]. These observations provide evidence for an excitation-excitation annihilation process that quenches the Stokes fluorescence at short times. At long times, the Stokes decays at the two excitation intensities exhibited the same decay behavior and approached the same constant exponential rate, indicating that the ions left in the excited state effectively have become isolated from each other. The solid curves in Fig. 2 are from theoretical modeling which will be discussed later.

When the excitation intensity was reduced low enough (such as 1 MW/cm^2) that anti-Stokes fluorescence was no longer observable, the fluorescence decay of the 16375 cm^{-1} state was still nonexponential. This provides evidence that, in addition to up-conversion, energy transfer occurs through other channels such as trapping and cross relaxation while the acceptor is initially in its ground state.[3] Cross relaxation and excitation transfer to traps can also cause nonexponential decays, but they are independent of excited donor ion density. In our system, cross relaxation can be ruled out because of the lack of intermediate energy levels. Substituted for Ce^{4+} ions, Bk^{4+} ions exist on two crystallographically nonequivalent sites[3,4]. The Bk^{4+} ions on one site may act as traps for the other site. Other species that might act as traps include Cf^{4+} and radiation-damage sites. Cf^{4+} is expected[2] to have 5f state energies (including vibronic states) which overlap the 16375 cm^{-1} emitting state of Bk^{4+}.

Trapping, in the sense of irreversible energy transfer from Bk^{4+} to Cf^{4+}, has been observed directly in our work. Emission from Cf^{4+} at 11543 cm^{-1} is found after excitation of the 17775 cm^{-1} state of Bk^{4+}. The observed Cf^{4+} fluorescence corresponds to emission from a Cf^{4+} level at 15595 cm^{-1} to the 4052 cm^{-1} component of the first excited multiplet of Cf^{4+}. Overlap of absorption bands of Cf^{4+} and the 16375 cm^{-1} emitting state of Bk^{4+} provides a resonant excitation transfer pathway. Excitation at 17460 cm^{-1} was used to directly excite Cf^{4+} and the resulting lifetime of the 15595 cm^{-1} state of Cf^{4+} was found to be about 10 μs [see Fig 3(b)] which is much shorter than the 550 μs lifetime of the 16375 cm^{-1} state of Bk^{4+}. Excitation at 17775 cm^{-1} predominantly excites Bk^{4+}, but also results in emission from Cf^{4+} on a time scale long compared to 10 μs [see Fig. 3(a)]. The decay of Cf^{4+} emission following 17775 cm^{-1} excitation of Bk^{4+} is comparable to that of the 16375 cm^{-1} state of Bk^{4+} [compare Fig. 2 to Fig. 3(a)]. The observed rise time of the energy transfer-induced fluorescence of Cf^{4+} was less than 100 ns. Both decays in Fig. 3 were monitored at 11543 cm^{-1}. The solid line through the data in curve (a) of Fig. 3 is a calculated fit to the experimental data using an energy transfer model discussed later.

Without consideration of excited-ion interactions that lead to up-conversion, incoherent energy transfer theories for disordered systems have been well-established since the fundamental work of Forster[12] and Dexter.[13] To interpret the dynamics of intrinsic ion fluorescence and the time evolution of emission from acceptors, Huber [14,15] and others [16] have developed theoretical models concerning energy transfer in various circumstances. When back transfer is negligible (i.e. trapping or cross relaxation are dominant), the Inokuti-Hirayama model[16] gives an exact description of the dynamics of donor fluorescence and is appropriate to fit our low-excitation intensity data. However, an exciton-exciton annihilation model is usually used to describe up-conversion with the assumption that the energy transfer rate is not site-dependent for either exciton-exciton or exciton-trap transfer.[6,7] With these assumptions, description of excited-state dynamics becomes very simple. The rate equation for exciton density, n, is simply given by $dn/dt = -\beta n - \gamma n^2$, where the constant β is the reciprocal lifetime of the exciton plus the rate of energy transfer to traps, and the second-order term represents the loss of excitation via exciton-exciton annihilation. Parameter γ is called the ensemble-averaged annihilation coefficient. For lanthanide (4f) and actinide (5f) ions doped into insulating crystals, this description is not appropriate because excited f-states in such systems are highly localized. Consequently, energy transfer probability is site dependent, particularly in the presence of traps. In this case, both up-conversion and energy transfer to unexcited traps have to be taken into account.

It is obvious that analysis of fluorescence dynamics influenced by both up-conversion and trapping processes requires modification of existing energy transfer models. Based on the Forster-Dexter energy transfer theory, we have developed a model that combines the Inokuti-Hirayama model and exciton-exciton annihilation models. In our new model, back transfer is neglected and exciton-exciton annihilation is treated as an energy transfer process between two excited ions in single-ion states.

In most circumstances, the reverse of the up-conversion process is negligible, except that some up-converted ions may refill the original excited state via radiative or nonradiative relaxation. In our system, an up-converted Bk^{4+} ion rapidly undergoes nonradiative relaxation to the 20350 cm^{-1} state from which the inverse of up-conversion is energetically impossible. In the trapping processes assumed, and even for transfer among donor ions within the inhomogeneous band profile, back transfer is negligible at low temperatures. The time-dependent probability that the ith initially excited ion, P_i, remains excited at time t after the excitation pulse therefore can be calculated from the rate equation

$$dP_i/dt = -\beta_0 P_i - \sum_j \alpha_{ij} P_i - \sum_k{}' \gamma_{ik} P_k P_i \qquad (1)$$

where β_0 is the reciprocal lifetime of the excited state in the absence of energy transfer processes involving excitation-excitation annihilation or transfer to traps, j is an index over all trap sites, k is an index (excluding the ith ion) over all initially excited ions, and P_k is probability that the kth ion remains in the excited state at time t. The second term in Eq. (1) involves energy transfer from the ith initially excited ion to surrounding traps while the third term accounts for the energy transfer among initially excited ions that results in up-conversion. The coupling parameters α_{ij} and γ_{ik} depend on interaction matrix elements and ion-ion distances. Following Forster-Dexter energy transfer theory[12-14], the coupling parameters due to electric multipole-multipole interactions between two ions, separated by distances R_{ij} and R_{ik}, respectively, are

$$\begin{aligned} \alpha_{ij} &= (R_0 / R_{ij})^s \alpha_0 \\ \gamma_{ik} &= (R_0 / R_{ik})^s \gamma_0 \end{aligned} \qquad (2)$$

where R_0 is the nearest-neighbor separation, α_0 is transfer-to-trap rate for nearest neighbor traps, and γ_0 is the excitation-excitation annihilation rate for nearest-neighbor excited ion sites. The value of s is 6, 8, or 10 for electric dipole-dipole, dipole-quadrupole, or quadrupole-quadrupole interaction, respectively.

In general, the excitation probability of intrinsic ions is different from one intrinsic ion site to another intrinsic ion site due to a random distribution of traps or defects. The resulting coupled rate equations are not solvable until further approximations are made. Note that for up-conversion to occur, the pair of initially excited ion sites involved must remain excited. Therefore, in comparison with trapping processes, the effect of up-conversion is important only in short times when most initially excited ions are still excited. An approximation of $P_k = P_i$ for all k in the third term of Eq. (1) then can be made. After configurational averaging, which has been carried out by an integration with the approximation of electric dipole-dipole interaction which is efficient for Cm^{4+} in CeF_4,[3] we obtain a solution of Eq. (1) in the form of an expression for n(t), the excited ion density at time t,

$$n(t) = \frac{n(0)(\beta_0 + C_t\alpha_0)}{(\beta_0 + C_t\alpha_0 + C_e\gamma_0)\exp[\beta_0 t + C_t(\pi\alpha_0 t)^{1/2}] - C_e\gamma_0} \tag{3}$$

where n(0) is the initial excited ion density, C_t is the fraction of all metal ion sites which are trap sites and C_e is the fraction of sites which contain initially excited ions.

Equation (3) has been used to fit the decay data for the 16375 cm^{-1} state of Bk^{4+} by a nonlinear least squares method in which parameters n(0), β_0, α_0, and $C_e\gamma_0$ were freely varied while C_t was fixed. The fit value for β_0 is $1.85X10^3$ s^{-1}. When C_t is fixed at 0.01 (i.e., assuming ground state Bk^{4+} on the other crystallographic metal ion site and Cf^{4+} act as traps), α_0 is $3.2X10^7$ s^{-1} for both high (28 MW/cm^2) and low intensity (1 MW/cm^2) data as plotted in Fig. 2. The fit value for $C_e\gamma_o$ is $6X10^5$ s^{-1} for high intensity data. We estimate that C_e is about $1X10^{-4}$ which results in $6X10^9$ s^{-1} for γ_o. For low-excitation intensity data, the parameter $C_e\gamma_o$ becomes undetermined in the fitting. When $C_e\gamma_0$=0 is set, the fitting gives the same values for β_0 and α_0 as that from fitting high-intensity data. This is consistent with the basic assumptions in our model. Because of the absence of up-conversion at low excitation intensity, the Inokuti-Hirayama model [$C_e\gamma_0$=0 in Eg.(3)] is expected to fit the decay data. As shown in Fig. 2, the difference between the two decay curves is quite small, indicating that the first order process, transfer to traps and impurities, is dominant even at high excitation intensity. As discussed earlier, trapping may indeed be the dominant energy transfer mechanism in this system due to a comparatively high number density of Cf^{4+} ions and radiation damage sites. As shown in Fig. 3(a), Eq. (3) has been used to fit the Cf^{4+} fluorescence decay following excitation of Bk^{4+}. The fit values are $1.8X10^3$ s^{-1} for β_0 and $6X10^8$ s^{-1} for α_0 when $C_e\gamma_0=0$ and $C_t = 0.01$ are set.

Because of the differences in energy structure between Bk^{4+} and Cf^{4+} and the presence of two metal ion sites in CeF_4, separation of the contribution of trapping from the Cf^{4+} impurities and the Bk^{4+} on different sites should be possible in more detailed studies. Moreover, studies at higher Bk^{4+} concentration are needed to more accurately determine the excited ion-ion coupling strength as excitation-excitation annihilation becomes the predominant energy transfer pathway for intrinsic Bk^{4+} ions and may aid in studying trapping between Bk^{4+} ions on each of the two metal ion sites in the absence of Cf^{4+}.

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38. We thank W. T. Carnall and M. Xu for helpful discussions, C. W. Williams for preparing and characterizing the sample, and the transplutonium element production facilities at Oak Ridge National Laboratory for supplying the ^{249}Bk used in this work.

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FIG. 1. (a) observed anti-Stokes fluorescence decay of Bk^{4+} (0.05 atom%) in CeF$_4$ containing circa 0.95 atom% Cf^{4+} at 4 K. The emission was recorded at 20360 cm^{-1} following excitation at 17775 cm^{-1}. (b) predominantly exponential decay of the 20360 cm^{-1} state following excitation at 28195 cm^{-1}. (c) indication of anti-Stokes fluorescence resulting from up conversion, which is obtained by subtracting from (a) an (0.7 μs) exponential decay based on (b).

FIG. 2. Excitation-intensity dependence of the Stokes fluorescence decay of Bk^{4+} (0.05 atom%) in CeF$_4$ containing circa 0.95 atom% Cf^{4+} recorded at 4 K using 17775 cm^{-1} excitation. The decay data (every tenth data point plotted) for 16375 cm^{-1} fluorescence following 28 MW/cm^2 excitation (○) and less than 1 MW/cm^2 excitation (●) are shown. The solid curves result from fits to the data using Eq. (3) discussed in text.

FIG. 3. Fluorescence decays of the 15595 cm^{-1} state of Cf^{4+}, monitored at 11543 cm^{-1}, following excitation at 17460 cm^{-1} (●), which directly excites an f-state of Cf^{4+}, and at 17775 cm^{-1} (○), which primarily excites an f-state of Bk^{4+}. The longer-lived emission from Cf^{4+} following excitation of Bk^{4+} is attributed to energy transfer from the 16375 cm^{-1} state of Bk^{4+} that results in population of the 15595 cm^{-1} state of Cf^{4+}. The solid curve is a fit of the Cf^{4+} decay data involving energy transfer from Bk^{4+} using Eq. (3) presented in the text.

Fig. 1

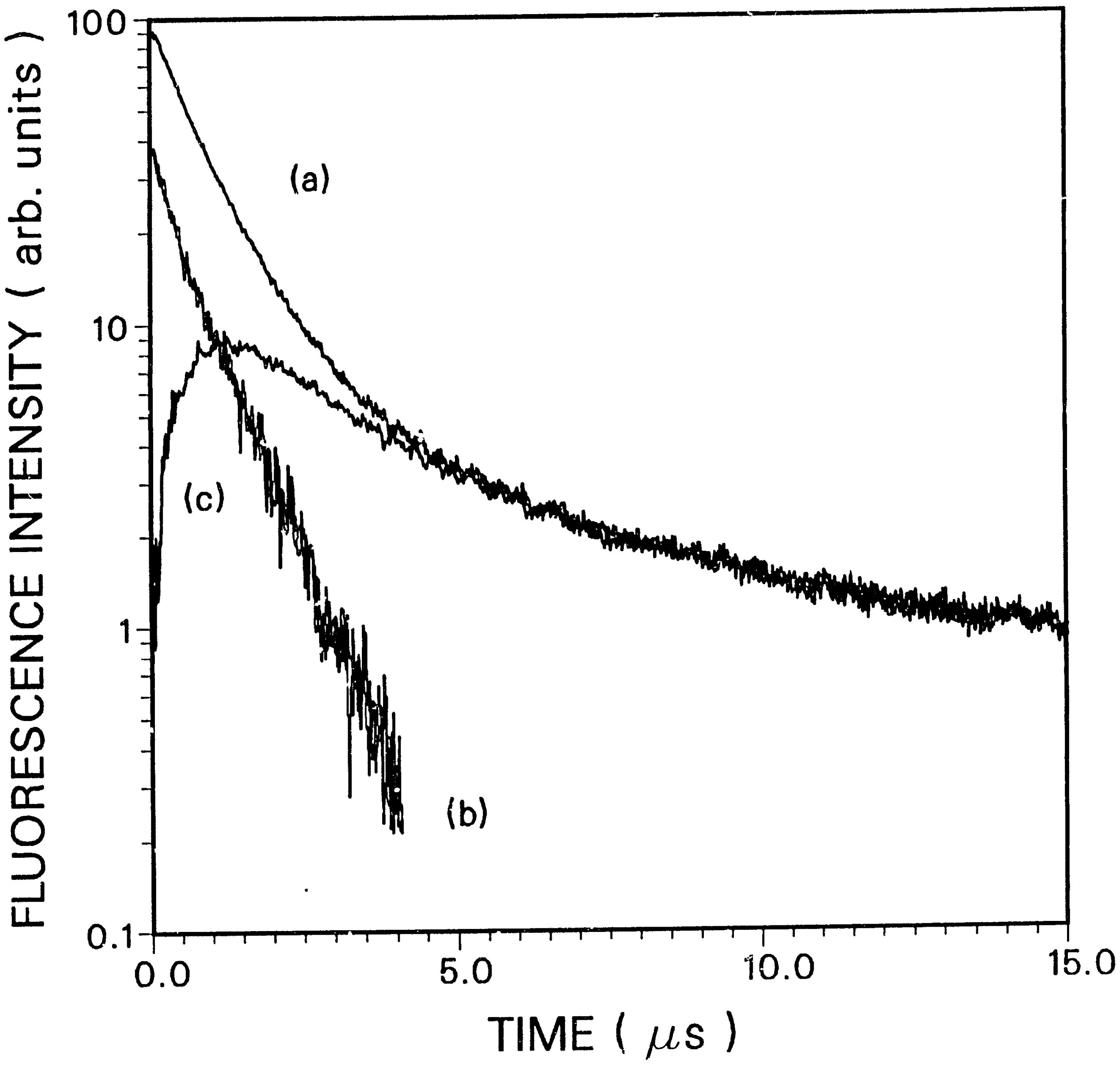
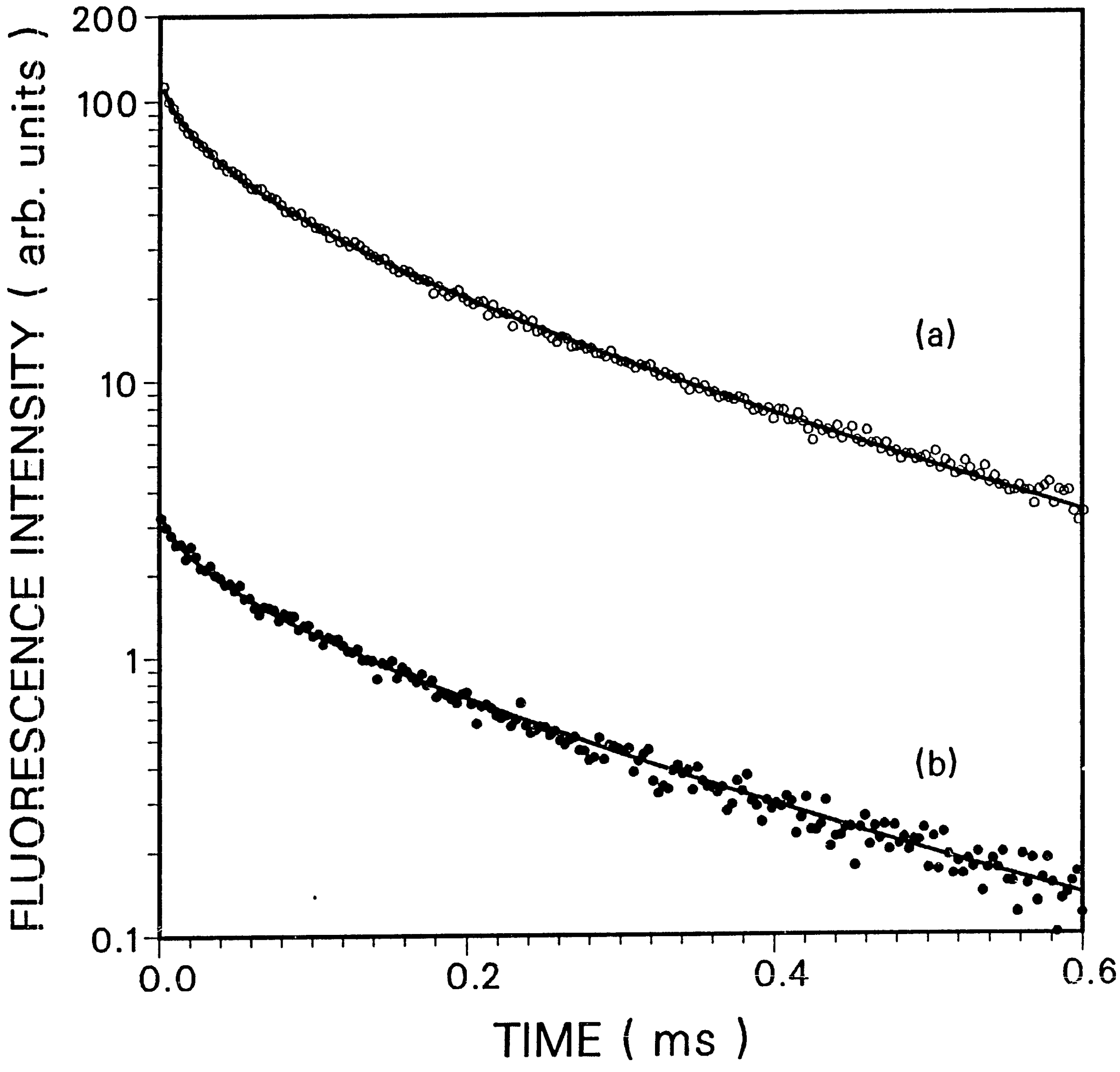

(a)
(b)
(c)
100
10
1
0.1
0.0
5.0
10.0
15.0
FLUORESCENCE INTENSITY (arb. units)
TIME (μs)

Fig. 2


FLUORESCENCE INTENSITY (arb. units)
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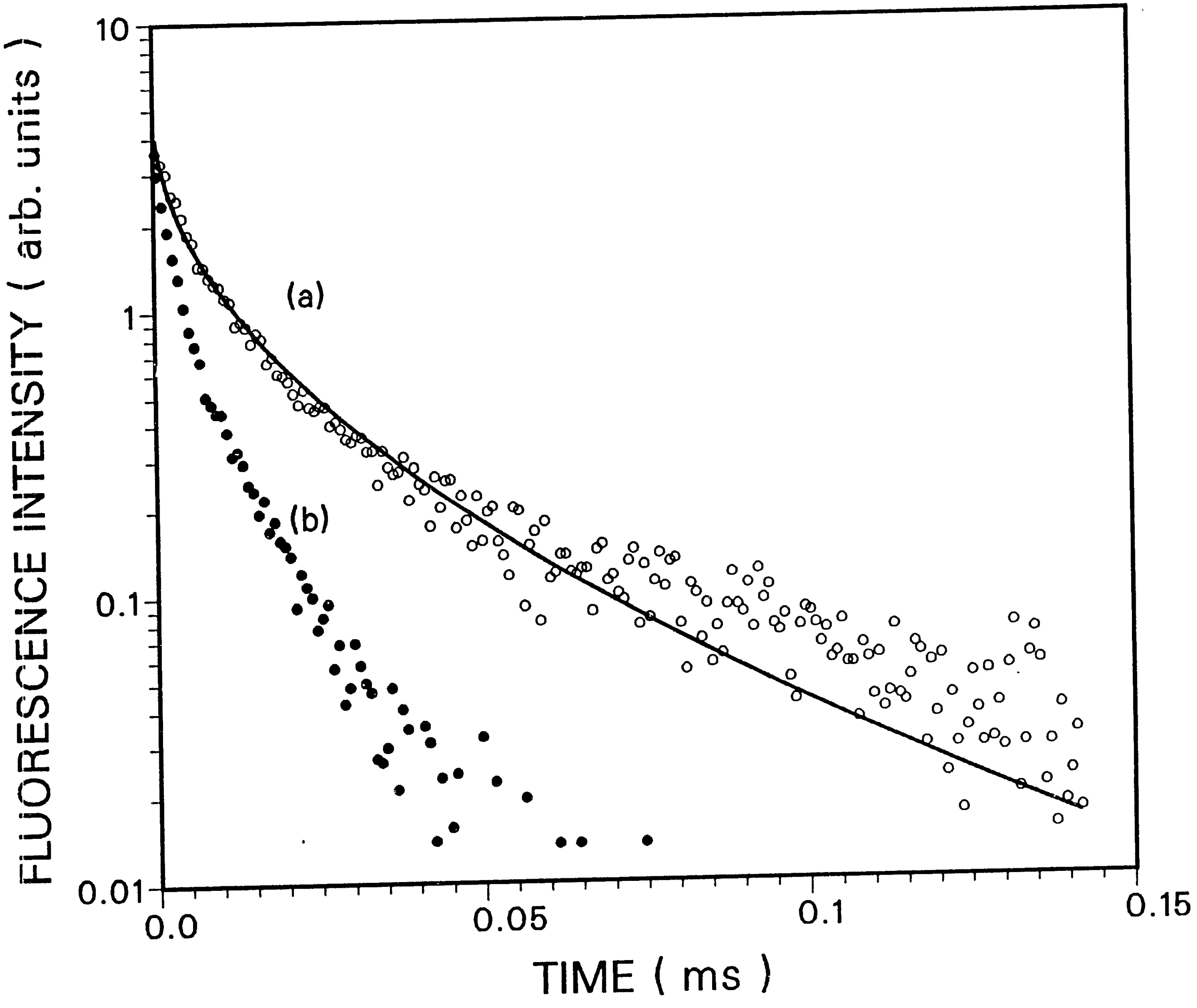
100
10
1
0.1
0.0
0.2
0.4
0.6
TIME (ms)
(a)
(b)

Fig. 3


FLUORESCENCE INTENSITY (arb. units)
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1
0.1
0.01
0.0
0.05
0.1
0.15
TIME (ms)
(a)
(b)

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