Luminescence decay times of KBr:Ga$^+$

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(Received 16 July 1976)

The kinetics of the luminescent decay of KBr:Ga$^+$ have been studied from 1.6 to 300 K. Below 45 K, a complex decay consisting of a slow (τ_s) and fast (τ_f) time constant is observed for both the A_T and A_X emissions. The temperature dependence of the A_T and A_X decay is explained in terms of the same model: in both A_T and A_X the emitting levels are twofold degenerate with a nondegenerate trap below, in agreement with recent calculations of Bacci *et al.* and Fukuda *et al.* From 45 to 55 K, the decay time τ_s of A_T is found to be equal to the rise time of A_X. Over the same range of temperature, the A_X emission increases at the expense of the A_T emission. Analysis of these data shows that A_T and A_X relaxed excited states are actually connected by a nonradiative process involving an activation energy B.

I. INTRODUCTION

In alkali halides containing heavy-metal ions with outer electronic configuration ns^2 such as Ga$^+$, In$^+$, Tl$^+$ one observes typically three absorption bands called A, B, C in order of increasing energy. An interesting feature observed in most phosphors is that excitation into the A band ($^1A_{1g} \rightarrow {}^3T_{1u}$) yields two emission bands designated as A_T (high energy) and A_X (low energy). Fukuda[1] explained the emission spectra by assuming that A_T and A_X emissions would occur from two types of minima coexisting on the $^3T_{1u}$ adiabatic-potential-energy surface (APES). As shown by Ranfagni,[2] Bacci *et al.*,[3] and Fukuda *et al.*,[4] coexistence of two kinds of minima on the $^3T_{1u}$ APES is allowed when considering (i) mixing effects with the higher $^1T_{1u}$ excited states due to large spin-orbit interaction[2] or (ii) bilinear terms in the electron-lattice interaction.[3,4] The symmetry and the energy-level structure of the two minima depend on the situation considered (for more details see Ref. 3). For Ga$^+$ situation (ii) seems to be appropriate since its spin-orbit interaction is small with respect to the exchange energy. In that case, one would expect a level structure for Ga$^+$ consisting of a doubly degenerate level with a trap below for both A_T and A_X minima. We have undertaken the present study of the kinetics of the KBr:Ga$^+$ fluorescence in the hope of obtaining information about the level structure of the A_T and A_X emissions.

II. EXPERIMENTAL

Emission was excited by illuminating into the A absorption band at 270 nm using a uv filter and either a deuterium flash lamp (TRW Model 88A) or a high-pressure oxygen flash lamp.[5] The deuterium lamp gave pulses of about 5-nsec duration, while those of the oxygen lamp were about 100 nsec. Decay times measured with both lamps were in complete agreement, but much higher intensities were possible with the oxygen lamp. The A_T or A_X emission was then selected by a broadband filter (centered at 450 nm for A_T and 550 nm for A_X) and measured with an EMI 9558 QB photomultiplier. The data were stored in a multichannel analyzer with a minimum channel width of 200 nsec. Regulated temperatures from 1.2 to 300 K were obtained with a gas flow cryostat. Temperatures were measured with a calibrated germanium resistance.

The results of the lifetime measurements of the A_X and A_T emissions after A excitation are shown in Figs. 1 and 2. As seen in Fig. 1, one observes a drastic change in the decay of A_T at 45 K. Thus, one can distinguish in the kinetics of the A_T and A_X decays a low-temperature part (for temperatures below 45 K)
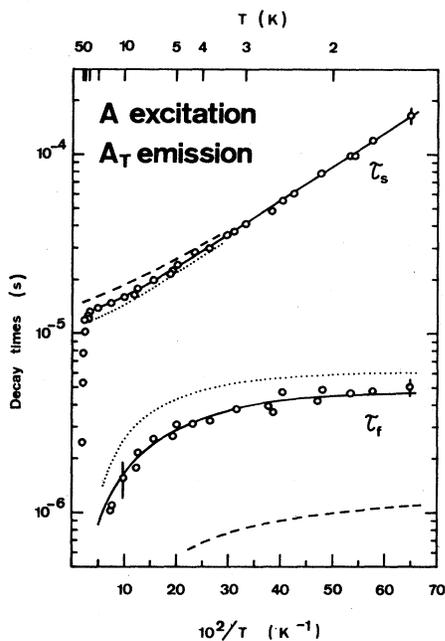
FIG. 1. Temperature dependence of the slow (τ_s) and fast (τ_f) time constants of the A_T decay. Best fits to the experimental data obtained with Eq. (5) and under the assumption of a one-phonon relaxation process between levels 1 and 2 are shown for different ratios of the degeneracies g_2 to g_1: $g = g_2/g_1 = 1$ (curve, broken line), 2 (curve, solid line), 3 (curve, dotted line).
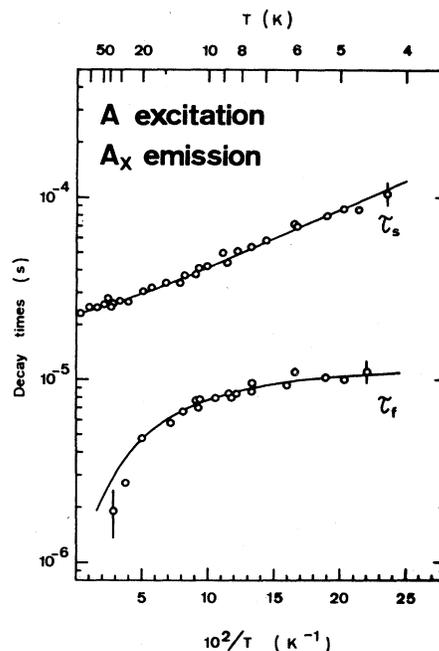
FIG. 2. Temperature dependence of the slow (τ_s) and fast (τ_f) time constants of the A_X decay. Best fit to the experimental data obtained with Eq. (5), under the assumption of a one-phonon relaxation process and for $g = g_2/g_1 = 2$, is given by the solid line.

and a high-temperature part (for temperatures above 45 K).

III. KINETICS OF THE FLUORESCENCE BELOW 45 K

A. Energy-level structure

Below 40 K the intensities of A_T and A_X emissions are temperature independent (see inset in Fig. 3). Thus, one can reasonably assume that the relaxed excited states of A_T are disconnected from those of A_X over the low-temperature range. On the other hand, the fluorescence kinetics of A_T and A_X behave in qualitatively the same fashion: both decays are characterized by two time constants τ_s and τ_f (see Figs. 1 and 2). This suggests that, as expected theoretically,[3,4] the same kinetic model involving only two sets of levels should apply for both fluorescence decays of A_T and A_X.

Our kinetic model is shown in Fig. 4. In the figure there is a group of levels, labeled 1, with a probability for radiative transition to the ground state k_1. A second group of levels, 2, is located at energy D above 1, and has a radiative transition probability for decay
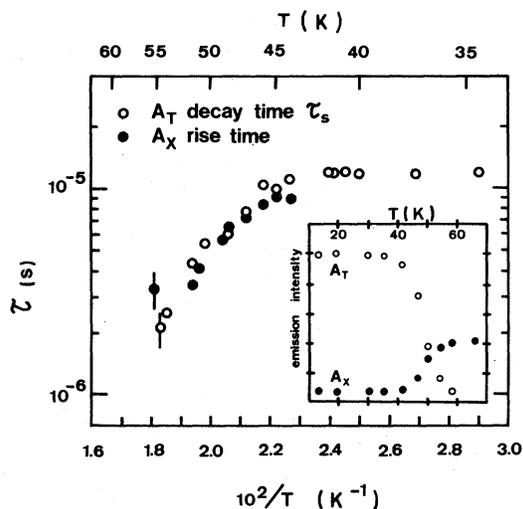
FIG. 3. Temperature dependence of the decay time τ_s of the A_T emission and the rise time of the A_X emission. The inset shows the temperature dependence of the A_T and A_X emissions.

to the ground state of k_2. The ratio of the degeneracies g_2/g_1 of the two groups of levels is called g. The nonradiative transition from $2 \rightarrow 1$ occurs with a probability k_{21}, while the reverse process has a probability

$$k_{12} = k_{21} \exp(-D/kT) \quad .$$

This model then gives the following rate equations:

$$\frac{dN_2}{dt} = -(k_{21} + k_2)N_2 + gk_{12}N_1 \quad , \tag{1}$$

$$\frac{dN_1}{dt} = k_{21}N_2 - (gk_{12} + k_1)N_1 \quad , \tag{2}$$

where N_2 and N_1 are respectively, the populations of levels 2 and 1 at any time. These equations have the solutions

$$N_2(t) = A_s \exp(-t/\tau_s) + A_f \exp(-t/\tau_f) \quad , \tag{3}$$

$$N_1(t) = B_s \exp(-t/\tau_s) + B_f \exp(-t/\tau_f) \quad . \tag{4}$$

The two roots of the quadratic equation

$$[gk_{12}k_2 + k_1(k_{21} + k_2)]\tau^2$$
$$- (k_{21} + gk_{12} + k_1 + k_2)\tau + 1 = 0 \quad , \tag{5}$$

give the two observed time constants τ_s and τ_f.

We assume for the moment that the relaxation process between levels 1 and 2 is a one-phonon process (or direct process), so that $k_{12} = Kn$, where n is the Bose-Einstein distribution function

$$n = [\exp(D/kT) - 1]^{-1}.$$

A value for g is chosen ($g = 1, 2, \text{or } 3$). Then there remain four parameters: $K, k_1, k_2,$ and D. These four parameters can then be determined from the best fit

to the experimental data: $\tau_s(T)$ and $\tau_f(T)$. The parameter k_1 could be dismissed at once, since at low temperatures $\tau_s(T)$ showed no tendency to level off, indicating values of $k_1^{-1} \gg 200$ μsec for A_T, and $k_1^{-1} \gg 100$ μsec for A_X. The calculated $\tau_s(T)$ and $\tau_f(T)$ depended strongly on the value chosen for the ratio g of the degeneracies. Best fit to the data was obtained with $g = 2$ (solid lines in Figs. 1 and 2). For comparison, tentative fits with $g = 1$ and 3 are also shown in Fig. 1 (dotted lines and broken lines). While an acceptable fit to τ_s could be found with $g = 1$ and 3, neither of these could simultaneously fit τ_s and τ_f at any temperature. In cases where only the slow component τ_s is observed, it is hard to unambiguously decide the degeneracy.[6] Although only the ratio of the degeneracies is obtained ($g = 2$), both relaxed excited states of A_T and A_X of Ga$^+$ in KBr likely consist of a radiative doublet with a metastable singlet below.[3,4] Table I summarizes the parameters which give the best fit to the data. The calculated values of the relaxation time between levels 1 and 2, i.e., $(k_{21} + 2k_{12})^{-1}$, at $T = 2$ and 20 K are given also in Table I. They show that at low temperatures, radiative transitions to the ground state occur before thermal equilibrium has been established in both A_T and A_X relaxed excited states. In the high-temperature range, when this relaxation time becomes very short with respect to the radiative decay k_2^{-1}, one measures a purely radiative lifetime

$$\tau_r = [(g + 1)/g]k_2^{-1} = 1.5k_2^{-1} \quad .$$

The possibility of a two-phonon relaxation process has also been considered. However, a Raman process leads to a T^7 temperature law, while a Orbach process gives rise to an even faster temperature dependence, i.e., $k_{21} \propto \exp(-\Delta/kT)$, where Δ would be the energy separation to some higher electronic state. Though agreement could be obtained for a given temperature,

FIG. 4. Energy-level scheme for A_T and A_X emissions. N_1^0 and N_2^0 are the initial populations of levels 1 and 2 just after the excitation pulse. g_1 and g_2 are the degeneracies of levels 1 and 2. Wavy arrows and straight arrows indicate, respectively, nonradiative and radiative transitions.

TABLE I. Values of the parameters giving the best fit for the data $\tau_s(T)$ and $\tau_f(T)$. Relaxation times between the radiative doublet and the trap below are calculated at $T = 2$ and 20 K.

	A_T	A_X
$1/K$ (μsec)	12 ± 2	59 ± 10
$1/k_1$ (μsec)	>200	>100
$1/k_2$ (μsec)	8.5 ± 1	15.4 ± 2
D (cm^{-1})	3.0 ± 0.3	3.9 ± 0.4
$g = g_2/g_1$	2	2

Calculated relaxation time, i.e., $(k_{21} + 2k_{12})^{-1}$:

| $T = 2$ K | 8.6 μsec | 48.8 μsec |
| $T = 20$ K | 0.89 μsec | 5.6 μsec |

neither of these two-phonon relaxation processes gives
the rather weak temperature dependence observed.

B. Relative intensities of fast and slow components—population rates

The intensity ratio of fast component to slow component A_f/A_s, which can be obtained from the solution (3) of the rate equations, will provide information about the way the levels are populated during the exciting pulse. Since the pulse length is short compared with all the characteristic times involved, the initial populations N_1^0 and N_2^0 of levels 1 and 2 are just proportional to the feeding rates of these levels. Then the ratio A_f/A_s at time $t = 0$ is given by

$$\frac{A_f}{A_s} = -\frac{gk_{12}N_1^0 + (-1/\tau_f + gk_{12} + k_1)N_2^0}{gk_{12}N_1^0 + (-1/\tau_s + gk_{12} + k_1)N_2^0} . \quad (6)$$

In Figs. 5 and 6 the solid lines give the calculated temperature dependence of the intensity ratio A_f/A_s at time $t = 0$, using the parameters listed in Table I, and assuming different ratios N of initial populations of levels 2 to 1 : $N = N_2^0/N_1^0$. Also shown in Figs. 5 and 6 are the measured ratios A_f/A_s at time $t = 0$. For the A_T emission the experimental points follow the calculated curve for $N = 10$ over the temperature range 1.5–20 K (Fig. 5), while for the A_X emission the data follow the $N = 2$ curve from 4 to 50 K (Fig. 6). This very different behavior of A_T and A_X should be em-

phasized. It appears that only the radiative levels of A_T are effectively populated, while on the other hand the three levels corresponding to the A_X emission are randomly populated $(N = g = 2)$, and this is true over a very large range of temperature.

IV. KINETICS OF THE FLUORESCENCE ABOVE 45 K

At temperatures below 45 K rise times for both A_T and A_X emissions are much less than 200 nsec, and thus cannot be measured with our multichannel analyzer. But over a narrow range of temperature (from 45 to 55 K) one can observe a slower rise time in the A_X emission (the rise time of A_X emission in KI:Tl$^+$ has recently been observed by Ishikane.[7] On the other hand, the A_T decay time τ_s, which has reached the steady value $\tau_r = 1.5k_2^{-1} = 12.8$ μsec, changes drastically with the temperature for $T \geq 45$ K. In fact the A_X rise time and the A_T decay time τ_s are found to be equal as can be seen in Fig. 3. Over the same range of temperature, the intensity of A_X emission increases while that of A_T decreases (see inset in Fig. 3). These experimental facts are strong evidence for the occurrence of a nonradiative process connecting A_T and A_X at high temperature. Let τ_{nr} be the characteristic time of this nonradiative process. Then, for $T \geq 45$ K, the A_T decay rate is given by

$$1/\tau_s = 1/\tau_r + 1/\tau_{nr} . \quad (7)$$

In the high-temperature range, the intensity of the A_T
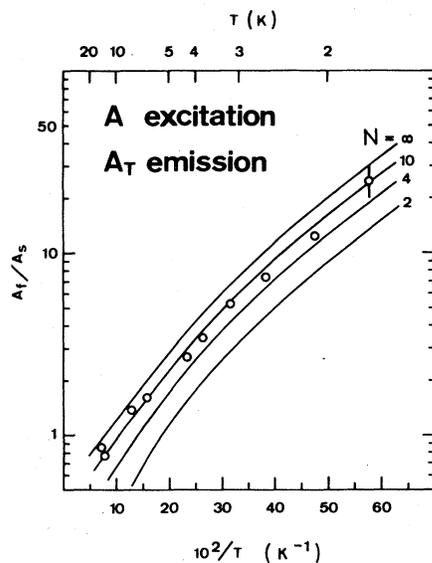
FIG. 5. Ratio of fast component to slow component intensity A_f/A_s of the A_T emission. Solid lines are the calculated intensity ratio [Eq. (6)] obtained with the parameters listed in Table I, and for various ratios of initial populations of levels 2 to 1:$N = N_2^0/N_1^0 = 2, 4, 10, \infty$.
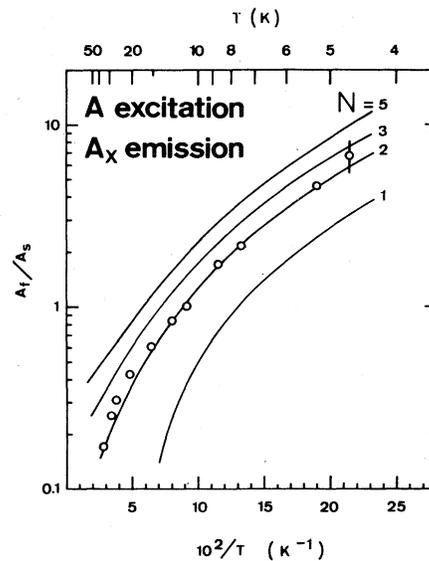
FIG. 6. Ratio of fast component to slow component intensity A_f/A_s of the A_X emission. Solid lines are calculated intensity ratio [Eq. (6)] obtained with the parameters listed in Table I, and for various ratios of initial populations of levels 2 to 1:$N = N_2^0/N_1^0 = 1, 2, 3, 5$.

emission is related to the radiative decay time by

$$I_0/I = \tau_r/\tau_s \ , \tag{8}$$

where I and I_0 are, respectively, the A_T intensity at temperature above and under 45 K. Combining (7) and (8) one gets

$$1/\tau_{nr} = 1/\tau_s - 1/\tau_r = 1/\tau_r(I_0/I - 1) \ . \tag{9}$$

It is found that the A_T decay time τ_s and the A_T emission intensity I satisfy relation (8). In fact, the experimental points for both

$$\ln(1/\tau_s - 1/\tau_r), \quad \ln[1/\tau_r(I_0/I - 1)]$$

fall on the same straight line when plotted against $1/T$ (see Fig. 7), leading to the following expression for the nonradiative process:

$$1/\tau_{nr} = A \exp(-B/kT) \ , \tag{10}$$

where $A = 8.6 \times 10^{11}$ s^{-1}, and $B = 550$ cm^{-1}.
B is the energy separation between the level a (see inset in Fig. 7) and the first excited level b from which a tunneling process towards A_X potential well becomes effective. This activation energy B can be either equal to or smaller than the height of the potential barrier between A_T and A_X wells on the $^3T_{lu}$ APES. Tunneling from higher levels than level b in
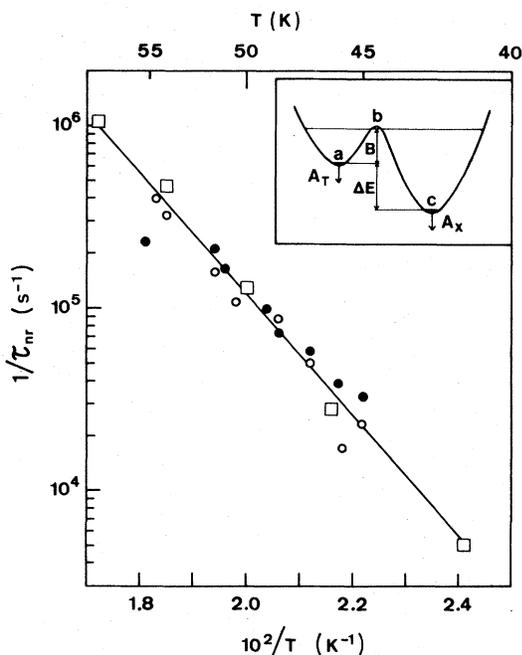
the temperature range 40 to 60 K seems unlikely, since τ_{nr}^{-1} exhibits a single exponential temperature dependence (see Fig. 7). Relaxation between levels a and b cannot occur through a one-phonon process, since no phonon of such an energy exists in KBr. Therefore, one has to consider successive absorptions of phonons which allow the system to climb along a "ladder" of vibrational levels defined in the A_T potential well. Since Raman scattering spectra of KBr:Tl$^+$ exhibit strong peaks in the range 70–150 cm^{-1},[8] one expects 5–10 intermediate levels between a and b. The characteristic rate A is then a combination of relaxation rates between these levels. The experimental Boltzmann factor takes into account the fact that the whole initial population of the level a has to go through the level b, whose population can never be larger than the Boltzmann equilibrium value.[9] As soon as τ_{nr} is smaller than the radiative lifetimes τ_r of A_T and A_X, which are about 10 μsec (see Table I), one obtains a Boltzmann distribution between levels a and c. For KBr:Ga$^+$, only A_X emission is observed at room temperature indicating that $\Delta E \geq 1000$ cm^{-1}. Finally, it should be noted that there is another mechanism active in populating level c (from which A_X emission occurs) other than the one discussed so far, since the A_X emission intensity is temperature independent in the low-temperature range.

V. CONCLUSION

The present study of the kinetics of the KBr:Ga$^+$ fluorescence is consistent with a model in which: (a) the energy-level structure in both A_T and A_X relaxed excited states consists of a radiative doublet with a trap below, (b) after A excitation, only the radiative doublet is populated in the case of A_T, while the three levels of A_X are equally populated, (c) radiative transition to the ground state occurs before thermal equilibrium has been established at $T \leq 4.2$ K in both A_T and A_X relaxed excited states, and (d) for $T \geq 45$ K, A_X minima are mainly populated by a direct transfer from A_T minima. This transfer actually is due to a nonradiative process involving an activation energy $B = 550$ cm^{-1}.

As pointed out by Bacci et al.[3] and Fukuda et al.,[4] coexistence of two types of minima on the $^3T_{lu}$ APES is allowed when including bilinear terms in the electron-lattice interaction. In that case, one would obtain a level structure for both A_T and A_X as in (a). However, there remains the problem of the A_T and A_X symmetry. The tetragonal symmetry of A_T has been well established,[10] while that of A_X is not so certain.[11] Point (b) is consistent with the correlation of linear polarization observed between the A absorption and the A_T emission of KBr:Ga$^+$,[10] which indicates more precisely that one can feed selectively one component of the radiative doublet.

Magnetic circular polarization of emission in various

FIG. 7. Temperature dependence of $1/\tau_{nr}$ [Eq. (9)]:time constants data are shown by open circles (decay time of A_T) and full circles (rise time of A_X), while open squares represent data on A_T emission intensity. Inset shows a qualitative cross section of the $^3T_{lu}$ APES.

phosphors has been studied by Fukuda[11]. In particular for KBr:Ga$^+$ at $T = 4.2$ K, a bump on the circular polarization curve of A_T is observed at a magnetic field H of 32 kG when H is parallel to a [100] axis. Such a bump on the circular polarization curve can be interpreted as due to a level crossing, but only under the condition that thermal equilibrium has not been established in the spin triplet.[12,13] This is exactly the situation of KBr:Ga$^+$. Furthermore from our results of a zero-field splitting $D = 3.0 \pm 0.3$ cm^{-1}, a level crossing at 32 kG leads to an effective value of $g \approx 2$, which is very close to the free spin spectroscopic splitting value. Thus, it can be concluded that the orbital angular momentum is severely quenched as would be the case for a strong Jahn-Teller coupling to E_g tetragonal modes of vibration in an orbital state T_{1u}.[14] Such

a situation has been observed with the triplet excited states of F centers in CaO.[15]

Note added in proof. After completion of this work, the optical detection of magnetic resonance in the relaxed excited states A_T and A_X has been undertaken in this laboratory.[16] The proposed level structure of A_T and A_X has been verified precisely, and their symmetry determined.

ACKNOWLEDGMENTS

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