PHYSICAL REVIEW VOLUME 138, NUMBER 1A 5 APRIL 1965

Lifetime of the Excited I^- Center in KCl†

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(Received 9 November 1964)

The lifetimes of two excited states of iodine centers in KCl single crystals were measured between 15 and 300°K, following flash excitation. Previous and new results of the fluorescent yield of these same emission processes are presented for comparison. At low temperatures the radiative lifetime is 1.7×10^{-4} sec and the yield $100\%\pm50\%$ for the blue-green emission process; for the ultraviolet emission the lifetime is 1.3×10^{-7} sec and the maximum yield $70\%\pm35\%$. In an intermediate temperature range, the radiative lifetime starts to decrease whereas the yield stays constant. At still higher temperatures, the lifetime and the fluorescent yield both decrease rather sharply.

INTRODUCTION

THE optical absorption of dilute mixtures of KI in KCl single crystals shows several new absorption bands in the transparent region of the host KCl crystal.[1] Absorption of light into these iodine bands gives rise to luminescence emitted into two groups of emission bands of different characteristics.[2] Figure 1 summarizes these previous results.

The aim of these investigations was to learn more about the detailed nature of absorption and re-emission processes in ionic crystals. The iodine centers (I^- centers) in KCl were chosen because a substitutional I^- ion is chemically close to the Cl^- ion it replaces, yet it can be studied in diluted form in the same KCl host lattice. The diluted system thus avoids some of the experimental and interpretative difficulties connected with intrinsic host absorption processes.

The experimental results obtained with such a chemically simple system showed, however, a complexity not anticipated from simple theories of two-level impurity systems (Franck-Condon models). It was concluded that several excited electronic states of the I^- center were involved in the absorption and re-emission processes. It was therefore of particular interest to learn more about these excited states in ionic crystals with the aim of elucidating the mechanism of changes from one excited electronic state of the system to others. This paper reports, then, measurements of the radiative lifetime of two different excited states, one giving rise to the emission of blue-green light the other giving rise to the emission of ultraviolet light (see Fig. 1).

Recent theoretical work[3] on the radiative lifetime of transitions in ionic solids and the observation of the unexpectedly long lifetime of the excited state of the F center and F_A centers in KCl[4] have also stimulated the present study.

EXPERIMENTAL ARRANGEMENT

A pulse of monochromatic light of very short duration was incident on the sample, giving rise to the emission of luminescent light (Fig. 2). The emitted light intensity could be monitored perpendicular to the direction of the incident radiation by a photomultiplier detector system, and this signal could be displayed on the screen of an oscilloscope. Light emitted into different emission bands could be selected by combining the spectral sensitivity of the photomultiplier with an adequate set of filters to form a window having the width of an emission band.

The light source, a spark gap in air, is extremely simple. It consists of a dc power supply capable of charging a capacitor of 10^{-9} to 10^{-7} F to about 3000 V. The capacitor was soldered with very short connections to a set of movable stainless-steel points forming a spark gap of adjustable spacing. A steady operation and spark sequence was assured by illumination of the gap with an intense uv point source (Black Light Eastern Corporation). The light pulse decayed exponentially with a half-width of about 50 nsec under optimum conditions. Considerable intensity was found in several narrow lines in the experimental range of 185 to 210 mμ.

KCl crystals containing known concentrations of iodine ions were grown in this laboratory from Cl_2-treated KCl in an argon atmosphere. Samples containing from 10^{17} iodine ions/cc to 2×10^{20} iodine ions/cc were used. The sample was mounted in a cryostat. Its temperature could be varied from about 15°K to room temperature.

RESULTS

Blue-Green Emission

The luminescent decay of blue-green light emitted from iodine-doped KCl crystals after flash excitation into certain exciting wavelength regions (see Fig. 1)

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† Work supported by the U. S. Office of Naval Research and the Advanced Research Projects Agency.

[1] H. Mahr, Phys. Rev. **125**, 1510 (1962); K. Nakamura, K. Fukunda, R. Kato, A. Matsui, and Y. Uchida, J. Phys. Soc. Japan **16**, 1262 (1961); K. Fukunda, R. Kato, K. Nakamura, and Y. Uchida, *ibid.* **15**, 1344 (1960); A. Smakula, Z. Physik **45**, 1 (1927); R. Hilsch and R. W. Pohl, *ibid.* **57**, 145 (1929).

[2] H. Mahr, Phys. Rev. **130**, 2257 (1963).

[3] W. Beall Fowler and D. L. Dexter, Phys. Rev. **128**, 2154 (1962); W. Beall Fowler, *ibid.* **135**, A1725 (1964).

[4] Robert K. Swank and Frederick C. Brown, Phys. Rev. **130**, 34 (1963); Phys. Rev. Letters **8**, 10 (1962); Giorgio Spinolo and Frederick C. Brown, Phys. Rev. **135**, A450 (1964); G. Gramm, Phys. Letters **8**, 157 (1964).

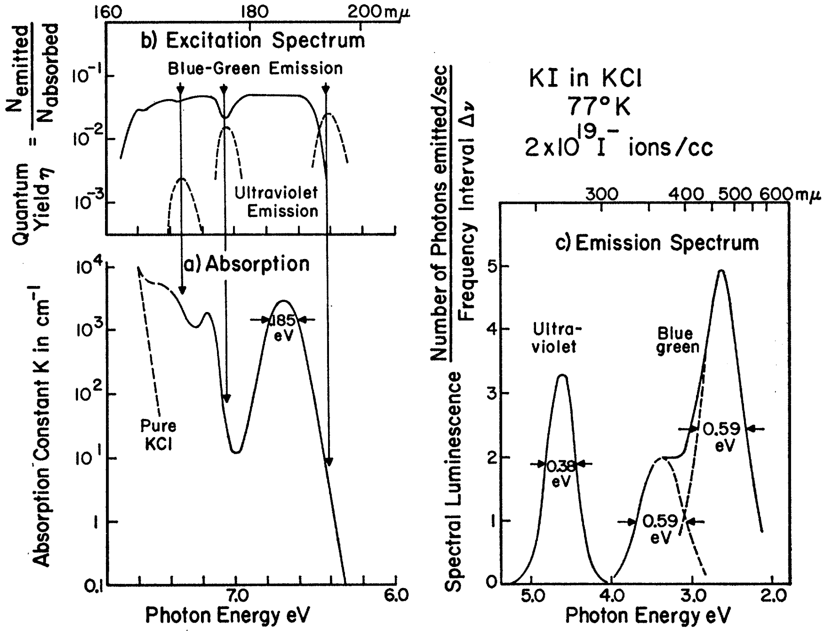

FIG. 1. Optical behavior of the iodine centers (I^- centers) in KCl crystals at 77°K. (a) Absorption spectrum: The absorption constant is plotted on a logarithmic scale versus the photon energy. The dashed line indicates the position of the absorption edge of pure KCl. (b) Excitation spectrum: The solid line represents the quantum yield for the blue-green component of the blue-green emission band. The dashed line shows the three regions of ultraviolet emission. These latter curves correspond to uncorrected values of total luminescence. The arrows point at coincident positions of a depression in the yield curve of the blue-green component emission, of excitation maxima for the uv emission, and of regions on the low-energy tail of the three absorption bands. (c) Emission spectrum: The spectral luminescence (arbitrary units) of the ultraviolet and blue-green emission is plotted versus photon energy. Note the different scale used for the photon energy. The blue-green emission consists of two components, a large blue-green and a smaller blue emission band.

could in all cases be fitted by an exponential time dependence $I_L=I_0e^{-t/\tau}$. The decay or lifetime τ was very long compared to the duration of the incident light pulse as schematically shown in Fig. 2(b). In addition to the lifetime the relative quantum yield could easily be obtained from photographed oscilloscope traces as indicated in Fig. 2(b).

The results of lifetime measurements for the blue-green emission is shown in Fig. 3. For a temperature range from 65 to 300°K the lifetime in μ sec is plotted logarithmically versus the reciprocal temperature. These data were obtained with a variety of samples of different iodine concentration. The wavelength of the exciting light was varied over the range of 185 to 200 mμ, which corresponds to light absorbed throughout the range of the first absorption band.

An absolute value of the yield of approximately 100%±50% at low temperatures (Fig. 3) was obtained through a new comparison with the yield of sodium salicylate at room temperature. This comparison was done in the direction of the incident light beam for an optimum thickness of the sodium salicylate layer as suggested by a recent calibration of this phosphor.[5] The values given in Fig. 1 and in a previous publication[2] were based on too low a value of the yield of sodium salicylate and should be multiplied by a factor of approximately 20. Relative values of the fluorescent yield were obtained from pulse measurements and with continuous light illumination in the temperature range shown for a variety of crystals containing different iodine concentrations. These data points (adjusted to 100% at low temperatures) are given in Fig. 3 (right-hand ordinate scale).

The results of Fig. 3 show that the lifetime of the blue-green emission process is independent of iodine concentration at least up to a concentration of 2×10^{20} iodine ions/cc or about 1 mole%. It is also independent of the wavelength within the region used. The quantum yield of the blue-green emission process reaches a saturation value below 150°K. In contrast the lifetime continues to rise by a factor of 3 between 150 and 65°K. At still lower temperatures it also saturates, as shown in Fig. 4. The final value of 170 μsec is remarkably long. The lifetime τ was found to be independent of the portion of the blue-green emission band that was used for its determination. The uncer-

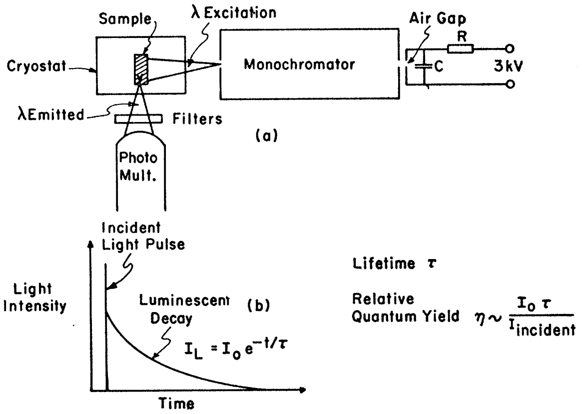

FIG. 2. (a) Schematic sketch of the experimental arrangement. (b) Schematic diagram of the oscilloscope trace of incident and luminescent pulse.

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[5] Rinda Allison, Jay Burns, and A. J. Tuzzolino, J. Opt. Soc. Am. 54, 747 (1964). But see also: N. Kristianpoller, *ibid.* 54, 1285 (1964).

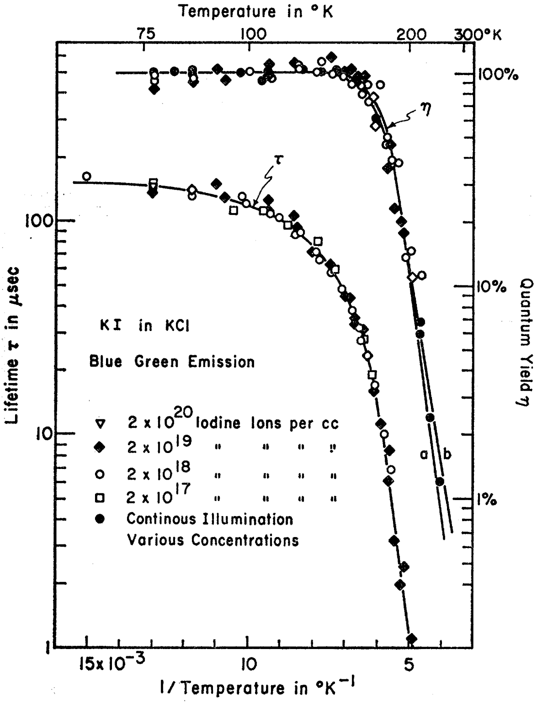

FIG. 3. Lifetime and fluorescent yield of the blue-green emission process as a function of sample temperature. The left-hand ordinate is a logarithmic scale of the lifetime in μ-sec; the right-hand ordinate is a logarithmic scale of the fluorescent yield η.

tainties in these spectral measurements were large, however.

Ultraviolet Emission

Excitation into narrow wavelength regions in the tail of the iodine absorption bands gives rise to the emission of ultraviolet light (see Fig. 1). The decay time of the ultraviolet emission after flash excitation was, unlike the blue-green emission, comparable to the flash duration. A direct evaluation of the exponential decay of the luminescence is therefore impossible. The following procedure—similar to a method described by Tomita and Rabinowitch[6]—was used to calculate the lifetime. It was found that the incident flash light pulse had an intensity distribution which was very nearly exponential in time: $I=I_0e^{-t/\tau_f}$. τ_f was found to be about 70 to 100 nsec. (Half-widths are 50 to 70 nsec.) The emitted light intensity can then be calculated as a function of time, assuming an exponential lifetime τ of the excited state. The results of such calculations are given in Fig. 5. The curves are one normalized trace curve of the incident pulse ($\tau=0$) and the shape of the traces for various lifetimes τ which are a multiple of τ_f. It was found that the observed oscilloscope traces resembled very closely those of Fig. 5. It was therefore felt that this analysis would give a rather accurate determination of the temperature variation of the lifetime although the absolute values might be less certain. The actual evaluation of the lifetime was accomplished by measuring the relative half-widths H/H_f of observed emitted and incident light pulses. τ was then obtained from Fig. 5(b). The results so obtained for the lifetime of the ultraviolet emission of I^- in KCl are given in Fig. 6 for the temperature range from 77 to 300°K. For comparison a new determination of the relative quantum yield of the luminescent process was obtained by using continuous illumination. These values are given in the figure (right-hand ordinate) together with earlier values. An absolute value of 70%±35% at 77°K was obtained through a new comparison with sodium salicylate.[5]

The lifetime of the ultraviolet emission is rather short, reaching a value of about 130 nsec at 77°K. Between 77 and 15°K a slight decrease was found; because of the indirect way of arriving at τ, however, a systematic error can not be excluded. Figure 6 shows that the values of the lifetime start to decrease at higher temperatures in a region where the fluorescent yield is still constant. It was established that the lifetime was independent of iodine concentration up to 2×10^{20} iodine ions/cc or about 1 mole%. The excitation region of the higher energy iodine band at about 175 mμ could not be used for flash excitation. Even after flushing the entire apparatus with N_2 gas, the flash light intensity was too small in that wavelength region.

CONCLUSIONS

The results obtained in this study are: (1) Two very different lifetimes are found for the blue-green and

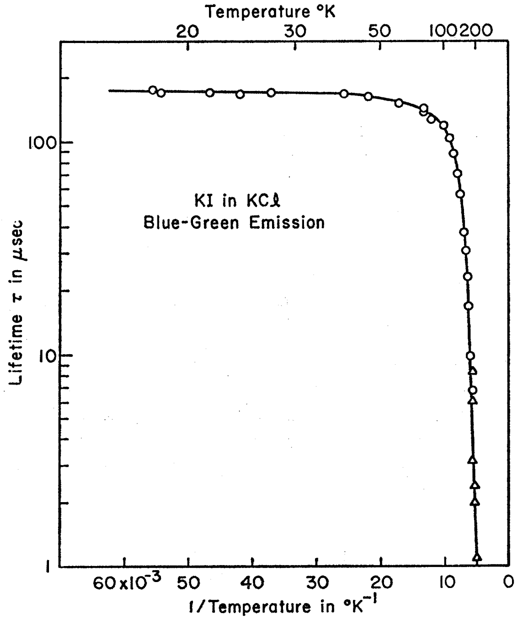

FIG. 4. Lifetime of the blue-green emission process in μ-sec.

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[6] Giti Tomita and Eugene Rabinowitch, Biophys. J. 2, 486 (1962).

ultraviolet emission of excited iodine centers in KCl, respectively. The lifetime of the blue-green emission process, 170 μsec at low temperatures, is unexpectedly long. (2) The lifetimes of the excited states exhibit a temperature dependence in low-temperature regions where the fluorescent yield has saturated. At still higher temperatures yield and lifetime decrease rather sharply.

We will first discuss the implications of the values of the lifetimes at low temperatures. Conclusions based on the temperature dependence of lifetime and fluorescent yield will be presented thereafter. We will be using the Born-Oppenheimer[7] approximation throughout our discussion, i.e., assuming that the total energy of our center system can be expressed well enough as the sum of the electronic energy and the vibrational energy of the system.

The discussion of optical phenomena in ionic crystals centers around Franck-Condon models.[7] This is because lattice relaxation after absorption of light amounts to an appreciable part of the total energy stored in the system. Central to the discussion is the Condon principle,[7] i.e., the assumption that the influence of the instantaneous position of the ions on the electronic matrix element of the transition of a two-level system is small and can be neglected. The Condon approximation predicts a Gaussian shape of absorption bands which, as with the iodine system in KCl, is normally observed near the absorption maximum. This same approximation also couples a radiative emission process with the absorption, thus predicting the Stokes' shift of the emission and the lifetime of the excited state. In a variety of impurity systems in ionic crystals, including the I^- center of KCl, the observed Stokes' shift was much larger than the predicted one.[8] It was also found that in the only systems of this type which have been measured so far, the F centers in alkali halides, the observed lifetime τ was larger than the predicted value.[4] Fowler and Dexter[3] have recently derived a formula to calculate the lifetime τ of an excited state from a knowledge of the integrated absorption coefficient $\Sigma=(1/N)\int Kd(h\nu)$ of a two-level transition in an ionic solid. With the measured value of the integrated absorption coefficient of the I^- band in KCl ($\Sigma=3.65\times10^{-17}$ eV cm^2 at 77°K) the calculated value of the lifetime[9] is $\tau_{\text{cal}}=4\times10^{-8}$ sec, assuming that the process is coupled directly to the absorption. The calculated lifetime is $\tau_{\text{cal}}=6.8\times10^{-9}$ sec in the case that the ultraviolet emission is coupled directly to the absorption. Both values are too small by a factor of more than 4000 and 19, respectively. We might recall[2] that the Stokes' shift was found too large—compared to a prediction using a conventional one-dimensional Franck-Condon model—by 3.4 eV for the blue-green emission[10] and by 1.4 eV for the ultraviolet emission.

These absorption-emission discrepancies can be resolved in either of two alternative ways:

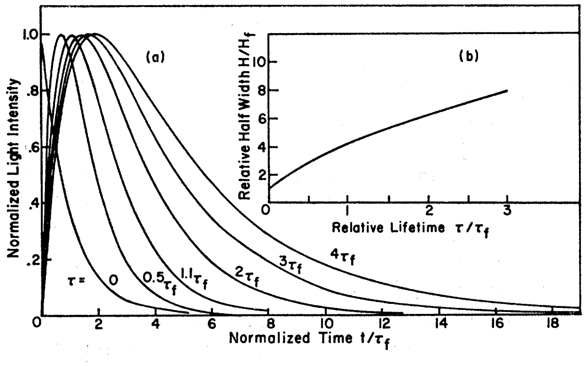

FIG. 5. (a) Normalized, calculated pulse shapes of incident and luminescent pulses for very short luminescent decay times τ. τ_f is the decay time of the incident pulse. (b) Plot of the relative half-widths of luminescent and incident pulses from (a) as a function of the relative lifetime of the luminescent process and the incident pulse.

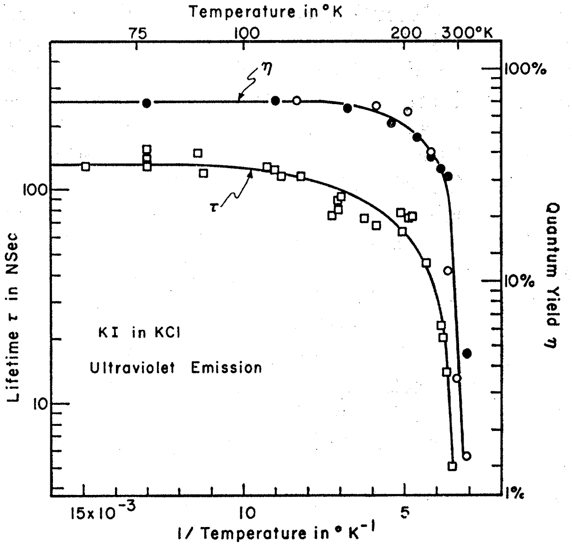

FIG. 6. Lifetime τ and fluorescent yield of the ultraviolet emission process as a function of sample temperature. The left-hand ordinate is a logarithmic scale of the lifetime in nanoseconds; the right-hand ordinate is a logarithmic scale of the fluorescent yield. The values of the yield were obtained from measurements with continuous illumination.

(1) Dexter and Fowler[3] proposed to drop the Condon approximation. Then the "average" electronic matrix

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[7] M. Born and J. Oppenheimer, Ann. Physik **84**, 457 (1957); J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959); D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 6; M. Lax, J. Chem. Phys. **20**, 1752 (1952), and D. E. McCumber, Phys. Rev. **135**, A1676 (1964).

[8] F. Lüty and W. Gebhard, Z. Physik **169**, 475 (1962); W. Gebhard and H. Kühnert, Phys. Letters **11**, 15 (1964); Ikuo Fujita, Sci. Light (Tokyo) **11**, 142 (1962); T. Timusk and W. Martienssen, Phys. Rev. **128**, 1656 (1962).

[9] This is true assuming the effective field to be $E_{\text{eff}}=(n^2+2)/3$ with $n_{\text{abs}}=1.80$, $h\nu_{\text{abs}}=6.7$ eV, $n_{\text{em}}=1.51$ or 1.57, $h\nu_{\text{em}}=2.64$ or 4.64 eV, respectively.

[10] We will limit the discussion from now on to the larger blue-green component of the blue-green emission process.

element for absorption (averaged over the relatively small thermal vibrations of the system in the ground-state position of the ions around the absorption center) would be different from the "average" matrix element in emission (averaged over small vibrations in new positions of the ions after a relatively large relaxation of the ions following absorption). Both the Stokes' shift and the lifetime of the excited state will now be uncoupled from the absorption matrix element. We will refer to this model as the "change of matrix elements" following the notation of Fowler and Dexter.[3]

(2) Another alternative would be to consider the effect of other electronic excited states of the same or different symmetry types. These certainly do exist, although they might not be reached directly from the electronic ground state by allowed optical transitions. Many total, vibronic states of the system (formed by these electronic excited states and the lattice vibrational states) will "overlap" or "cross over" due to the effect of lattice vibrations and lattice relaxations. This means that after excitation of the system the total energy of two excited vibronic states can be the same at some instant of time, although the electronic energy and the lattice displacement are both different for each state. Transitions will then be induced and the system can thus end up in an excited state which is different from the one reached in absorption. This situation will include cases where after absorption of light the center undergoes structural changes like the formation of halogen-molecule centers. We will refer to this as "different excited states." Again absorption and emission are completely uncoupled; the Condon approximation is, however, retained in each case.

The absorption-emission discrepancy of the blue-green emission process of I$^-$ in KCl is certainly so large that a mere change of matrix elements could not explain the whole misfit. We would rather propose that this emission originates from a vibronic state which is different from the one reached in absorption.

The situation is less certain in the case of the ultraviolet emission process. A discrepancy of a factor of 19 in the lifetime might well be attributed to a change of matrix element. This explanation was recently favored in the case of the F center in KCl where a discrepancy of a factor of 7 in the lifetime has been reported.[3,4] No detailed calculation has however been made of how such a change of matrix elements would affect the shape of the absorption and emission bands. The shape of the I$^-$ band in KCl has been measured over a rather wide range of photon energies thus probing an appreciable fraction of the energetic distance to the emission bands. The shape of the band can, however, be analyzed on the basis of the Condon approximation.[11]

A simple theory of the temperature dependence of the luminescent process in solids between an electronic two-level system assumes two different decay modes for the excited state.[12] One is by radiation with a radiative transition probability $P_r = 1/\tau_r$, where τ_r is the radiative lifetime of the excited state. Another decay mode is possible through lattice vibrations. The system can "cross over" an energy barrier ΔE into other electronic states of the system (conduction-band state or ground state). This transition is assumed to be temperature-dependent and its probability assumed to be given by $P_{nr} = \nu_0 e^{-\Delta E/kT}$. The model predicts the following behavior of the lifetime τ and the fluorescence yield η of an excited state[4,12]:

$$\tau = \tau_r / (1 + \tau_r \nu_0 e^{-\Delta E/kT}), \qquad (1)$$

$$\eta = \tau/\tau_r = 1/(1 + \tau_r \nu_0 e^{-\Delta E/kT}). \qquad (2)$$

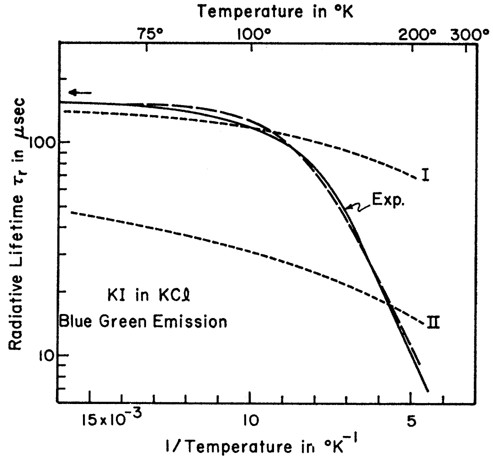

FIG. 7. Radiative lifetime τ_r of the blue-green emission process as a function of sample temperature (solid line). These values have been obtained by dividing the lifetimes of Fig. 3 by the corresponding values of the normalized fluorescent yield. The dashed line is an attempt to fit the results by Eq. (4). The two dotted curves are an attempt to fit the results by Eq. (3) with $\hbar\omega = 17.2\times10^{-3}$ eV and 3.4×10^{-3} eV, respectively.

For both the ultraviolet and the blue-green emission process the lifetime starts to deviate from its low-temperature value in a temperature region where the fluorescent yield is still constant (see Figs. 3 and 6). We presume, looking at Eqs. (1) and (2), that this temperature variation originates in τ_r, the radiative lifetime. The smoothed experimental results of the lifetime τ for the blue-green emission were therefore divided by the yield to give τ_r as a function of temperature. The result is shown in Fig. 7 (solid line).

The rather long radiative lifetime and its temperature dependence suggest[13] that the corresponding transition is an "electronically forbidden" transition which is "partially allowed" through lattice vibrations. In this case theory predicts a temperature dependence of the

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[11] H. Mahr, Phys. Rev. **132**, 1880 (1963).

[12] C. C. Klick and J. H. Schulman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

[13] R. Kubo and Y. Toyozawa, Progr. Theoret. Phys. (Koyto) **13**, 160 (1955); R. S. Knox, J. Phys. Soc. Japan **18**, Suppl. II, 268 (1963).

radiative lifetime given by[13]

$$\tau_r = \tau_r^0 \tanh(\hbar\omega/kT). \qquad (3)$$

The dotted lines of Fig. 7 are calculated from Eq. (3) using two different values of $\hbar\omega$: 17.2×10^{-3} eV and 3.4×10^{-3} eV. The agreement is extremely poor. We found empirically, however, that the function

$$\tau_r = \tau_r^1[(1+e^{-\Delta E/kT})/(1+Ae^{-\Delta E/kT})], \qquad (4)$$

with $A=760$ and $\Delta E=0.07$ eV, fits the experimental results rather nicely, as indicated by the dashed curve. A possible explanation is as follows: The electronic levels of two different vibronic excited states differ by 0.07 eV, and both states are coupled through lattice vibrations. If their respective radiative lifetimes for transitions to the ground state are $\tau_r^1=1.7\times10^{-4}$ sec and $\tau_r^2=(1/A)\tau_r^1=2.2\times10^{-7}$ sec, the common lifetime τ_r due to the decay of excitations from both states in thermal equilibrium is then given by formula (4) with $A=\tau_r^1/\tau_r^2$. The emission from either state would have to contribute to the same wide emission band[10] of 0.59-eV half-width. We have no additional experimental evidence of these various excited states. It might be pointed out that in the case of Tl^+ impurities in alkali halides a similar richness of excited states was actually observed in absorption and emission studies.[14]

At higher temperatures both the yield and the lifetime decrease rather steeply. This behavior is predicted by formulas (1) and (2). For the blue-green emission the fluorescent yield was calculated from Eq. (2) using two different pairs of parameters. For curve (a) of Fig. 3 $\nu_0=3.5\times10^{13}$ sec^{-1} and $\Delta E=0.31$ eV were used; curve (b) was calculated from $\nu_0=3.9\times10^{12}$ sec^{-1} and $\Delta E=0.27$ eV. Values of the radiative lifetime were taken from Fig. 7. Both sets of values give a rather nice fit through the data points, indicating a rather large uncertainty in the determination of ν_0 but a satisfactory determination of ΔE from such graphs. The frequency $\nu_0=3.9\times10^{12}$ sec^{-1} is identical with the characteristic frequency obtained previously[1,2] from the temperature variation of the half-width of absorption and emission bands.

In addition it was found that upon quenching of the ultraviolet emission above 200°K a strong F coloration of the crystals was observed. A study of this process is still in progress. No such coloration of the crystals was observed after prolonged stimulation of blue-green emission around room temperature. These observations suggest that the quenching of the blue-green emission process might be due to a direct "crossover" from the excited state to the ground state via nonradiative transitions.[15] Using the characteristic frequency $\nu_0=3.9\times10^{12}$ sec^{-1}, a one-frequency Franck-Condon model[7,12] has been constructed (Fig. 8) from experimental values[1,2] obtained at 77°K. The vibronic state parabolas of the ground state and the state giving rise to blue-green emission[10] (blue-green component) show a crossover with a ΔE very close to the observed value of $\Delta E=0.29$ eV. Considering that here the harmonic approximation has been used over a range of about 400 vibrational levels, or more than 6 eV, this was a rather unexpected result. We do not mean to imply that exact quantitative conclusions can be drawn from such a simplified one-dimensional model but we feel that qualitative features, like the crossover with the ground state, are certainly borne out. It might be added that a similar model for the state giving rise to the ultraviolet emission process would by far miss the ground-state parabola within an energy difference ΔE attainable through thermal vibrations of the system.

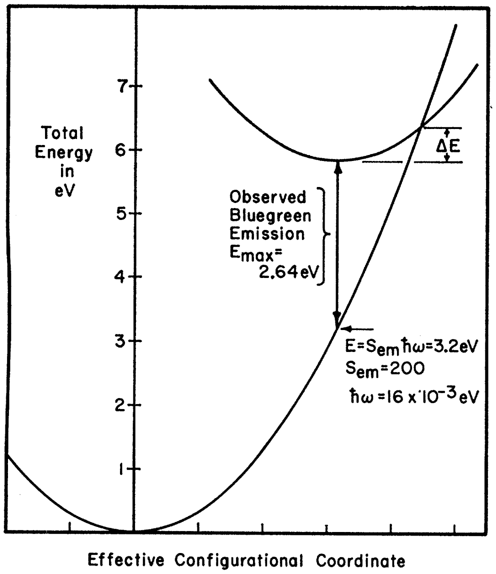

FIG. 8. Configurational coordinate model of the iodine center in KCl. The ground state and the excited state giving rise to the emission of blue-green light (large blue-green component) are traced using an effective frequency $\nu_0=3.9\times10^{12}$ sec^{-1} ($\hbar\omega=16\times10^{-3}$ eV) and a Huang-Rhys factor $S=200$, determined from absorption and emission studies.

Because of the indirect way of arriving at values of the lifetime of the ultraviolet emission a detailed discussion was not attempted. The radiative lifetime decreases only slightly in an intermediate temperature range and the final sharp decrease at higher temperatures has a slope indicating a quenching process over an energy barrier of $\Delta E=0.2$ to 0.3 eV.

ACKNOWLEDGMENTS

The authors would like to thank Professor R. O. Polh and J. Francis of the Crystal Growth Facility of Cornell University's Material Science Center for generously providing the high-purity single crystals used in the present experiments. The advice given by Professor P. L. Hartman and Dr. D. Frohlich during various stages of the experiments is greatly appreciated.

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[15] D. L. Dexter and C. C. Klick, Phys. Rev. **100**, 603 (1955).