PHYSICAL REVIEW VOLUME 135, NUMBER 2A 20 JULY 1964

Lifetime of the Excited F_A Center*

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(Received 12 March 1964)

Recent experimental results show that the radiative lifetime of the F center is as long as 0.58 μsec in KCl and 1.1 μsec in KBr. We now report similar pulsed luminescence and photoconductivity measurements on the F_A center in KCl and KBr. In these cases the radiative lifetimes are somewhat shorter as follows: KCl:Na, $\tau_R=0.53$ μsec; KBr:Na, $\tau_R=1.0$ μsec; KBr:Li, $\tau_R=1.0$ μsec. Although the F_A absorption band is double, only one emission band has been observed. A single radiative lifetime is found. The observed lifetimes and ionization energies of F_A centers are discussed and compared with the properties of F centers. The results suggest that the relaxed excited state of the F center is quite spread out in the lattice.

I. INTRODUCTION

CONSIDERABLE attention, both experimental[1,2] and theoretical,[3,4] has recently been given to the excited F center. The F center is a thoroughly studied defect in solids and should serve as a model luminescent center. It is one of the few cases where both the integrated absorption and radiative lifetime have been carefully measured. There exists, however, an observed discrepancy in these two quantities. Although a simple model consisting of an s ground state and a p excited state seems to apply, the lifetime of the excited state is observed to be about an order of magnitude larger than predicted on the basis of absorption strength.

Two possible hypotheses have been suggested[2] to explain the lifetime discrepancy. (a) The large lattice relaxation that is evidenced by a Stokes shift in emission alters the wave function of the excited state so that the overlap integral with the ground state is drastically reduced. This may come about by a size effect or through a change in symmetry. For example, it has been pointed out[3] that Jahn–Teller distortion of the lattice following excitation can produce matrix element effects which are sizable. (b) After absorption, the electron may drop into a lower excited but metastable state. One possibility is that this state has the same parity as the ground state; for example, the $2s$ energy level lies below the $2p$ in the relaxed lattice. Transitions to the ground state could then take place by thermal excitation to the $2p$ state or by violation of selection rules due to unsymmetrical lattice vibrations. In this case the radiative lifetime might be quite sensitive to changes in the environment of the F center.

One way of changing the immediate environment of the F center is to convert to the so-called F_A centers.[5–10] The F_A center is an F center with one of the six nearest neighbors replaced by a different, usually smaller, alkali ion. These centers are formed in doped, additively-colored crystals by illumination in the F band at a proper temperature near room temperature. The F_A center has two absorption bands but only one emission band.[11] It exhibits dichroic behavior in absorption but not in emission. The absorption characteristics of the center are undoubtedly explained by the fact that the excited wave function (p like) overlaps two different alkali ions in one of its three possible orientations. The two F_A bands have a Stokes shift which are different by about 20% so that on the basis of hypothesis (a) one might expect slightly different lifetimes. On the other hand, if hypothesis (b) were correct the lifetime of F_A centers might be very different than the lifetime of F centers because of different symmetry and the possibility of an altered local vibration.

In order to obtain a better understanding of both F and F_A centers, we have measured directly the lifetime of fluorescence and photoconductivity of the F_A center, as well as the efficiency of these processes as a function of temperature. This has been done in the following impurity-doped systems: KCl:Na, KBr:Na, and KBr:Li.[12] We plot our results in terms of the equations used in Ref. 2. New results are given for the F_A-center lifetime τ_R, the ionization energy ΔE and the frequency factor $1/\tau_0$. In addition, the emission spectrum for the F_A center in KBr has also been measured for the first time. These results are discussed with the aim of understanding the emission of the F center in detail.

II. EXPERIMENTAL DETAILS

The crystals were grown by the Kyropoulos method and were additively colored with potassium up to 10^{16} F centers per cm^3. The optical density of a typical specimen of KCl:Na is shown in Fig. 1 after conversion

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* Supported in part by the U. S. Air Force Office of Scientific Research Grant No. AF62-215.

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[12] KCl:Li appears to be an interesting and anomalous case. Work on this center is underway at the Physikalisches Institut der Technischen Hochschule, Stuttgart (private communication with Dr. F. Lüty).

from F to F_A centers by exposure in the F band at $-40°C$ in an optical cryostat. The conversion F to F_A for KBr:Na and KBr:Li was accomplished at room temperature. For KCl:Na and KBr:Na, care was taken to avoid the further products of the photochemical reaction, namely, the B center.[7] In KBr:Li the absorption band associated with the B center did not appear.

After recording the absorption spectrum to ensure that the conversion was almost complete, the crystal was transferred under safety light to a liquid-helium cryostat especially designed for fluorescence and photoconductivity lifetime measurements. As a further check, a second absorption spectrum was obtained following the measurement. During the experiment, an average of 100 light pulses fell on the specimen. Each light pulse contained about 10^{11} quanta in the F-band region; this means that a maximum of 10^{13} F_A centers can be destroyed. A very small change in the absorption spectrum results, of the order of a few percent.

The exciting light was a nitrogen spark of high intensity and 2×10^{-8} sec duration. The stability of light intensity was within 5%.[2] To detect fluorescence, an RCA-7102 photomultiplier was used with a CS 7-56 Corning filter which attenuates the visible and transmits near infrared radiation. Only the luminescence of the KCl:Na F_A center was observed since it lies within the spectral sensitivity of the photomultiplier. To excite the two bands of the F_A center in KCl:Na two different sets of filters were used which we denote by A_1 (Corning CS 4-94 and CS 3-66) and A_2 (Corning CS 4-94 and CS 4-64).

In the photoconductivity measurements the electric fields applied to the crystal were in the range from 2 to 9 kV/cm. Care was taken to apply the fields only at temperatures below $-100°C$ to avoid ionic polarization; if the field was applied at room temperature, very strong polarization effects were detected. The lifetimes of fluorescence and photoconductivity in KCl:Na were compared by applying a correction of 0.68°K for 1 kV/cm of applied field.[13] The integrated pulses, after amplification, were displayed on the screen of a Tektronix Type-517 oscilloscope and photographed. Then, with the aid of a projector, the beam deflection was plotted as a function of time on semilogarithmic paper. A convenient way of doing this is to determine the maximum pulse height and read displacements from this asymptotic value.[14] A correct choice of the maximum pulse height then gives a straight line. The slope of these plots gave the lifetime of the excited state of the F_A center. In this way the lifetime was measured as a function of temperature. The height of the pulses was a measure of the relative fluorescence or the quantum yield of photoconductivity.

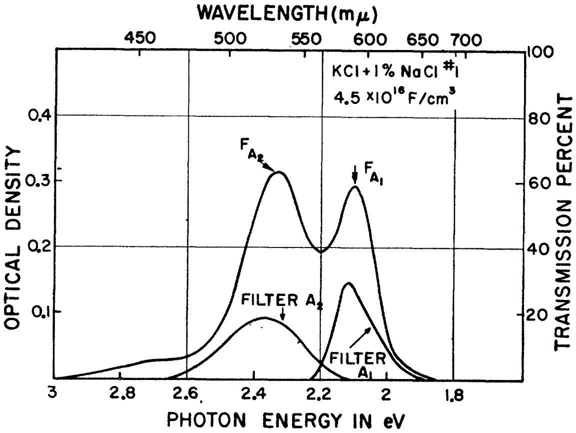

Fig. 1. Absorption spectrum for F_A center in KCl:Na at liquid-nitrogen temperature and transmission curves of the sets of filters used for exciting in the two bands (the scale to the left refers to the absorption of the crystal; the scale to the right refers to the transmission curves of the sets of filters).

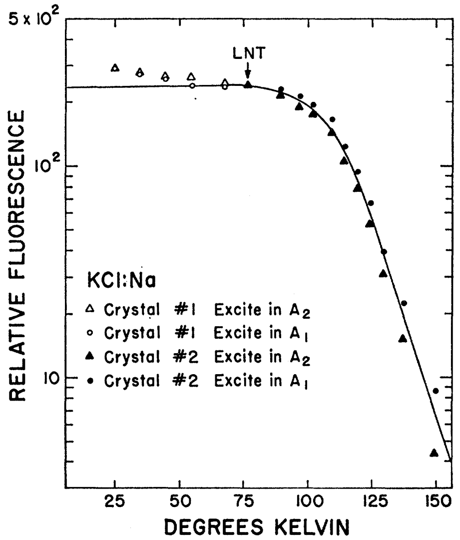

Fig. 2. Relative fluorescence of the F_A center in KCl:Na. (Sample No. 1 has 4.5×10^{16} F/cm^3; sample No. 2 has 2.7×10^{16} F/cm^3.) The solid line is theoretical.

The steady excitation luminescence spectra were obtained by analyzing the emitted light with a Perkin-Elmer infrared monochromator using a PbS cell cooled to dry-ice temperature as a detector. The exciting light was obtained by selecting the proper band from a 1000-W tungsten lamp with interference filters.

III. EXPERIMENTAL RESULTS

A. KCl:Na

In Fig. 1 we show the F_A bands in KCl:Na. Transmission curves of the two sets of filters A_1 and A_2, chosen to reject the band not under study, are also shown. In Fig. 2 the theoretical curve is a plot of the equation $1/\eta_R=1+(\tau_R/\tau_0)\exp(-\Delta E/kT)$,[2] where η_R

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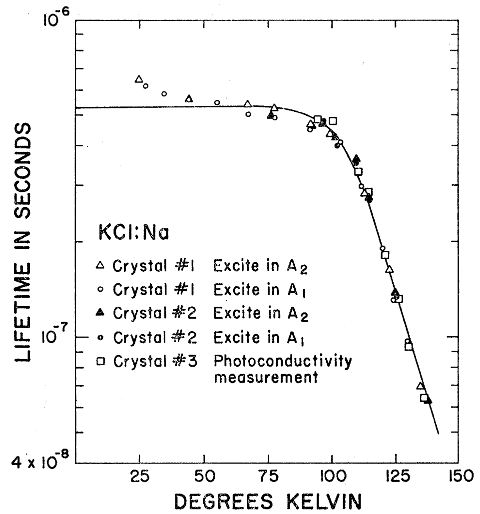

FIG. 3. Lifetimes of fluorescence and photoconductivity for the F_A center in KCl:Na. (Sample No. 1 has 4.5×10^{16} F/cm³; samples Nos. 2 and 3 have 2.7×10^{16} F/cm³.) The solid line is theoretical. In the photoconductivity measurement, the excitation was obtained using a Corning filter CS 4-94.

is the relative yield of fluorescence, τ_R the radiative lifetime, $1/\tau_0$ the frequency factor, and ΔE the ionization energy. Two sets of experimental points for η_R are shown corresponding to excitation in the F_{A_1} tnd F_{A_2} band. The two sets of measurements are normalized at 77°K. The values of the adjustable parameters which gave the best fit between theory and experiment are $\Delta E=0.137$ (±0.003) eV and $\tau_R/\tau_0=0.75$ $(\pm0.25)\times10^6$. The deviation of the experimental points from theory at low temperatures are thought to be connected with the shift of the luminescence band to higher energies with decreasing temperature; this shift happens in a wavelength region where the detector has a rapidly changing spectral sensitivity.

In Fig. 3 we see the lifetime of the excited state of the F_A center obtained by analyzing the shape of the luminescence and photoconductivity pulses at different temperature. The points from the photoconductivity measurements have been shifted in temperature, as mentioned above, to make them coincide with the luminescence lifetime data. In this figure, the lifetimes obtained from excitation in the two absorption bands are plotted, and it can be seen that they coincide within experimental error. This fact is consistent with previous results[11] which show that the maximum of the emission curve occurs at the same wavelength whether one excites in the F_{A_1} or the F_{A_2} band. The observed lifetime corresponds to the lifetime τ which is related to the probability for spontaneous emission $1/\tau_R$ and the probability for thermal ionization $1/\tau_i=(1/\tau_0)e^{-\Delta E/kT}$ by means of the equation $1/\tau=(1/\tau_R)+(1/\tau_i)$. Comparing these relations with experiment yields the following values: $\tau_R=0.53$ (±0.02) μsec, $\Delta E=0.122$ (±0.06) eV, and $1/\tau_0=0.70$ $(\pm0.15)\times10^{12}$ sec^{-1}. Here, as in previous work,[2] the ΔE given by fluorescence yield is of the order of 10% higher than the ΔE given by lifetime measurements. From the height of the pulses used to plot Fig. 3, we have obtained the yield of photoconductivity versus $1/T$; analysis of this data shows that $\Delta E=0.14$ (±0.005) eV and $1/\tau_0=3$ $(\pm1)\times10^{12}$ sec^{-1} (assuming $\tau_R=0.53$ μsec).

The B centers, when present, influence our measurements in the high temperature region, in a way similar to that reported for the effect of M centers on F-band data.[2] We measured the emission spectrum of the B center at 77°K exciting in the absorption band which peaks at 637 mμ. We found a broad emission band that has a maximum at ~1.24 μ; the half-width is ~0.3 eV.

B. KBr:Na and KBr:Li

In Fig. 4 we see the absorption spectra of KBr:Na and of KBr:Li at 77°K. The samples were prepared by quenching the colored crystal from 450°C on a copper plate and subsequently converting the pure F center to F_A by irradiating with F light at room temperature. This was carried out in a Cary Model-15 spectrophotometer using maximum slit width and a tungsten light source. Four minutes exposure time was necessary for KBr:Na and 40 min for KBr:Li.

In Fig. 5 the luminescence spectra of the F, F_A(Na) anf F_A(Li) centers in KBr are shown. Excitation using interference filters was carried out at 600 mμ for the pure F center and at 666 mμ for the F_{A_1} bands of the F_A(Na) and F_A(Li) centers.

The data obtained from the measurements shown in Figs. 4 and 5, together with the results of other authors[6,10] are given in Table I. We notice that in absorption the difference in energy between the peaks of the two F_A bands is greater in KCl than in KBr. Further, in KCl there is a greater difference between

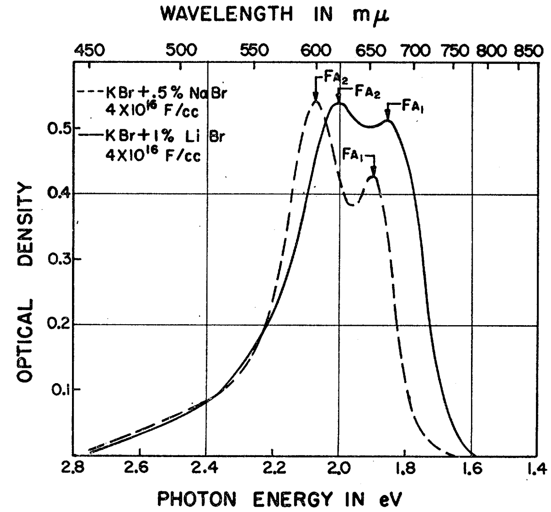

FIG. 4. Absorption spectrum for F_A center in KBr:Na and KBr:Li at liquid-nitrogen temperature.

TABLE I. Spectral position of the F and F_A absorption and emission bands in KCl and KBr.[a]

	F abs. peak	F_{A_1} abs. peak	F_{A_2} abs. peak	F emiss. peak	F_A emiss. peak
KCl:Na	2.30	2.105	2.348	1.22	1.11
KCl:Li		1.971	2.242		0.46[b]
KBr:Na	2.056	1.898	2.066	0.938	0.835
KBr:Li		1.842	2.003		0.785

[a] The values are in eV and the measurements are taken at liquid-nitrogen temperature.

[b] Private communication with Dr. F. Lüty.

the two F_A bands for Li than for Na; in KBr the opposite is true. In luminescence, the shift from the "pure" F to F_A(Na) and F_A(Li) emission bands is greater for KCl than for KBr.

The lifetime of photoconductivity in KBr for F_A(Na) and F_A(Li) together with those of the F center[2] are plotted versus temperature in Fig. 6. The lifetimes for F_{A_1} and F_{A_2} excitation were found to be coincident at 77°K as expected. This has been measured for both F_A(Na) and F_A(Li). The values for τ_R, ΔE, $1/\tau_0$ that we find from the analysis of the data of Fig. 6 are shown in Table II.

In Fig. 7 $[(1/\eta_i)-1]$ versus $1/T$ for F_A(Na) and F_A(Li) is plotted. This is done in terms of the equation[2] $[(1/\eta_i)-1]=(\tau_0/\tau_R)\exp(\Delta E/kT)$ where η_i is the yield of free electrons and the other quantities have already been defined. The data of Swank and Brown[2] on the F center are shown for comparison. Assuming $\tau_R=1$ μsec for F_A(Na) and F_A(Li) centers and 1.1 μsec for F centers we evaluate $\Delta E=0.142$ eV for the F center and 0.140 and 0.138 eV for F_A(Na) and F_A(Li) centers, respectively. Here too, the ΔE obtained from photoconductivity yield measurements are slightly higher than those obtained from lifetime of photoconductivity.

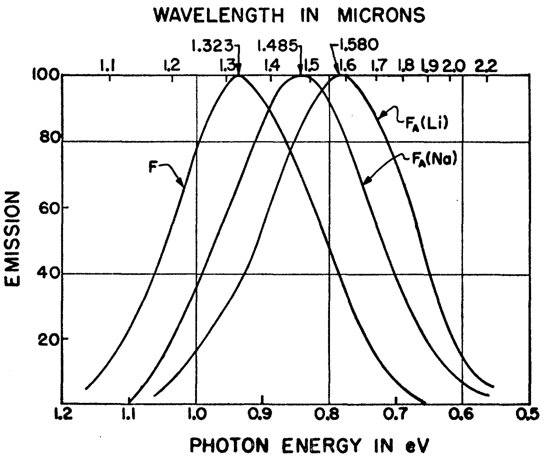

FIG. 5. Emission spectrum for pure F centers, F_A(Na) and F_A(Li) in KBr at liquid-nitrogen temperature. The exciting wavelength was 600 mμ for F center and 666 mμ for both F_A centers (selected with interference filters).

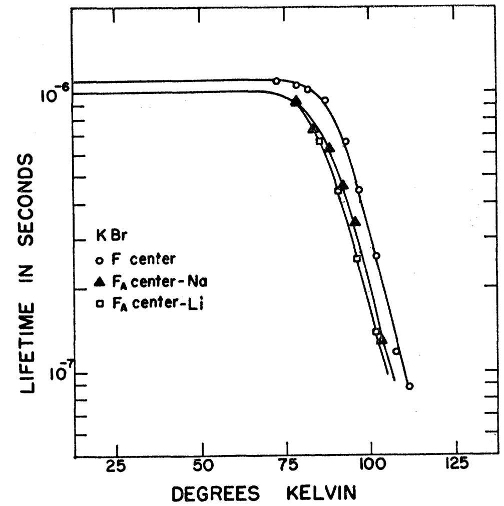

FIG. 6. Lifetime of photoconductivity for F (Ref. 2), F_A(Na), and F_A(Li) centers in KBr uncorrected for field effects. The fields were 2.5 kV/cm for the F centers, 2.5 kV/cm for F_A(Na), and 2.9 kV/cm for F_A(Li).

It should be pointed out that in the temperature region between 50 and 4.2°K a small, fast transient photocurrent appeared and increased with decreasing temperature. This has also been observed in the pure F system.[2] Qualitative measurements using infrared cutting filters indicate that this photoconductivity is excited on the long wavelength side of the F_A bands.

IV. DISCUSSION

The experimental results indicate that: (a) The radiative lifetime is equal, within experimental error, for excitation in both F_{A_1} and F_{A_2} bands in all cases studied. (b) The lifetime of the F_A center is somewhat shorter than that of the F center. (c) In the F_A case at low temperature, there is an increase in lifetime which is of the same order as that for the F center. (d) The different perturbing ion, namely, Na or Li, does not have any significant effect on the τ_R and ΔE of KBr. These

TABLE II. Radiative lifetime τ_R; depth of the excited state below the conduction band ΔE; frequency factor $1/\tau_0$ for the F and F_A centers.

	τ_R (μsec)	ΔE (lifetime) (eV)	ΔE (yield of fluor. or photoconductivity) (eV)	$1/\tau_0$ (lifetime) (10^{12} sec^{-1})
KCl-F[a]	0.577	0.143	0.157	1.12
KCl-F_A(Na)	0.53	0.122	0.138	0.70
KBr-F[a]	1.11	0.135	0.142	14.00
KBr-F_A(Na)	1.0	0.126	0.140	7.8
KBr-F_A(Li)	1.0	0.122	0.138	6.6

[a] The values for KCl-F and KBr-F are taken from Ref. 2.

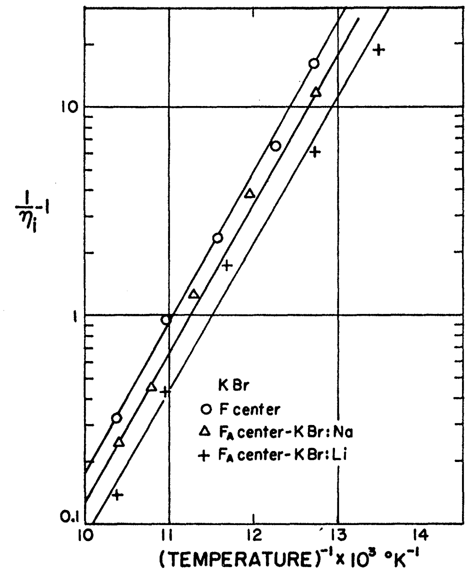

FIG. 7. Plot of $(1/\eta_i)-1$ from photoconductivity measurements for F_A(Na), F_A(Li), and F centers (Ref. 2) in KBr. These data are taken from the same pulses as Fig. 6. No correction for the field effect has been applied.

quantities have been found to be very similar in F_A(Na) and F_A(Li). (e) The ionization energy is equal for both excited states F_{A_1}* and F_{A_2}* and is slightly smaller than that of the F center. This has only been done carefully for F_A(Na) in KCl. (f) The $1/\tau_0$, main interacting frequency, is smaller for the F_A than for the F center. (g) The ionization energy obtained from the plot of fluorescence or photoconductivity yield, as well as $1/\tau_0$ which depends very strongly on ΔE, is higher than the ionization energy obtained from the lifetime of fluorescence or photoconductivity. This is also true for the F center where it was found that the ΔE determined by fluorescence efficiency is ~10% higher than the ΔE of lifetime measurements.[2] An average of the values of ΔE given by fluorescence efficiency[2] agrees very well with the ΔE given by photoconductivity yield.[15]

The model of the luminescent center used is not adequate to explain the effects described in (c) and (g).

The ΔE is very similar for F, F_A(Na), and F_A(Li); on the other hand, the difference in energy at the maxima of the emission peaks for these centers is appreciable. This means that the excited and relaxed level of the F center is not greatly perturbed by the disturbing ion, but the ground state after relaxation around the excited state has occurred, is nearer to the bottom of the conduction band, the lighter the perturbing ion. It is known from electron-spin-resonance data that the ground-state wave function is about 80% inside the vacancy. On the other hand, the excited and relaxed wave function is much more spread out on the neighboring ions, so that one can understand at least intuitively why the excited state is less affected by the Na or Li ion than the ground state.

Our results are in poor agreement with the metastable-state hypothesis (b). The presence of the foreign ion should destroy the inversion symmetry of the center. If the metastable excited level is of the 2*s* type in a cubic environment it should acquire some *p* character through mixing due to the perturbing impurity ion and to unsymmetrical local vibrations. The transition downward should become partially allowed and the lifetime substantially shorter. Going from F_A(Na) to F_A(Li) the amount of admixture of 2*s* and 2*p* should be different and consequently so should τ_R. However, in KBr at least, this does not appear to be the case. In addition, there are theoretical reasons[3] for supposing that the 2*s* level is not below the 2*p*.

Recent work has been done[16] on the determination of the configurational coordinates of the F center. Without employing a commonly used approximation, it was found that the shape of the F band is a "modified Gaussian"; the experimental points fitted the theoretical curve very well.

On the other hand, this approach gives a wrong emission energy for the F center. These authors[16] suggest that probably the level in emission is different from that involved in the absorption. This idea is also contained in the work of Fowler and Dexter[3] and might be considered as a matrix element effect. At present, however, it is not clear whether the difference between the absorbing and emitting level arises from symmetry changes or from simply a size effect. The results of our experiments indicate the latter. Considering the fact that the emitting level is very near (0.16 eV in KCl, F center) to the continuum, one would argue that the orbit of the electron is much larger before emission than just after absorption. Consequently, it is possible that the size effect is predominant in reducing the matrix element of emission. The larger size of the excited, relaxed wave function, which overlaps many lattice sites, would also explain why the lifetime is not very sensitive to substitution of a different alkali ion for one of the six nearest neighbors.

ACKNOWLEDGMENTS

The authors would like to acknowledge helpful discussions with Dr. W. B. Fowler, Dr. D. Y. Smith, Dr. F. Lüty, and Dr. R. K. Swank. Thanks are also due to Professor W. D. Compton and R. J. Spry especially in connection with the luminescence measurements.

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