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THE ELECTRONIC EXCITED STATE OF Pb^{++} IN KCl : IONIC REORIENTATION AND RADIATIVE LIFETIMES OF THE PHOTOSTIMULATED LUMINESCENCE

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Résumé. — On a diffusément étudié la réorientation de dipôles ioniques dans leur état électronique fondamental tels que, par exemple, les dipôles lacune-impureté dans les halogénures alcalins. Récemment un phénomène de réorientation a été observé même à très basse température quand les dipôles L. I. ont absorbé de la lumière, c'est-à-dire, quand ils se trouvent dans l'état électronique excité (e. e. e.). L'effet est dû à l'abaissement de la barrière ionique d'énergie, induite par l'excitation du système électronique (modèle à diffusion). D'après ceci on a écrit des équations dans le but de discuter les procès de réorientation qui ont lieu dans l'e. e. e. du Pb^{++} dans une structure ordonnée de dipôles L. I. (phase de Suzuki) dans KCl. L'efficacité de réorientation dans l'e. e. e. est thermiquement activée et sa distribution spectrale est étroitement liée au spectre d'absorption optique.

On a étudié les vies moyennes radiatives entre 78-300 K dans KCl : Pb soit quand Pb^{++} est lié à un défaut simple soit quand il fait partie de la phase complexe de Suzuki. On a trouvé trois vies moyennes différentes : deux d'entre elles sont indépendantes de la température, tandis que la troisième croît, lorsque la température baisse. Enfin on a analysé les spectres d'excitation et d'émission de photoluminescence dans KCl : Pb entre 20-300 K, en employant une très bonne résolution.

Abstract. — The reorientation of ionic dipoles in their electronic ground state (e. g. s.), such as, for example, Impurity-Vacancy dipoles in alkali halides, was extensively studied. Recently reorientation was found even at very low temperatures, when I. V. dipoles have absorbed light, i. e. when they are in the electronic excited state (e. e. s.). The effect is due to the lowering of the ionic energy barrier induced by the excitation of the electronic system (diffusion model). On this basis rate equations are written in order to discuss the reorientation processes which occur in the e. e. s. of Pb^{++} embedded in an ordered structure of I. V. dipoles (Suzuki phase) in KCl. The reorientation efficiency in e. e. s. is thermally activated and its spectral distribution is closely related to the optical absorption spectrum.

The radiative lifetimes in the temperature range 78-300 K are studied in KCl : Pb both where, Pb^{++} belongs to a simple defect (I. V. dipole) and in the complex Suzuki phase. Three distinct lifetimes were found ; two of them are temperature independent while the third one increases by decreasing the temperature.

The analysis of the excitation and the emission spectra of photoluminescence in KCl : Pb was performed in the range 20-300 K by using a very good resolution.

1. Introduction. — The reorientation of ionic permanent dipoles, for instance impurity vacancy (I. V.) dipoles in alkali halides, has been extensively investigated by using different techniques such as dielectric and mechanical losses and ionic thermoconductivity (ITC). All the works have dealt with the dipoles in which the impurity was in the electronic ground state (e. g. s.).

However if the impurity electron system can be raised to the electronic excited state (e. e. s.) by the absorption of proper light, one expects that the ionic reorientation parameters of the ionic dipole can be changed. In fact, as stressed by Slifkin [1] recently, if the electronic configuration (still in e. g. s.) changes, as it happens along the transition metal series, the ion motion parameters change as well.

In principle, when the impurity in the I. V. dipole is in e. e. s., one can expect that the activation energy

for the reorientation is lower than the one in the e. g. s., in analogy with the diffusion model proposed by Dreyfus [2] for the reorientation of the F_A centers induced by absorption of polarized light at very low temperatures. As a consequence the relaxation time of the dipole in e. e. s. τ_2 becomes shorter than that in the e. g. s. τ_1 and one can expect that the dipole in e. e. s. can be reoriented at such a low temperatures where its motion, in e. g. s., is hindered.

On this basis we investigated if the diffusion model holds also for divalent cation impurity centers in alkali halides, for instance, I. V. dipoles, which show a permanent electric dipole moment. If light induced reorientation in e. e. s. occurs, it can be monitored by means of ITC technique [3]. In a previous work [4] we showed that photostimulated disorientation of I. V. dipoles in KCl : Pb was possible at such a low temperatures where the relaxation time of I. V.

dipoles in e. g. s. is very long (10^7 - 10^8 s). In this work we are concerned with the heterogeneous occlusions which grow in KCl : Pb upon proper annealing. Due to the large amount of cation vacancies, polarization can be induced by an applied electric field : the thermally stimulated release of the frozen in polarization is responsible for an ITC peak at 278 K [9]. In this case the light induced excitation of Pb in e. e. s. is expected to lower the energy wall for the migration of cation vacancy rather than for the reorientation of the isolated I. V. dipole : actually we are dealing with a photostimulated diffusion of defects.

Both in the photostimulated reorientation of simple dipoles and in photostimulated diffusion, the barrier lowering induced by the excitation can be evaluated quantitatively from the reorientation experiments if the radiative lifetime of the lead excited state in various defect configurations is known as well.

On this purpose the luminescence emission spectra and lifetimes were studied by starting with the dilute solid solution containing the simplest defects such as I. V. dipoles and extending them to more complex environments as those which characterize the Suzuki phase.

2. Scheme of the experiment. — If one assumes that the dipole reorientation takes place through a diffusion activated mechanism both in the electronic ground state (e. g. s.) and in electronic excited state (e. e. s.), one introduces energy barriers ε_1 and ε_2 which separate two equivalent positions of the dipole in e. g. s. and in e. e. s. respectively (see Fig. 1a).

The relaxation times in e. g. s. and in e. e. s. can be written as :

$$\tau_1 = \tau_{01} \exp(\varepsilon_1/kT) \quad (1)$$

$$\tau_2 = \tau_{02} \exp(\varepsilon_2/kT). \quad (2)$$

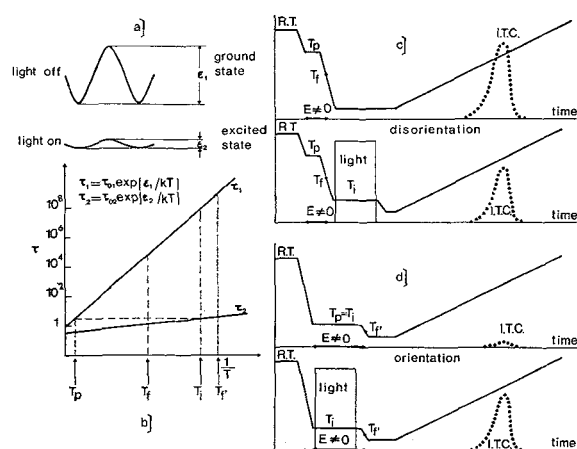


FIG. 1. — Scheme of dipole reorientation in e. e. s. : a) Energy wall which separates two equivalent dipole orientations in e. g. s. and in e. e. s. ; b) Semilogarithmic plot of τ_1 and τ_2 vs $(T)^{-1}$; c) ITC cycles in order to detect the disorientation of dipoles in e. e. s. at very low temperatures ; d) ITC cycles in order to detect the orientation process in e. e. s. at very low temperatures.

A semilogarithmic plot of τ_1 and τ_2 vs $1/T$ gives the straight lines of figure 1b.

The dipole reorientation in e. e. s. can be put in evidence through : a) disorientation and b) orientation experiments, by exploiting ITC versatility [3]. Both approaches are schematized in figure 1c and 1d respectively.

The upper part of figure 1c shows the usual ITC cycle in order to put in evidence the dipole orientation e. g. s.

1) The electric field E is applied at a temperature T_p where the relaxation time in e. g. s. τ_1 is short (Fig. 1b), in order to orient the dipoles up to the saturation value of the polarization, P_s given by

$$P_s(T_p, E) = \alpha N_d \frac{Ed^2}{kT_p} \quad (3)$$

where α is a geometrical factor depending on the possible orientations of the dipoles, N_d the dipole concentration and d the dipole moment in e. g. s.

2) The temperature is lowered to T_f , where τ_1 is very large (see Fig. 1b). Even if now the field is turned off, the previously induced polarization remains frozen in.

3) The sample is heated at linearly increasing temperature : in this way τ_1 becomes shorter and shorter. The dipoles gain mobility and the thermally stimulated depolarization current peak is detected. The area subtended under the peak gives P_s and hence N_d .

The subsequent scheme of figure 1c illustrates the photostimulated *disorientation*. Steps 1) and 2) are repeated, then the temperature is lowered to $T_i < T_f$ where $\tau_1(T_i)$ is extremely long (see Fig. 1b). The light absorbed by dipoles is turned on ; as a consequence the relaxation time drops from $\tau_1(T_i)$ to $\tau_2(T_i)$ (see Fig. 1b) and a fraction of dipoles, oriented during steps 1) and 2), is allowed to move towards random orientations.

The step 3) is then repeated in order to detect the fraction of still oriented dipoles. The area difference between the former ITC curve and the latter gives the concentration of dipoles which have undergone the photostimulated disorientation.

The dipole orientation in e. e. s. can be detected by means of ITC in a similar way (see Fig. 1d).

In a conventional ITC cycle, performed through steps 1), 2) and 3) by choosing $T_p \equiv T_i$ and $T_f = T_f$ (see Fig. 1d upper part) no appreciable ITC peak is detected : in fact $\tau_1(T_i)$ in e. g. s. is very long (see Fig. 1b) and the polarization induced by the electric field is negligible.

On the contrary when the step 1) is performed at $T_p \equiv T_i$, but with light on, the relaxation time drops to the value $\tau_2(T_i)$, which is short enough to allow the orientation of dipoles by the applied field. Then the light is turned off. During the subsequent step 3) an appreciable ITC peak, related to the photostimulated *orientation* of dipoles in e. e. s. is detected.

For the sake of simplicity the scheme of experiment and the reorientation kinetics analysis (see § 5) are discussed for simple non interacting dipoles, such as I. V. dipoles, however the whole picture holds in more general cases, for instance in the present one for the polarization phenomena connected with Suzuki phase occlusions [6]. Infact, as in the case of I. V. dipole reorientation, also in the present case the set up and/or the release of the polarization is characterized: 1) by a time constant or relaxation time τ , which is thermally activated [6]; 2) by a monomolecular first order kinetics; 3) by a linear relationship of the frozen in polarization vs the polarizing electric field up to relatively high fields [6].

3. Experimental details. — Due to the lack of space the experimental details are here omitted. We send the reader for the single techniques to the quoted references as follows.

For the reorientation experiments monitored by ITC, see [5]. For the lifetime measurements see [7]. The details concerning the high resolution emission and excitation spectra will be reported in a further paper. For the preparation of sample see [5] and [6].

4. Experimental results. — **4.1 « REORIENTATION » EXPERIMENTS IN THE E. E. S., MONITORED BY ITC.** — In this part we are concerned with the heterogeneous phase occlusions induced by Pb^{++} in KCl [6]. The occlusions are an ordered arrangement of I. V. dipoles in n. n. n. coordination (Suzuki phase [8]). They are responsible for the Maxwell-Wagner relaxations, which can be detected by means of ITC technique. The related ITC peak (B band) is located in the high temperature side with respect to the I. V. dipole peak ($T_{M,I.V.} = 222$ K) (see for instance Fig. 2).

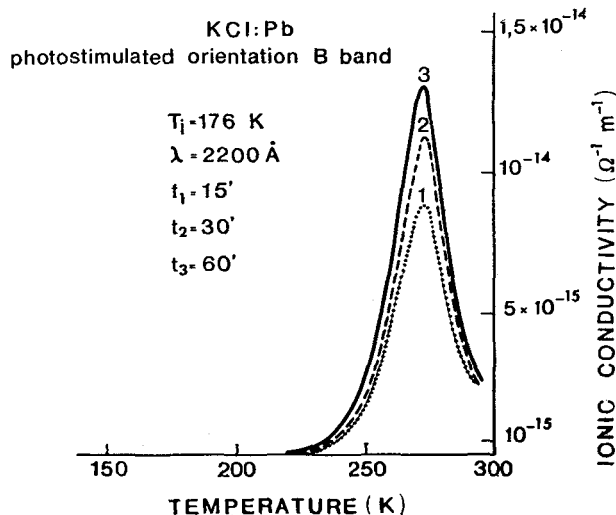


FIG. 2. — Photostimulated orientation for ITC-B band in KCl : Pb (1.7×10^{-4} m. f.) for different light doses.

The activation energy, which characterizes the relaxation, was determined from the ITC plot in the usual ways [3]. The value found, 0.7 eV, agrees with

the activation energy for cation vacancy motion in KCl [9], supporting the hypothesis that ITC B-band originates from the thermally activated displacement of cation vacancies within the Suzuki phase. The presence of the Suzuki phase occlusions, which grow at expense of I. V. dipoles by annealing at high temperatures, also modifies the optical absorption bands [6]. The well known A, B and C optical absorption bands [10] decrease, while a more complex spectrum grows (see for instance Fig. 4, full line). Moreover a strong light scattering, which is an increasing function of the frequency, overlaps to the optical absorption spectrum.

The KCl (with Pb^{++} occlusions) system, even if it is more complex than the simple I. V. dipole, is suitable to test the expected lowering of the energy wall for the ionic motion whenever the Pb^{++} electronic system is in an excited state. Infact: 1) The Pb^{++} electronic system can be excited by absorption of u. v. light in a wide spectral range (see Fig. 4 full line); 2) the ionic motion (specifically the cation vacancy motion) biased by the applied electric field at a suitable temperature, induces a polarization which can be thermally relaxed in absence of the field, as shown by the ITC B-band.

Disorientation and orientation experiments were performed at $T_i = 176$ K by shining the sample with 2200 Å light. In figure 2 the ITC B-band growth upon the contemporary application of the electric field and of the U. V. light is shown for different light doses (orientation). The induced polarization (orientation) and the still surviving polarization (disorientation) are function of the light dose and of the temperature T_i , at which the irradiation is performed: these results are summarized by figure 3, where the wavelength used was 2200 Å.

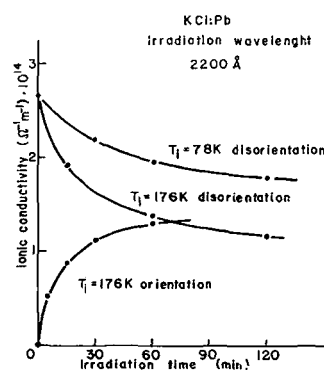


FIG. 3. — Photostimulated orientation and disorientation process versus the light dose at different irradiation temperatures.

The spectral efficiency of the disorientation process was also investigated, see figure 4. The light in the spectral range between 2400 and 2900 Å was particularly efficient in reducing the previously frozen in polarization. On both sides of this range an efficiency fall was observed: it was complete in the visible

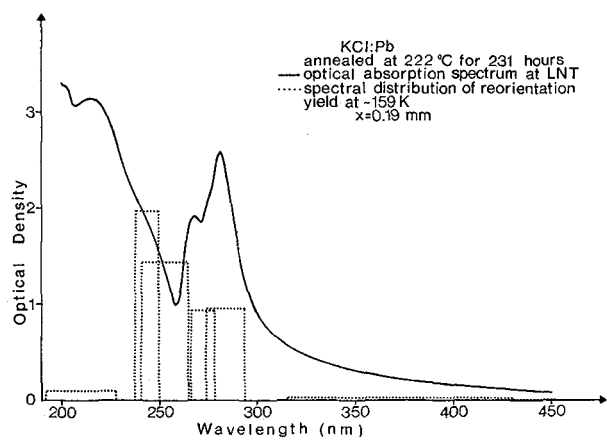


FIG. 4. — Optical absorption spectrum for KCl : Pb containing Suzuki phase (full line). The dotted rectangles are related to the spectral disorientation yield at 159 K. The rectangle basis is related to the filter pass band.

range, as expected, due to the lack of absorption. The fall of disorientation efficiency in the low wavelength side, where the light is strongly absorbed, rules out the possibility that the observed effect is ascribed either to radiation damage or to photoelectric effect.

Optical absorption spectra taken before and after the irradiation with u. v. light ruled out any optical bleaching of the absorption bands, which in principle could be responsible for the observed decrease of ITC B-band.

4.2 PHOTOLUMINESCENCE EXCITATION AND EMISSION SPECTRA. — The absorption, excitation and emission spectra were studied in the temperature range between 78 and 320 K, chiefly for very diluted solid solutions ($4 \div 6$ ppm) quenched in order to obtain only I. V. dipoles.

The excitation in the A-lead band induces the well known emission at 3390 \AA at LNT and 3350 \AA at RT, whose half-width broadens from 0.262 eV at LNT to 0.499 eV at RT and whose intensity weakens.

No appreciable differences are detected both in the emission and excitation spectra by changing the wavelength ($4 \div 10 \text{ \AA}$ bandwidth) either of the exciting or of

the emitted light respectively, notwithstanding the high resolution used.

However the emission band is slightly asymmetric and the excitation spectrum does not coincide, at least at LNT, with the A-absorption spectrum, being the former wider than the latter. A careful analysis of the shape of the emission band shows that at low temperatures ($T < 120 \text{ K}$) two gaussians are responsible for the peak, while at higher temperatures a third one starts to grow on the high energy side.

The study of the excitation and emission spectra of samples containing Suzuki phase occlusions have been done in a preliminary way. The spectra appear more complex and their detection and interpretation become rather difficult due also to the overlapping of light scattering. However by exciting in the A band region, emission in the region of 3400 \AA was found as well, hence allowing the measurement of the lifetime, whose knowledge is of key importance for the interpretation of the photostimulated diffusion, see § 5.

4.3 LIFETIMES. — In very diluted samples the time decay of the luminescence excited in the A band and emitted in the region of 3400 \AA was studied as well as a function of the temperature. The signal detected was a complex function of the time. A careful analysis allowed to distinguish three exponential decays, hence three lifetimes $\tau_{r,1}$, $\tau_{r,2}$ and $\tau_{r,3}$. Two of them were rather short and practically independent of the temperature, while the third one, which was the longest, was strongly dependent on the temperature and increased by decreasing the temperature. The intensity and lifetime of the decays are summarized in table I.

For samples containing Suzuki phase occlusions (see above) three lifetimes were found as well with a behaviour roughly similar to those related to the diluted solid solutions. However the temperature dependent lifetime was slightly longer than the one related to the simpler I. V. dipole see figure 6.

5. Discussion. — If the diffusion model holds for the reorientation of dipoles in e. e. s., the disorientation process induced by the light at a given tempera-

TABLE I

Photoluminescence for I. V. dipoles : excitation in A band, emission in the 3400 \AA region. Thermal stability, temperature dependence and length of the lifetimes τ_r and luminescence intensity of the three observed decays.

Decay	Temperature range in which the decay is detected	Temperature dependence of τ_r	Length of τ_r (ns)	Intensity (on increasing T)
1	$80 \text{ K} < T < 280 \text{ K}$	independent	~ 30	decreases
2	$140 \text{ K} < T < 280 \text{ K}$	independent	~ 160	increases
3	$80 \text{ K} < T < 300 \text{ K}$	increases on increasing T	230 at $\sim 300 \text{ K}$ 2×10^4 at $\sim 80 \text{ K}$	const. for $T < 250 \text{ K}$ increases for $T > 250 \text{ K}$

ture T_i is described by a simple rate equation, as in the case of dipole disorientation in e. g. s., i. e. :

$$\frac{dn_{or}}{dt} = -\frac{n_{or}^{exc}(t)}{\tau_2(T_i)} \quad (4)$$

where $n_{or}(t)$ is the concentration of still oriented dipoles $n_{or}^{exc}(t)$ is the concentration of still oriented dipoles which are in the electronic excited state, due to the light absorption and $\tau_2(T_i)$ is the relaxation time in e. e. s. (see § 2). $n_{or}^{exc}(t)$ is given by :

$$n_{or}^{exc}(t) = n_{or}(t) \cdot F(\lambda, T_i) \cdot \tau_r(T_i) \quad (5)$$

where $\tau_r(T_i)$ is the radiative lifetime of the e. e. s. at the temperature T_i and $F(\lambda, T_i)$ is the probability per unit of time that a photon of wavelength λ is absorbed by a dipole and causes the population of the e. e. s. of the dipole.

$F(\lambda, T_i)$ depends : 1) on the optical properties of the sample, such as optical absorption coefficient $\mu(\lambda, T_i)$ and reflectivity $R(\lambda)$; 2) on the transparence of the interference filter $\mathcal{C}(\lambda)$; 3) on the source intensity $I(\lambda)$ which is supposed time independent and 4) on the number of dipoles effectively struck by light \mathcal{N} . In principle $F(\lambda, T_i)$ depends on the temperature T_i through the absorption coefficient μ . A more intricate temperature dependence can be expected if the excited levels are populated with a different probability and through different channels for different T_i , as in the case of KI : Tl [11].

By taking into account that at $t = 0$ the number of oriented dipoles is given by

$$n_{or}(0) = \frac{P_s(T_p, E)}{d} = \frac{\alpha N_d E d}{k T_p} \quad (6)$$

(see eq. (3)), one finds :

$$n_{or}(t) = \frac{N_d \alpha E d}{k T_p} \exp \left[-\frac{\tau_r(T_i)}{\tau_2(T_i)} \cdot F(\lambda, T_i) \cdot t \right] \quad (7)$$

Hence the concentration of still oriented dipoles depends on the light dose (through $F(\lambda, T_i) \cdot t$), on an ionic motion parameter such as $\tau_2(T_i)$ and on a parameter related to the nature of electronic transition, such as the radiative lifetime $\tau_r(T_i)$.

The exponential dependence of $n_{or}(t)$ on the light dose (or on irradiation time t) expected by (7) is verified by our experimental results (see Fig. 3 curves b and c).

Both eq. (7) and experimental results of figure 3 indicate that the disorientation process in e. e. s. depends on the temperature T_i at which the irradiation is made. A better insight on this point is obtained through a rearrangement of (7). For a fixed light dose of a fixed wavelength λ^* and under the hypothesis that $F(\lambda, T_i)$ does not depend on T_i , i. e. $F(\lambda^*, T_i) \cdot t^* = D = \text{const.}$, one has :

$$\ln [-\ln \tilde{n}(T_i)] = \ln [\tau_r(T_i)/\tau_2(T_i)] + \ln D \quad (8)$$

where $\tilde{n}(T_i)$ is the fraction of still oriented dipoles after the sample has been shined with the fixed light dose D at the temperature T_i , i. e.

$$\tilde{n}(T_i) = n_{or}(t^*) \left/ \frac{\alpha N_d E d}{k T_p} \right.$$

In the frame of diffusion model, the temperature dependence of τ_2 is given by (2). In order to discuss eq. (8), two simple cases can be taken into account :

- 1) τ_r is temperature independent, i. e. $\tau_r = \tau_{o,r}$ and
- 2) τ_r is temperature dependent in a simple way, i. e.

$$\tau_r(T_i) = \tau_{o,r} \exp \varepsilon_r/kT_i \quad (9)$$

From (2) and (9) one can rewrite (8) as :

$$\ln [-\ln \tilde{n}(T_i)] = \ln (\tau_{o,r} D/\tau_{o,2}) + \frac{\varepsilon_r - \varepsilon_2}{kT_i} \quad (10)$$

The former case is contained in (10) if one assumes $\varepsilon_r = 0$. In both cases a semilog plot of $[-\ln \tilde{n}(T_i)]$ vs $1/kT_i$ gives a straight line whose slope is $-\varepsilon_2$ in the former case and $\varepsilon_r - \varepsilon_2$ in the latter.

In this way the study of disorientation efficiency vs. T_i coupled with the measurement of the temperature dependence of radiative lifetime allows to evaluate the energy barrier for ionic motion in e. e. s. Figure 5 shows the semilog. plot of $-\ln \tilde{n}(T_i)$ vs. $1000/T$ for the experimental results obtained from disorientation measurements on B band (with $\lambda = 2850 \text{ \AA}$ and $t^* = 60'$).

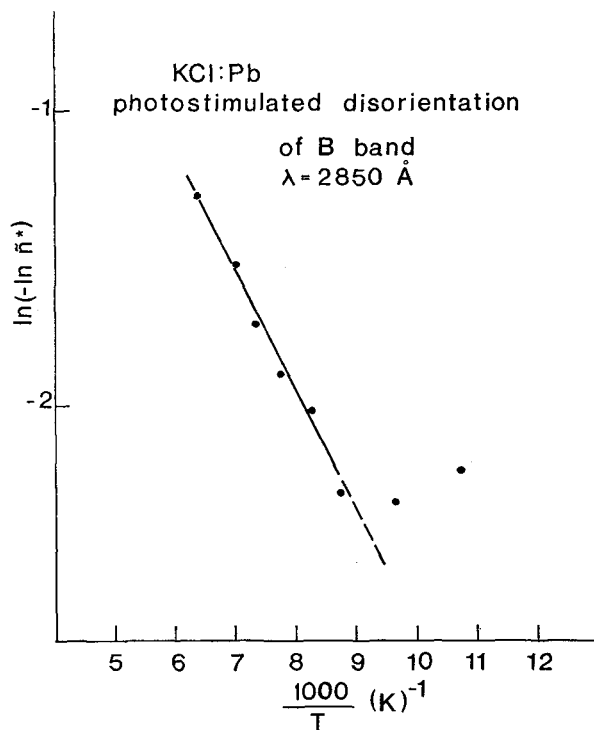


FIG. 5. — Photostimulated disorientation of ITC-B band as a function of the irradiation temperature.

In the temperature range $107 \text{ K} \leq T_i \leq 176 \text{ K}$ a straight line is observed indicating that the photostimulated reorientation occurs through the proposed diffusion model. At lower temperatures, the experimental points are far from the straight line. The departure from the straight line can be accounted for, if one considers : 1) a more complex dependence of τ_r on T_i and or 2) the dependence of $F(\lambda, T_i)$ on T_i , which was assumed constant for the sake of simplicity (see above). However the observed temperature dependence of the lifetime reported in figure 6, does

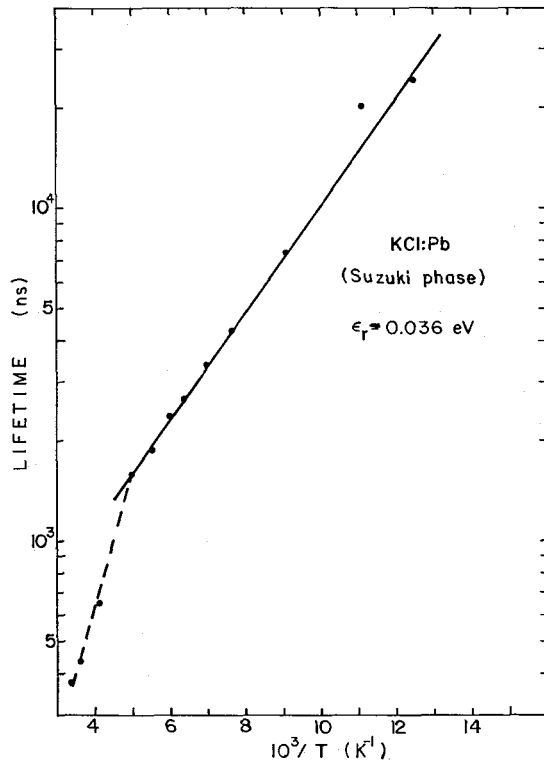


FIG. 6. — Temperature dependence of the longest radiative lifetime $\tau_{r,3}$ detected by exciting in A band the emission in the 3 400 Å region in KCl : Pb with Suzuki phase.

not show any abrupt change which can directly account for the anomalous behaviour of disorientation yield at low temperature. The explanation of this can be found in the excited level population, which can change with the temperature or in the existence of long-lived excited levels which can escape the detection by the apparatus built for the analysis of very fast decays.

Of course in samples with Suzuki-like phase occlusions a complex situation is expected and more than one effect can concur to the deviation. From the above preliminary lifetime measurements and from the yield of disorientation one can try to estimate roughly from eq. (10) the activation energy for *reorientation* in e. e. s. : it turns out 0.07 eV. In this way the barrier in e. e. s. decreases of nearly a factor of ten with respect to that in e. g. s.

As shown by the experimental results, the overall picture of the spectral distribution and of the time behaviour of the lead photoluminescence turns out to be complex yet in the case of simple I. V. dipoles, where three lifetimes and, possibly, three overlapping emission bands were found. Actually a structure in the emission spectra is expected both due to the presence of the charge compensating vacancy and due to the Jahn-Teller effect.

In fact the excited state from which A emission takes place consists of two different adiabatic potential energy surfaces (APES) called ${}^3T_{1u}$ and ${}^3A_{1u}$ that originate respectively from the atomic states 3P_1 and 3P_0 . The ${}^3A_{1u}$ APES is characterized by equivalent minima and the transition from these minima to the ground state could be responsible for the component strongly temperature dependent. This transition forbidden in principle could be in part allowed as suggested in [13]. The three minima on ${}^3T_{1u}$ APES are no longer equivalent due to the presence of the vacancy [12] which lowers the symmetry : two minima (which we call M_1) remain unchanged while the third one (which we call M_2) is shifted in energy (the reverse can occur as well). The transition from the minima M_1 to the ground state is allowed and one can associate the shortest lifetime $\tau_{r,1} = 30 \text{ ns}$; the intermediate lifetime $\tau_{r,2} = 160 \text{ ns}$ can be tentatively attributed to the decay from M_1 minima which are populated through a tunneling process from M_2 minima. $\tau_{r,2}$ is practically accounted for by the tunneling time.

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DISCUSSION

N. ITOH. — Is there any possibility that your experimental result could be understood on the basis of the enhancement of the dipole orientation because of the local mode excitation due to the non-radiative recombination ?

R. CAPELLETTI. — In principle the *hot spot* model could explain the photon induced reorientation, however, the dependence of the process on the temperature should be rather weak. In our case the reorientation (disorientation) turned out to be thermally activated as expected for a *diffusion model*.

J. DURAN. — 1) Have you tried some experiments using polarized light for pumping the crystal ?

2) I ask for this question because I cannot see the implications of the Jahn-Teller effect in your reorientation model. Could you comment on the way the orientation of the electronic orbitals via the J. T. effect could play a role in the model which you suggest ?

R. CAPELLETTI. — 1) Up to now we have not performed irradiation with polarized light, but we planned to do it.

2) Obviously the preferential orientation of the electronic orbitals can affect the reorientation yield.