G. G. Liĭd'ya. *Decay of Triplet-State Luminescence of the Autolocalized Exciton ($X_2^{2-}$ Quasimolecule) of Alkali Halide Crystals in a Magnetic Field.* The excited quasimolecule $X_2^{2-}$, where X = I, Br, Cl, or F, appears in alkali halide crystals (AHC) either on relaxation of an exciton or as a result of recombination of an electron with a $V_k$ center. Kabler established in[1] that the broad (~0.4 eV) longwave band in the luminescence of pure AHC is emitted by quasimolecules from the triplet state $^3\Sigma_u^+$. The $^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ transition is allowed by virtue of an admixture of the singlet $^1\Pi_u$, which is governed by spin-orbital interaction. In a $D_{2h}$ local symmetry field, the triplet splits into a pair of nearly degenerate radiative levels $b$ ($B_{2u}$, $B_{3u}$) and a metastable level $a$ ($A_u$). We have established that the quenching of luminescence at low temperatures consists of two exponential components,[2] study of whose temperature dependence[3] made it possible to determine the probabilities of the radiative transitions $p_{bg}$ and $p_{ag}$ to the ground state $g$, the probabilities of nonradiative transitions $p_{ba}$ and $p_{ab}$ between the components of the triplet, and the energy splitting $E_{ab}$. At low temperatures, $kT \lesssim E_{ab}$, the nonradiative transitions are single-phonon and $p_{ba} = p_0(1+\bar{n})$, $p_{ab} = 2p_{20}\bar{n}$, where $\bar{n} = [\exp(E_{ab}/kT) - 1]^{-1}$. Table I gives certain parameters for KI and KBr.

The magnetic field $H$ mixes the components of the triplet and shifts the corresponding levels. The electron transition probabilities change, and this is reflected in the luminescence kinetics, which was studied

TABLE I.

| Crystal | $E_{ab}/k$, °K | $p_{bg}$, sec$^{-1}$ | $p_{ag}$, sec$^{-1}$ | $p_0$, sec$^{-1}$ |
|---|---|---|---|---|
| KI | 7.9 | $0.88 \cdot 10^6$ | $< 10^4$ | $0.98 \cdot 10^6$ |
| KBr | 0.35 | $1.27 \cdot 10^4$ | $0.17 \cdot 10^4$ | $7 \cdot 10^2$ |

by Kabler[7,8] and by this author.[9,10] The change in the radiative-transition probability reduces to mixing of wave functions (the change in the transition energy $\Delta E_{bg} \approx g\mu_B H \ll E_{bg}$ makes practically no contribution). The change in the probabilities of the radiative transitions reduces to two effects: 1) shifting of levels, which is taken into account by the factor $P_{ij} \sim E_{ij}^3(1+\bar{n})$, and 2) a change in the nature of the electron-vibrational interaction.[9,10] Usually, only the former effect is taken into account (see, for example,[7,8]).

In the case of KI, where single-phonon nonradiative transitions predominate at 4.2 °K ($kT < E_{ab}$), the latter effect asserts itself in the decay kinetics. At $H = 0$, the transitions $A_u \leftrightarrow B_{2u}$, $B_{3u}$ are induced by the vibrations $B_{2g}$ and $B_{3g}$, and the fully symmetric $A_g$ vibrations, which are characterized by a large coupling constant, do not contribute to $p_0$. When $H \neq 0$, the $A_g$ vibrations result in a rapid increase in the probabilities of nonradiative transitions between the components of the triplet, which contain parts of identical symmetry that appear and increase with the magnetic field. Curve 3 in Fig. 1, which approximates the experimental $H$-dependence of the decay time of the long luminescence component in KI, merges smoothly with curve 1, which was calculated without consideration of effect 2), into curve 2, which was calculated for the thermal-equilibrium ($p_{ab}$, $p_{ba} \gg p_{ag}$, $p_{bg}$). The only parameter determined from experiment (the difference of the diagonal elements of the perturbation matrix $(\partial E_{ij}/\partial Q_{ij})Q_{ij}$, where $Q_{ij}$ is the local coordinate of the vibration) give a good description of the decay of the two components and the various orientations of the field.[10]

In the case of KBr, where $E_{ab}/k = 0.35$ °K and multiphonon transitions predominate even at 2 °K, the decay

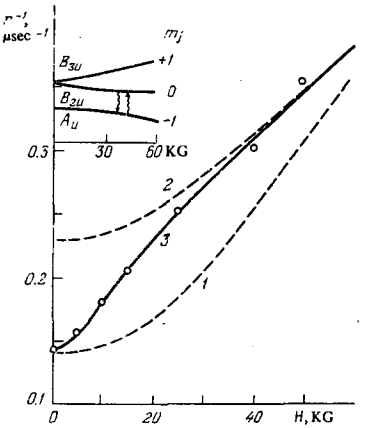


FIG. 1. Decay time of triplet luminescence in KI vs. magnetic field intensity H ∥ [001] at 4.2 °K. The plotted points represent experiment for the slow damping component. The significance of the theoretical curves (1–3) is explained in the text. The splitting of the $^3\Sigma_u^+$ term for $I_2^-$ molecules whose axes form 45° angles to H is indicated in the upper-left corner.

in the magnetic field is described on the basis of the simple theory (effect 2) is not taken into account).[10]


[1] M. N. Kabler and D. A. Patterson, Phys. Rev. Lett. 19, 652 (1967).
[2] R. A. Kink, G. G. Liid'ya, and T. A. Soovik, Opt. Spectrosk. 30, 279 (1971).
[3] P. A. Kask, R. A. Kink, G. G. Liid'ya, and T. A. Soovik, *ibid.* 37, 942 (1974).
[4] P. A. Kask, R. A. Kink, G. G. Liid'ya, and T. A. Soovik, Izv. Akad. Nauk SSSR, Ser. Fiz. 38, 1264 (1974).
[5] P. Kask and T. Soovik, Izv. Akad. Nauk EstSSR, Ser. Fiz. Matem. 23, 291 (1974).
[6] J. V. Fischbach, D. Fröhlich, and M. N. Kabler, J. Luminescence 6, 29 (1973).
[7] M. N. Kabler, M. J. Marrone, and W. B. Fowler, Izv. Akad. Nauk SSSR, Ser. Fiz. 37, 341 (1973).
[8] W. B. Fowler, M. J. Marrone, and M. N. Kabler, Phys. Rev. B8, 5909 (1973).
[9] P. Kask, V. Mihkelsoo, and T. Soovik, ENSV TA Toimetised, füüs. mat. 24, 230 (1975).
[10] P. A. Kask, G. G. Liid'ya, V. T. Mikhkel'soo, and T. A. Soovik, Tr. IF Akad. Nauk EstSSR 45, 5 (1976).