

Ultrafast vibrational relaxation and hot luminescence of Tl^+ centers in KI

G. S. Zavt, V. G. Plekhanov, V. V. Khizhnyakov, and V. V. Shepelev
Institute of Physics, Academy of Sciences of the Estonian SSR, Tartu

(Submitted 29 June 1982; resubmitted 20 August 1982)

Pis'ma Zh. Eksp. Teor. Fiz. **36**, No. 7, 235–238 (5 October 1982)

Hot luminescence bands are observed in KI–Tl crystals. These bands are interpreted as emission from the first classical turning point in the process relaxation of the configurational coordinate, which represents a complex nonmarkovian process with scale time ~ 0.5 ps.

PACS numbers: 78.60. – b, 63.75. + z

1. Single-atom impurity centers in ionic crystals are characterized by strong vibronic interaction with nearest neighbor ions and high energy and high rate of vibrational relaxation.¹ The study of this relaxation process is of interest as an example of a nonmarkovian process in a simple but nontrivial system, which cannot be understood in terms of kinetic equations. Moreover, the generalized Nakadzhim and Zvanzig kinetic equations are not applicable here either, since it is impossible to define the initial state: Because of the high relaxation rate, the creation of the nonequilibrium state and its relaxation overlap in time. An adequate approach here is an examination of the vibrational relaxation as the phonon response to the exciting pulse, i.e., including in the analysis interaction of the center with the photon packet and the dispersion (dephasing) of the phonons caused by this interaction.² Using this approach, we investigated the vibrational relaxation in the excited (3p) state of Tl^+ centers in KI and its manifestation in the hot luminescence (HL) spectrum.

2. In the centers being examined, the width of the HL spectrum is large compared to the characteristic phonon frequency ($\bar{\omega}$). This allowed us to restrict the analysis to the envelope of the spectrum, which is described by the following equation for the pulsed quasimonochromatic excitation with frequency ω_1 (Ref. 2)

$$I(\omega, t) = \int dq \rho(q, t) \delta(\omega - V_q). \quad (1)$$

Here $V_q = H_1 - H_0$ is the difference in the vibrational Hamiltonians of the excited and ground electronic states, $\hbar = 1$; q is the configurational coordinate chosen in such a way as to take into account exactly the linear part of the vibronic interaction $V_q^{(0)} = V_0 + aq$;

$$\rho(q, t) = \text{const} \int_0^\infty d\tau \Delta_\tau^{-1/2} \exp\left[-\gamma\tau - \frac{(q - q\tau)^2}{2\Delta_\tau}\right] I(t - \tau) \quad (2)$$

is the distribution of q at time t ; γ is the damping constant of the excited state; $q_{0n} = q_n + (\omega_1 - V_0) \langle \{q_n, q\} \rangle_0 / 2a \langle (q - q_0)^2 \rangle_0$, where $q_n = \langle q(t) \rangle_0$ is the classical relaxation of the configurational coordinate $\langle q(t) \rangle_n = \exp(itH_n) q \exp(-itH_n)$; $n = 0, 1$; $\hat{q}_t = q(t)_1 - q_t$, and $\Delta_t = \langle \hat{q}_t^2 \rangle_0 - \langle \{ \hat{q}_t, q \} \rangle_0^2 / 4 \langle (q - q_0)^2 \rangle_0$ is the dispersion of the in-

stantaneous distribution of q ; $\langle \hat{q}_t^2 \rangle$ is the temporal behavior of the quadratic fluctuation of the configuration coordinate; $\langle \{ \hat{q}_t, q \} \rangle_0$ is the correlation function for excitation of oscillations and their relaxation; and $I(t)$ is the intensity of excitation at time t [with stationary excitation $I(t) = \text{const}$]. The distribution function (2) and spectrum (1) are expressed exactly² in terms of the Fourier transform [$G(\omega)$] of the vibrational Green's function $G(t) = -i_\rho(t) \langle [q(t)_0, q] \rangle_0$, including the linear and quadratic vibronic interaction. The calculations were performed in the model for interaction with nearest neighbors. The shell model was used to describe the dynamics of the system.

3. Equations (1) and (2) are valid for nondegenerate electronic states. In the centers being examined, in the initially totally symmetrical configuration, the excited ${}^3T_{1u}$ level is three-fold degenerate and strongly interacts with a_{1g} , e_g , and t_{2g} vibrations. However, during the relaxation the degeneracy is removed due to the Jahn-Teller effect. For this reason, if the small part of the radiation spectrum which overlaps with absorption is ignored (i.e., resonant Raman scattering), then the basic effect of degeneracy reduces to the possibility of relaxation along different channels, leading to the existence of tetragonal (T) and trigonal (X) distortions of the center³ and two (A^T and A^X) luminescence bands [transitions 1 and 2 in Fig. 1(c)]. Thus, it is necessary to sum two relaxation channels and, in addition, in the T channel relaxation occurs due to the interaction with a_{1g} and e_g vibrations of the lattice, while in the X channel with ca_{1g} and t_{2g} vibrations. In addition, it is necessary to take into account the fact that each minimum of the adiabatic surface (AS) of the 3p state contains an emitting doublet

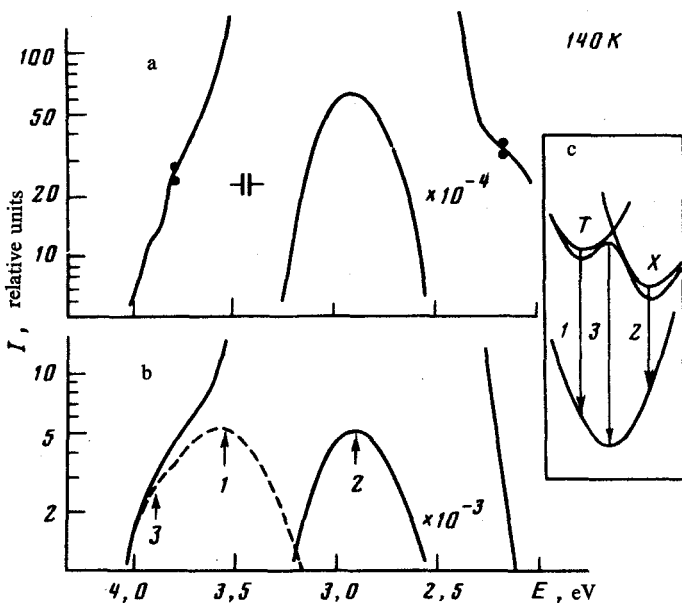


FIG. 1. Emission spectra [experiment (a), theory (b)] and cross section (c) of the adiabatic surface of the ground and excited states along the line connecting the tetragonal (T) the trigonal (X) minima. The dashed line represents the spectrum of the total 1 + 3 emission, calculated in a model with sinusoidal form of the cross section of the emitting sheet of the adiabatic surface.

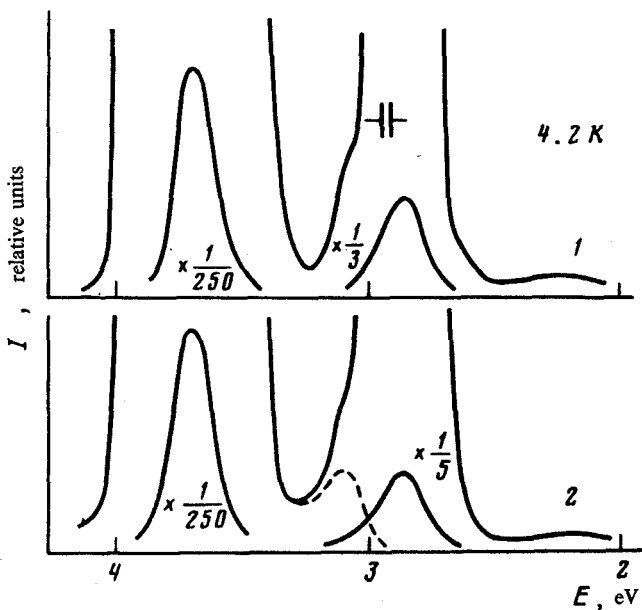


FIG. 2. Emission spectrum. (1) Experiment and (2) theory. Spectral resolution is indicated.

let and a metastable singlet situated beneath it⁴ [see Fig. 1(c)]. This leads, together with the possibility of transitions between radiating states, to a strong temperature dependence of the quantum yield, emission persistence and relative intensity of the A_T and A_X bands of the standard luminescence (UL).⁵ For this reason, the parameters γ (γ_T and γ_X), which determine the HL intensity from the relation to UL in the two channels depends on the experimental conditions.

4. The spectra were measured on the setup described previously in Ref. 6. The specimens consisted of freshly cleaved plates of perfect single crystals with Tl^+ concentration less than 10^{-3} moles/%.

The radiation observed at 4.2 K with excitation (through a double DMB-4 monochromator in the A band (4.4 eV) is illustrated in Fig. 2. The maxima at 3.69 and 2.86 eV are the well-known A_T and A_X bands.⁵ The features at 3.15 and 2.2 eV were first observed in this work. Their excitation spectra are the same as those for the main bands, while the intensities are nearly independent of temperature. We conclude from this that these features represent HL. This interpretation was confirmed by calculations of the total UL + HL spectrum (curve 2 in Fig. 2). The linear vibronic interaction parameters necessary for the calculation were determined from independent experimental data by the method described in Ref. 7. The change in the force constants in the excited states was determined from the temperature dependence of the widths of the A_T and A_X bands, while in the ground state it was determined from the Raman scattering data⁸ and turned out to be equal to $\Delta k_1/k = -0.4$; and $\Delta k_0/k = -0.1$, respectively, for the T minima and $\Delta k_0 \sim \Delta k_1 \sim 0$ for the X minima (k is the central force constant in the perfect lattice). The decay constants in (2) were found from the

relation of the intensities in observed spectra: for 4.2 K, $\gamma_T^{-1} \sim 0.5$ ns, $\gamma_X^{-1} \sim 0.02$ ns; at 140 K, $\gamma_T^{-1} \sim 2 \times 10^{-3}$ ns and $\gamma_X^{-1} \sim 6$ ns. The calculations of the relaxation law $q_i = \pi^{-1} \text{Im}G(\omega) \cos \omega t d\omega$ show that most of the vibrational energy is transferred to the lattice over a time of the order of one-half the period of the actual vibrations, i.e., 0.5 ps, so that the features in the HL spectrum are related only to the first classical turning point and are situated on the long-wavelength UL wings.

As the temperature is increased, the shape of the spectrum changes dramatically because of the exponential quenching of A_T and heating of A_X bands. At 140 K, two features were observed in the region 3.7–3.9 eV (Fig. 1). In accordance with the model presented, the feature at 3.7 eV should be understood as strongly quenched emission from T minima, which the 3.9-eV shoulder should be understood as emission from rhombic saddle points on AS (transition 3 in Fig. 1). The excitation spectra, temperature dependence of the intensity, as well as estimates of the position and widths of these features agree with this interpretation. This indicates the fact that the T and X minima of the AS indeed arise as a result of Jahn–Teller distortions of the centers in the same electronic state.

We thank A. A. Maaros for providing the specimens.

¹N. N. Kristofel', *Teoriya primesnykh tsentrov malykh radiusov v ionnykh kristallakh* (Theory of Impurity Centers With Small Radius in Ionic Crystals), Nauka, Moscow, 1974.

²V. V. Hizhnyakov, *Izv. Akad. Nauk Est. SSR, fiz.-mat.* **31**, 106 (1982); *Solid State Commun.* (1982) (in press).

³M. F. Trinkler and I. S. Zolobkina, *Izv. Akad. Nauk Est. SSR, ser. fiz.-tekh. Nauk* **4**, 117 (1975).

⁴V. Hizhnyakov, S. Zazubovich, and T. Soovik, *Phys. Status Solidi B* **66**, 727 (1974).

⁵R. Ederton and K. Teegarden, *Phys. Rev. A* **136**, 1091 (1964); A. Fukuda, *Phys. Rev. B* **1**, 4161 (1970).

⁶V. V. Hizhnyakov, V. G. Plekhanov, V. V. Shepelev, and G. S. Zavt, *Phys. Status Solidi B* **108**, 531 (1981).

⁷G. Benedek and N. Terzi, *Phys. Rev. B* **8**, 1746 (1973).

⁸R. T. Harley, J. B. Page, and C. T. Walker, *Phys. Rev. B* **3**, 1365 (1971).

Translated by M. E. Alferieff

Edited by S. J. Amoretty