K. K. Rebane and P. M. Saari. *Hot Luminescence and Relaxation Processes in the Luminescence Centers of Crystals.* Hot luminescence (HL) can be represented in good approximation as the emission of a luminescence center during the first few moments after an excitation event, up to the time of establishment of thermal equilibrium between the center and its environment (equilibrium with the lattice vibrations in the case of an impurity atom molecule in a crystal).

Since HL originates from unrelaxed substates (vibrational, rotational, etc.) of an excited electronic state of the center, it gives information on the relaxation processes of these substates. The overwhelming majority of luminescence centers in crystals are fast-relaxing—the vibrational relaxation time is reckoned in picoseconds and is several orders of magnitude smaller than the lifetime of the excited electronic state. Thus, HL can be used to investigate processes of picosecond duration under the conditions of continuous excitation of moderate power that are the rule for luminescence measurements.

A consistent description of HL has been given within the framework of a unified two-photon approach to the formation of secondary luminescence.[1] In this approach, the entire secondary luminescence flux is calculated for a given fast-relaxing center (or complex of centers[2]) and the photon flux incident on this center, and is then separated into the ordinary luminescence, scattering, and a residual part whose properties are intermediate between them—the HL.

The basic distinctive properties of HL have been demonstrated clearly in a series of experiments in which HL was observed on impurity NO_2^- molecules in alkali halide crystals.[3] Of particular importance among these properties for experimental separation of the HL are the appearance of vibrations not only of the ground state, but also of the excited electronic state in the low-temperature spectra, which makes it possible to calculate the positions of the hot lines in the spectrum, and the characteristic dependence of the HL spectrum on the wavelength of the exciting light within the same electronic transition (see Fig. 1). HL is much less subject to temperature and other types

of quenching than ordinary luminescence.

HL has now been observed and investigated in various objects: frozen organic solutions (Shpol'skii systems),[4] semiconductors,[5] nonimpurity molecules and ionic crystals, etc. (see the review[6]).

Under continuous excitation, information on relaxation processes in the excited electronic state is reflected in the intensity of the HL (which is very low compared to that of ordinary luminescence in fast-relaxing systems). The measured (with spectrally selective excitation to various levels) intensities of the HL lines can be used in combination with other spec-
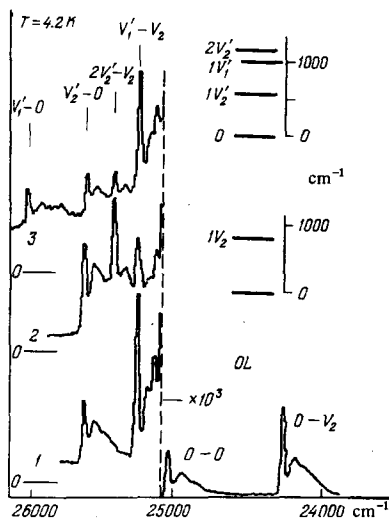

FIG. 1. HL spectrum of $KCl = NO_2^-$ vs. wavelength of exciting light. The figure shows the scheme of the lower intramolecular vibrational levels of NO_2^- in the excited and ground electronic states and the positions of the corresponding hot lines in the spectral range to the shortwave side of the ordinary luminescence (OL). Data on the intensities of the HL lines have made it possible to determine the relaxation times of transitions from the vibrational levels $1\nu_2'$, $1\nu_1'$, and $2\nu_2'$; for example, the lifetime of the $1\nu_2'$ level with respect to vibrational relaxation is 550 oscillation periods or 30 psec, and the total lifetime of the level ($\tau = 18$ psec) is shorter due to the competing nonradiative deactivation ($\tau_{1_T}' = 45$ psec) of the electronic state.

troscopic data to obtain highly detailed information on relaxation kinetics. This method was used in[3] to determine the times of vibrational (rotational) relaxation and those of other non-radiative transitions in systems in which HL is observed. The shortest of the lifetimes determined—those of the vibrational levels of the anthracene molecule in frozen n-hexane—ranged from 1.5 to 5 psec.[6] The effects of various factors (type of base matrix, temperature, pressure) on the relaxation processes have also been investigated.

If relaxation occurs simultaneously in different degrees of freedom of the system, the spectra of the HL originating from various levels of one degree of freedom reflect the time dependence of the HL in another degree of freedom. "Time samples" of the rotational relaxation process were obtained in this way in the case of KCl-NO$_2^-$ in[6]; to a certain degree, they are similar to those that can be obtained experimentally with flash excitation and time resolution in the picosecond range.

Most of the material of the paper was published in[6];

the latest results from experimental study of HL will be published in Izv. Akad. Nauk SSSR, Ser. Fiz. (papers at 23rd All-Union Conference on Luminescence).

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