Temperature dependence of hot luminescence in solid xenon: theory and experiment

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Vibrational relaxation of self-trapped excitons in solid xenon has been investigated both experimentally and theoretically. Hot luminescence spectra of the crystal have been measured in a wide temperature range (from liquid helium temperature to 100 K), using x-ray and two-photon excimer laser (ArF and KrF) excitation. The theoretical analysis is based on a recent nonperturbative relaxation theory and on a rigorous quantum mechanical Franck−Condon approach.

Introduction

Self-trapped excitons (STE) in rare gas crystals (RGC) are strong vibrational excitations very similar to free diatomic excimers R_2^* (R = Xe, Kr, Ar, Ne), whose level spacings considerably exceed the maximum phonon energies. Therefore, to adequately describe vibrational relaxation of such STE, one definitely has to use a nonperturbative quantum mechanical approach. This kind of concept has been recently elaborated [1], and is most suitable for the rigorous analysis in solid Xe, where two- and three-phonon relaxation processes are dominant. The theory predicts an abrupt increase of the relaxation rate around a critical level ($n_{cr} = 22$ in Xe), which results in a dramatic population drop of the levels in this characteristic region.

Useful information of the relaxation processes in R_2^* centres contains in their hot luminescence (HL) spectra, whose explicit calculation is a rather demanding task for several reasons. First, one needs to construct reasonable potential curves for the system. Second, one has to determine the relaxation rates and relative populations for all vibrational levels of interest. Third, one has to ascertain a huge set of correctly normalized Franck−Condon (FC) factors for bound-free and bound-bound transitions. Moreover, one cannot use the convenient «reflection» approximation of the FC principle [2,3], which ignores the quantum structure of the final state and therefore fails to take a correct account of the transitions to the scattering states near the dissociation limit and to the bound states, just most important in our case. To overcome these complicated computational-technical problems we used a rigorous quantum mechanical method by one of the authors [4,5].

In this paper we present new experimental data on the temperature dependence of HL in solid Xe, and a relevant theoretical analysis. The choice of Xe crystal for testing the reliability of the new nonperturbative relaxation theory [1] is not accidental. Compared with R_2^* centers in other RGC, a much larger range of vibrational levels (from $n = 14$ to $n = 40$ for the potential curve used) is involved in two-phonon relaxation processes, in which case the most pronounced acceleration effect around n_{cr} is expected.

Experimental results

Bulk Xe crystals of volume 2 cm^3 were grown from liquid near the triple point in a special tube made of organic glass (see [6] for more details). Two methods have been applied for the excitation purposes: irradiation by a tungsten x-ray source (40 kV, 15 mA) through a Be window, and the two-photon ArF (193 nm) or KrF (248 nm) excimer laser radiation. The HL spectra have been recorded with the help of a 2m double vacuum monochromator, which ensures spectral resolution of 10–15 meV and the light dispersing factor less than 10^{-5}.

An important specific feature of good-quality Xe crystals is the existence of two broad emission bands, as shown in Fig. 1. Here we do not discuss the origin of these bands because this has been already done more than 20 years ago [7]. In the present context we put
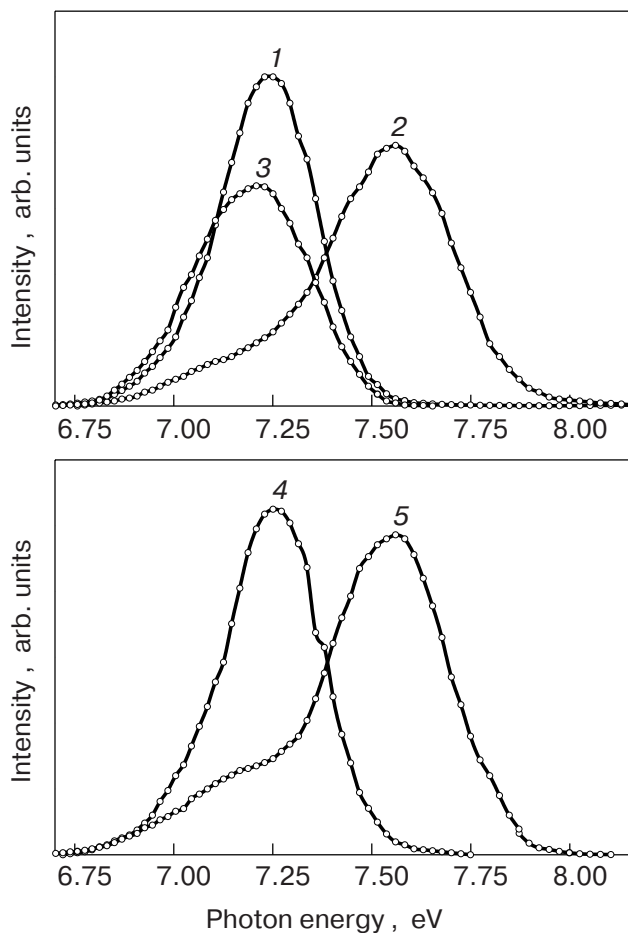
Fig. 1. Overall luminescence spectra of STE in Xe crystal corresponding to different excitation methods: ArF laser excitation (spectra *1* and *2*), x-ray excitation (*3*), KrF laser excitation (*4* and *5*). Curves *1*, *3* and *4* have been measured at $T = 10$ K, while *2* and *5* correspond to $T = 90$ K.
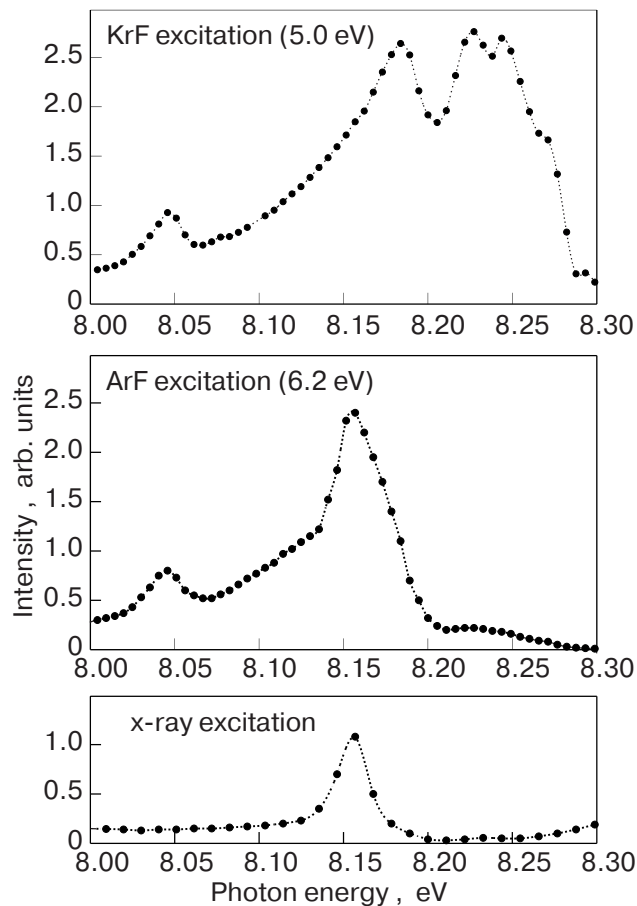

Fig. 2. Experimental emission spectra of Xe crystal in the supposed HL region at $T = 10$ K under different excitation, as shown in the graphs. Intensities are given in arbitrary but comparable units.

emphasis on their intrinsic nature and will use the same abbreviation STE for both 7.2 and 7.6 eV bands. Figures 2 and 3 demonstrate the high-energy wings of the luminescence spectra, where we observed several weak bands (their intensity being less than 1% compared with that at the maximum of the STE bands), which at least partially can be attributed to HL. There always persists a spectral feature with maximum at 8.14−8.17 eV depending on temperature and the method of excitation. This band has been reported earlier [8] and is probably related to surface excitons, in accordance with relevant absorption [9] and reflectivity [10] data. However, we cannot completely exclude its possible relationship with HL. At low temperatures and under laser excitation another weak band shows up near 8.05 eV, whose origin is unknown.

According to our earlier interpretation [11,12] the «real» HL band is the feature with maximum at 8.22−8.23 eV, which is most effectively induced by

two-photon KrF laser excitation, while other excitation methods tend to bring forth the 8.15 eV feature (cf Figs. 2 and 3). We will discuss the fine structure of the 8.23 eV band in more detail below. One can see that separation of the «pure» HL part from the variety of weak emission bands is rather complicated. Moreover, we observed clear correlation between the temperature dependence of the HL and the intensity redistribution of the main STE bands (see Fig. 1), which makes the adequate theoretical analysis even more difficult.

Theoretical results

In recent paper [5] a thorough FC analysis has been performed for free xenon excimers. In particular, exactly solvable multi-component reference potentials for the 0_u^+ ($^3P_1$) state and for the ground state 0_g^+ of Xe_2 have been constructed and their agreement with available spectroscopic data demonstrated. As the same electronic states play the key role in formation of the main STE emission bands in solid Xe (including
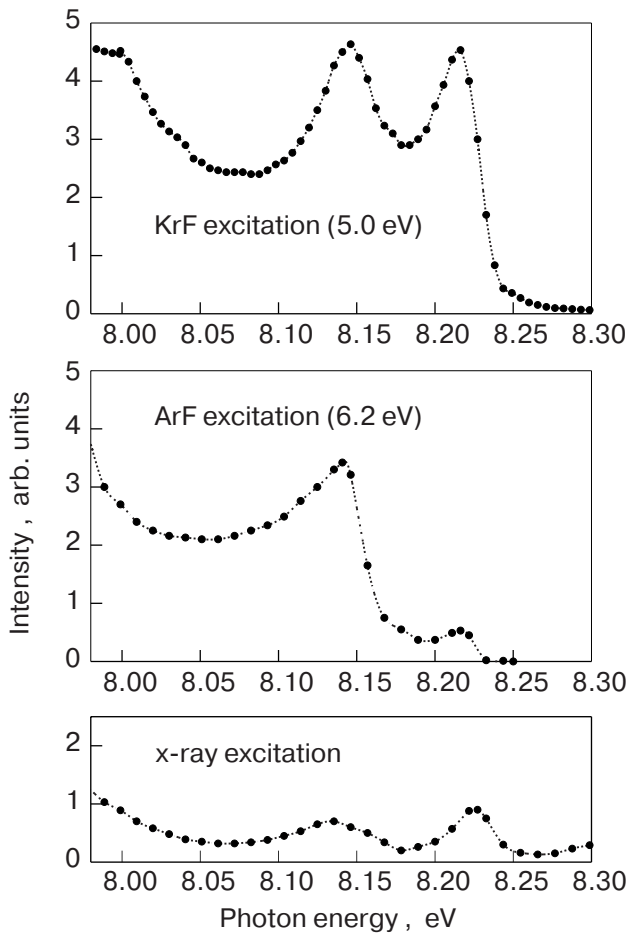
Fig. 3. The same spectra shown in Fig. 2, but measured at temperature $T = 70$ K.

HL), one would expect to receive some benefit from the results of this gas phase analysis. To this end, however, one has to adjust the free excimer's potential curves to the crystal environment.

Spectral characteristics of the 7.2 eV STE emission band are quite close to those of the well-known second continuum in the gas phase, while the free exciton peak ($E_{ex} = 8.359$ eV [13]) is about 80 meV red-shifted compared with its gas phase analogue — the $^3P_1$ atomic resonance line (8.437 eV). In view of these experimental facts we slightly deformed our free 0_u^+ ($^3P_1$) excimer's potential curve, but left the ground state potential unchanged. We also did not change the equilibrium position ($R_e = 3.00 \pm 0.01$ Å, $U(R_e) = 7.885$ eV [5]) of the 0_u^+ ($^3P_1$) potential well, but the overall curve was proportionally compressed to fit its dissociation limit with E_{ex}. Of course, there is no real dissociation limit for a quasimolecular center in the crystal, but this is of secondary importance for our treatment, because all needed FC factors nicely converge in rather narrow distance range. In the upper graph of Fig. 4 one can see a direct comparison be-
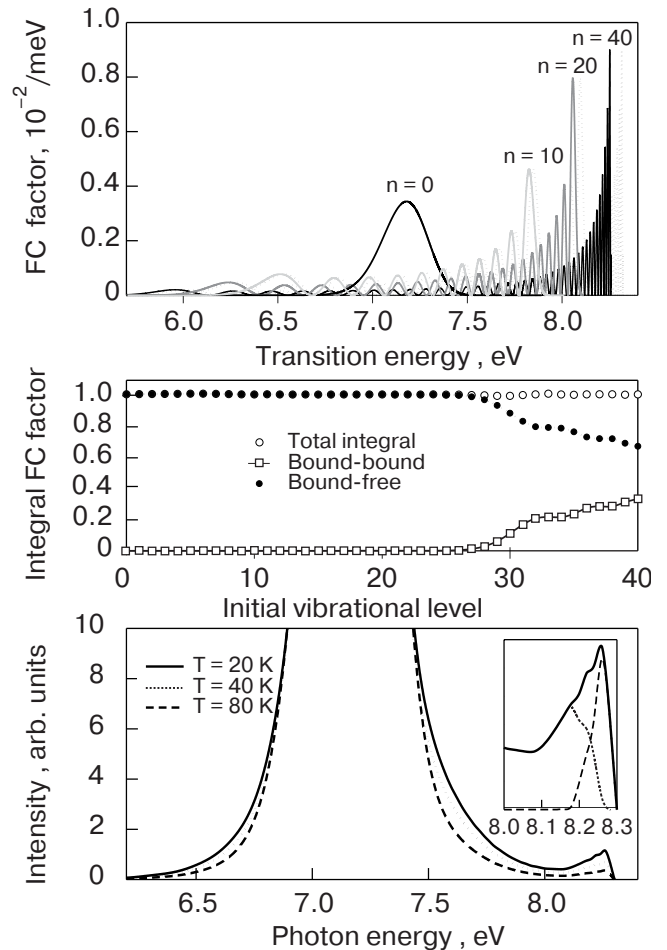

Fig. 4. Visualization of the main theoretical results of the work. The upper graph compares two sets of calculated FC factors for bound-free transitions from the selected vibrational levels ($n = 0, 10, 20$ and 40) of the 0_u^+ ($^3P_1$) state. The dotted lines correspond to the potential curves constructed in [5] for free molecules Xe_2, while the solid lines show the FC factors for the same levels related to the «deformed» potential curve of the 0_u^+ state, whose dissociation limit coincides with $E_{ex} = 8.359$ eV [13]. Note that $n = 0$ curves are indistinguishable. The middle graph demonstrates excellent agreement with the rigorous sum rule expressed by Eq. (1). Contributions from both bound-bound and bound-free transitions can be seen. The lowest graph depicts the calculated luminescence spectra for Xe_2^* in solid Xe at different temperatures. Thanks to the rigorous quantum mechanical approach, one can elucidate the substructure of the HL band. This is shown in the inset: the dotted line there corresponds to bound-free transitions, while the dash curve is related to bound-bound transitions. All spectra have been averaged with spectral resolution of 20 meV.

tween the bound-free FC factors related to free Xe_2^* excimers and their crystal analogues just described.

Normalization of the FC factors is determined by the rigorous sum rule

$$\int_0^\infty \left[\int_0^\infty \psi(E,r)\varphi_i(r)\,dr \right]^2 dE +$$

$$+ \sum_j \left[\int_0^\infty \psi_j(r)\varphi_i(r)\,dr \right]^2 = 1 \qquad (1)$$

which directly results from the fundamental property of the Schrödinger equation − completeness of the system of its eigenfunctions. Here $\varphi_i(r)$ is the wave function of the initial (0_u^+) bound state, while $\psi_j(r)$ and $\psi(E,r)$ represent the full set of normalized bound $(E < 0)$ and scattering state $(E = \hbar^2 k^2/2m \geq 0)$ wave functions, which are related to the final electronic state $(0_g^+$ in our case). Therefore, $\psi(E,r) = 2\cos(kr - \delta)/F(E)$ (δ being the phase shift), where $F(E) = [4\pi\sqrt{E\hbar^2/2m}\,]^{1/2}$ [14]. The quantities in the square brackets are recognized as the FC overlap integrals for bound-free and bound-bound transitions. Excellent agreement with Eq. (1) is explicitly demonstrated in the middle graph of Fig. 4 for all vibrational levels $(n = 0-40)$ of the 0_u^+ state that have been used in our HL analysis.

The next step is to ascertain the vibrational relaxation rates for the vibrational levels of the quasimolecule Xe_2^*. For this purpose we calculated the probabilities $\Gamma_{n,n-1}$ (relaxation rates at $T = 0$) of the multi-phonon transitions from level n to $n - 1$ according to [1], using the value $\beta = 0.3$ for the characteristic displacement parameter (see Fig. 1 in [1]), and taking $n_{cr} = 22$. The probability $\Gamma_{n-1,n}$ of the reverse transition $n - 1 \to n$ is determined by the principle of detailed balance, i.e. $\Gamma_{n-1,n} = \exp(-\Delta_n/kT)\Gamma_{n,n-1}$, where Δ_n is the spacing between the levels. Thereafter, we solved the system of kinetic equations including the levels from 0 to 40, and assuming the radiative decay rate $\Gamma_R = 2 \cdot 10^8$ s^{-1} [15] to be constant for all levels. The quantity Δ_{40} nearly equals to the maximum phonon energy in Xe (5.3 meV). We therefore assume that the levels $n > 40$ give very small contribution to HL, because fast one-phonon relaxation processes are allowed for them.

Finally, we summed the FC factors according to the relaxation law to get the luminescence spectrum for $Xe_2^*(0_u^+)$ centers in solid Xe. The results are presented in the lowest graph of Fig. 4 for three different temperatures. The calculations nicely reproduced the overall 0_u^+ component of the 7.2 eV STE band, including its HL part shown in the inset. As can be seen,

the relative intensity of HL in theoretical spectra gradually diminishes with increasing T, which was experimentally confirmed only for relatively high temperatures. The possible reason for this partial disagreement is discussed in the next section.

Conclusions

It is well known that luminescence properties of RGC strongly depend both on temperature and on the sample's structural quality. As has been demonstrated in this paper, the intensity of emission in the far high-energy edges of the main luminescence bands, which can be associated with HL of STE in solid Xe, strongly depends on the method of excitation as well. We got some new evidences to support our earlier hypothesis that the «real» HL feature in Xe is the band near 8.23 eV. Indeed, this weak emission band is most effectively induced by KrF laser excitation (5.0 eV), which supports two-photon transitions from the upper sub-band $(j = 3/2)$ of the highest spin-orbit splitted valence band into the lowest conduction band. Consequently, such an excitation is most effective in producing delocalized $\Gamma(3/2)$ excitons, the precursors of STE we are examining. In contrast, ArF laser excitation (6.2 eV) seems to support formation of STE via capturing electrons by trapped holes. This may be the cause for the weakness of the «real» HL under ArF laser excitation at low temperatures (see Fig. 2). As regards x-ray excitation, its penetration depth in solid Xe is only about 0.5 mm [6]. It means that a lot of emission centers are created near the surface, which could explain relatively high intensity of the surface-sensitive 8.15 eV feature compared with the 8.23 eV band.

The 8.23 eV band is also well pronounced in our calculated emission spectra based on the potential curves for the quasimolecular centers Xe_2^* in solid Xe. Both bound-bound and bound-free transitions contribute to the intensity distribution of this HL feature, the former being much more important for establishing its maximum position and substructure. The calculated spectra presented in the lowest graph of Fig. 4 represent averaged curves with resolution 20 meV, which nearly corresponds to the real experimental resolution at the moment. Our prediction is that one would see an abundant fine structure of the 8.23 eV band, if the experimental resolution could be essentially improved, because the band actually represents a line spectrum against the background of a continuum. Experimental efforts in this direction would therefore be of great importance for the verification of our HL concept.

As already reported earlier [12] the actual temperature dependence of the HL intensity is more compli-

cated than just the monotonous decrease predicted theoretically. Independent of the excitation method we observed an abrupt drop in the intensity of the 8.23 eV band at about $T = 40$ K, followed by rapid rise in the range from about 50 to 65 K (under KrF excitation), and gradual vanishing at still higher temperatures. Such a behavior clearly correlates with the intensity redistribution between the 7.2 and 7.6 eV bands (see Fig. 1), which possibly means that both these STE bands have HL constituents at nearly the same spectral positions. We have not succeeded to work out a more detailed model to explain this phenomenon, but this is one of the main goals of our forthcoming research.

Acknowledgment

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