

Visible luminescence of desorbed atoms resulting from the dynamics of self-trapped excitons in neon

I. Ya. Fugol', A. G. Belov, V. N. Samovarov, V. N. Svishchev,
and V. M. Zhuravlev

Physicotechnical Institute of Low Temperatures, Academy of Sciences of the Ukrainian SSR

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The amplitude and phase characteristics of the cathodoluminescence spectra of solid neon in the visible region have been measured. A series of narrow lines is shown to result from a self-trapping of p excitons near the surface of the crystal and a subsequent desorption of excited atoms into vacuum.

The emission spectrum of solid neon in the interval 585–750 nm exhibits a hot luminescence which has no analog in other cryogenic crystals. This spectrum takes the form of a multicomponent series (26 terms), each component of which contains a narrow line and a broad band. The entire series can be linked with radiative transitions between highly excited levels of the neon atom, $2p^53p_i \rightarrow 2p^53s_k$ ($i = 1-10$, $k = 1-4$). The nature and mechanism for the formation of lines and bands, however, are still being debated.^{1,2} In an effort to resolve these questions, we have used a cathodoluminescence method to carry out a multifaceted study of the spectra, varying the electron energy, the thickness and temperature of the samples, the role of impurities, etc. In addition, we used a phase-modulation method to measure the cathodoluminescence decay time. Modulating an electron beam at a frequency $\omega = 6.78 \times 10^7$ Hz, we determined the phase angle between the excitation and the luminescence. The measured phase included a population time τ^p and a radiative-transition time τ^R of the luminescing state.

Figure 1 shows a part of the spectrum of solid neon, recorded with resolution

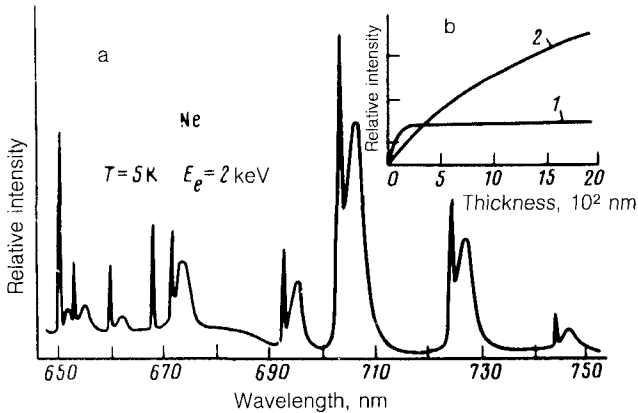


FIG. 1. a: Spectrum of the visible cathodoluminescence of solid neon in the interval 650–750 nm ($T = 5$ K, $E_e = 2$ keV). b: Intensity of the 703-nm line (1) and of the 706-nm band (2) versus the sample thickness.

$\sim 0.3 \text{ cm}^{-1}$. Corresponding to each $3p_i \rightarrow 3s_k$ transition are a narrow line with a half-width less than 0.3 cm^{-1} and a band with a half-width $\sim 60 \text{ cm}^{-1}$. The positions of all the lines agree within $\pm 0.3 \text{ cm}^{-1}$ with the frequencies of the free atom, while all the bands are shifted $\sim 60 \text{ cm}^{-1}$ down the energy scale. The intensity distribution in the series of lines and bands differs sharply from the spectrum of a gas: The transitions from low-lying $3p_i$ terms are more intense. The brightest luminescence appears in the 706-nm band and the 703-nm line, from the lowest-lying $3p[1/2]_1$ level. This distinction between the distribution in this case and the distribution in the case of the gas indicates that these series of features result from the excitation of solid, rather than gaseous, neon. Further evidence of this conclusion comes from the dependence of the intensities of the lines and bands on the sample thickness (Fig. 1b), the temperature, the impurity concentration, and so forth. As the temperature is raised, the intensities of all the lines decrease, while those of the bands increase.

Analysis of the changes in the line and band intensities as the sample thickness is

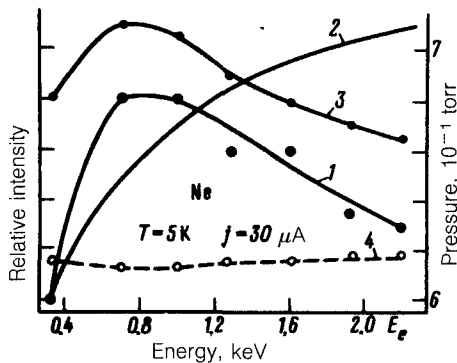


FIG. 2. Intensities of the 703-nm line (1) and of the 706-nm band (2) versus the energy of the exciting electrons. 3—Change in the pressure in the volume of the test chamber as E_e is increased; 4—control pressure in each experiment, in the absence of the electron excitation of the sample.

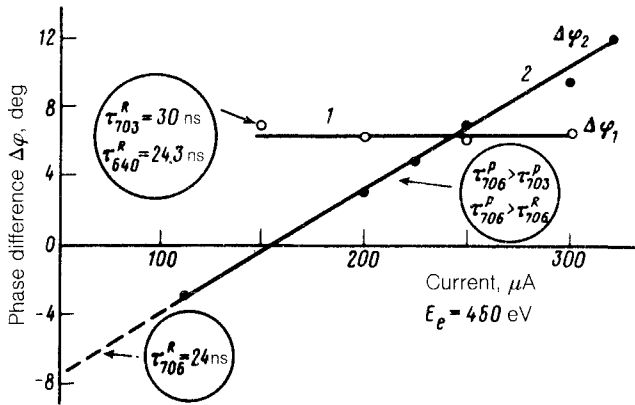


FIG. 3. The phase difference $\Delta\varphi$ versus the current of the electron gun, j . $T = 5$ K, $E_e = 450$ eV. 1— $\Delta\varphi = \varphi_{703} - \varphi_{640}$; 2— $\Delta\varphi_2 = \varphi_{706} - \varphi_{703}$.

increased (Fig. 1b) and as the energy of the exciting electrons is increased (Fig. 2) and also an analysis of the changes in the phase as a function of the electron density (Fig. 3) show that the lines and bands are filled in different parts of the crystal. As the sample thickness is increased, the intensities increase and gradually reach saturation. However, there is a series of lines which is predominant at small thicknesses, where the surface plays a large role, while a series of bands is predominant in thick crystals, where the interior plays a greater role. Correspondingly, the lines are very intense at low electron energies (small penetration depths), while the bands always intensify with increasing E_e and become predominant in the spectrum as soon as the energy E_e exceeds the maximum of the energy loss in solid neon, which is $E_e^{\max} \approx 800\text{--}1000$ eV (the excitation maximum is in the interior of the sample in this case).

Phase measurements were taken for eight lines and the 706-nm band at an electron energy of 450 eV. Since the radiative time τ^R and the filling time τ^P are related to the phase by the relation $\varphi = \arctan\omega\tau^R + \arctan\omega\tau^P$, it is interesting to analyze the difference between the phases for several lines and also the difference between a line and a band. Figure 3 shows plots of the phase difference ($\Delta\varphi_1$) between the lines at 703 and 640 nm and of the phase difference ($\Delta\varphi_2$) between the band at 706 nm and the line at 703 nm versus the current density. We see that $\Delta\varphi_1$ does not depend on the current, and a behavior of this sort is characteristic of the phase difference between any lines. For these cases, the filling time is the same, and the values of $\Delta\varphi_1$ include only the difference between radiation times. We find a completely different picture for $\Delta\varphi_2$, which turns out to depend on the electron density in the sample. This result means that the recombination time $\tau^R \approx (\alpha n)^{-1}$, where α is the recombination coefficient, and n is the density of electrons in the sample, should be taken into account in the filling cascade. According to our measurements, we have $\tau_{706}^P > \tau_{703}^P$ or $(\alpha n)_{706} < (\alpha n)_{703}$; i.e., the electron density in the part of the crystal where the lines are formed is greater than that in the part of the crystal where the centers responsible for the emission of the 706-nm band form. Since low-energy electrons, with

$E_e < E^{\max}$, were used in these experiments, the electron density should have been higher near the surface. Taken together, these measurements thus prove that the filling of the centers responsible for the emission in the lines occurs near the surface, while the filling of the centers responsible for the bands occurs in the bulk of the crystal.

The lifetimes of all the measured lines agree within ± 2 ns with the gas values for the neon atom. This agreement, combined with the complete agreement of the frequencies of all the lines in the cathodoluminescence spectrum with the gas lines, is evidence that the emission occurs at some distance from the surface of the crystal; in other words, the excited atom desorbs into vacuum and emits in vacuum. The radiative lifetime of the interior centers can be estimated by extrapolating $\Delta\varphi_2$ to a zero current. For the band at 706 nm we have $\tau_{706}^R = 24$ ns, which is 6 ns shorter than the value $\tau_{703}^R = 30$ for a desorbed atom. These results verify that the band adjacent to a line results from the same transition, but the emission occurs in the interior of the crystal.

The linkage between the entire series of lines and desorbed neon atoms was confirmed in experiments in which we simultaneously measured the pressure in the sample chamber and the changes in the line intensity while varying the electron energy (Fig. 2). We found a clear correlation between the nonmonotonic behavior of the pressure and of the line intensity as functions of E_e . At low energies, $E_e < 1$ keV, the pressure in the chamber increases with increasing E_e as a result of desorption, and we observe a simultaneous intensification of the lines. At $E_e \gtrsim 1$ keV, the electron-ion density near the surface of the sample begins to fall off; correspondingly, there is a decrease in the desorption rate and thus the pressure in the chamber and the line intensity. The intensities of the broad bands continue to increase.

These results show unambiguously that the desorption studied here is of a non-thermal nature and is a consequence of an erosion of the surface by electron impact. The line emission from the high-energy $3p$ states of neon is preceded by an intense interaction of excitons with the lattice, as can be seen from several systematic features (primarily the shift with respect to the excitation spectrum). It is thus logical to link the observed desorption of atoms with a rapid self-trapping of p excitons near the surface, in a process similar to the surface self-trapping and subsequent desorption from s -exciton states which occur in neon.^{3,4} It is possible to draw a noncontradictory picture of the self-trapping dynamics of the $3p_i$ states of Ne: During electronic excitation of the crystals, electron-hole pairs are produced. As these pairs subsequently recombine, p excitons form. The self-trapping of p excitons which develops at the surface is accompanied by the release of an energy ~ 0.6 eV, which is substantially greater than the binding energy of the atom with the lattice. Accordingly, during self-trapping at the surface, the $3p$ atoms become unbound from the lattice and are ejected into vacuum, where they subsequently emit.

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