Quasiline emission solid neon for transitions between excited states

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A series of bands, corresponding to transitions between excited $2p^5 3p \rightarrow 2p^5 3s$ states, have been found in the luminescence of solid Ne. A scheme is proposed for the formation of quasiatomic localized $3p$ states and their selective occupation on the basis of dissociative recombination processes.

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Cryocrystals of the inert elements are broad-band dielectrics and are characterized by intense luminescence in the far UV spectral region, arising from transitions from the lowest excited states into the ground state.[1] A weak continuous emission,[2] the origin of which in the solid phase is still not clear, is observed in the visible and near UV spectral regions in solid Xe, Kr and Ar. There is practically no continuum in the emission spectrum of solid Ne, but a group of lines between 6150 and 7950 Å was already noticed in Ref. 2, which could not be ascribed to any extraneous impurities. A detailed study of the cathodoluminescence spectrum of neon cryocrystals, which we have carried out, showed that at least 26 narrow bands, practically lines, appear in the red spectrum, which can be completely matched to the transitions between the two excited terms of the neon atom $2p^5 3p \rightarrow 2p^5 3s$. Each band consists of a narrow phonon-free line and a phonon wing. The wavelengths of the phonon-free lines agree with the atomic wavelengths within an accuracy of 1 Å. This surprisingly close agreement of the frequencies forced us to perform control experiments, showing that the emission occurs from the solid sample and not the gas. The temperature characteristics and concentration quenching of the spectrum were investigated. A possible scheme was

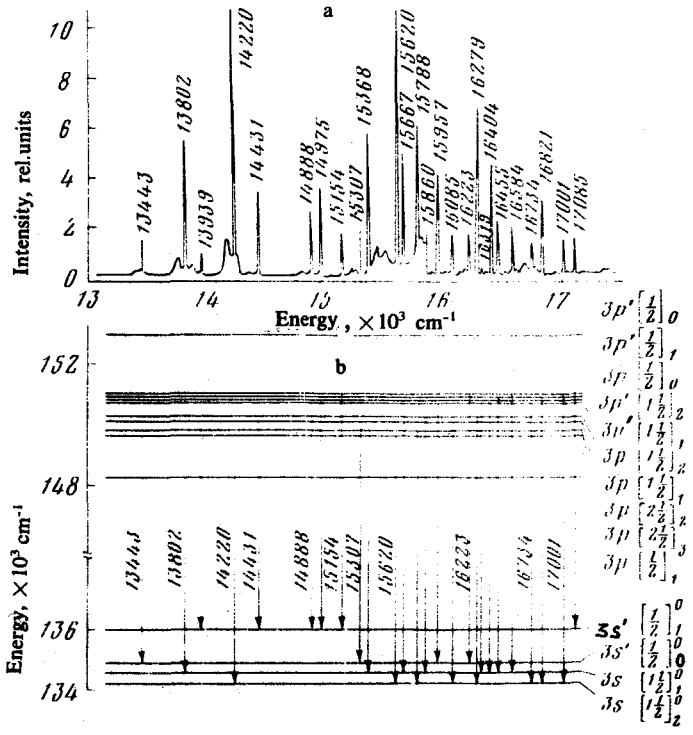

FIG. 1. (a)—Luminescence spectrum of crystalline neon in the region of the $2p^5 3p \rightarrow 2p^5 3s$ transitions; (b)—Corresponding identification.

suggested for the creation of local quasiatomic $3p$ states and their selective occupation in neon cryocrystals.

The solid neon test samples were grown by condensation of the gas on a metallic substrate, cooled by liquid helium. The neon crystallites, with a size larger than 1000 Å, were stimulated by a beam of electrons with an energy of 100 to 500 eV. The emission was recorded by means of a monochromator and a detection system for individual photons. The spectral resolution was 1–1.5 cm^{-1}. The visible luminescence of solid Ne occurred in the 8000–600 Å region and comprises a group of 26 bands, the width of which does not exceed 1.5 cm^{-1}. The observed spectrum and its identification as a series of $2p^5 3p \rightarrow 2p^5 3s$ transitions are shown in Fig. 1. The intensity distribution in Fig. 1 is significantly different from the gas-discharge spectrum and the luminescence of the gas above a cold surface at $T = 80$ K, and it is closer to the spectrum of the dense gas at pressures above 1 atm.[3]

First of all, the observed neon spectrum raises the question of whether it is the gas above the cold surface, bunched by the electron beam, that is glowing or the solid specimen? In order to answer this question a layer of xenon up to 1 μ-thick was deposited on top of the crystalline neon film, and the emission spectrum of the Xe-Ne sandwich was examined. The observed spectrum contained the same group of Ne bands, somewhat attenuated and located on the background of the continuous emission of solid Xe. Other control experiments involved investigations of the spectra of solidified O_2 + Ne mixtures as the O_2 concentration was varied. A sharp attenuation

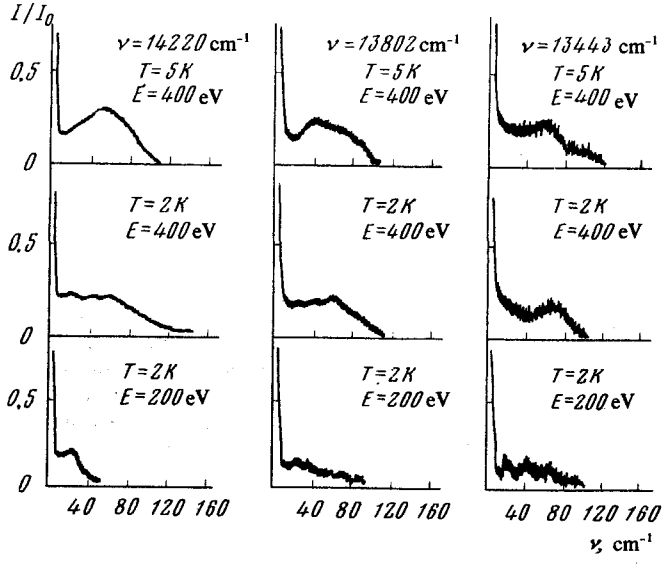

FIG. 2. Intensity distribution in phonon satellites as a function of the temperature and the energy of the stimulating electrons.

of the intensity of the narrow Ne bands and their broadening was observed in the ratio $1:5\times10^{-1}:7\times10^{-2}$ for oxygen concentrations of $10^{-2}:1:4$ mol%, respectively. As the intensity of the Ne bands decreased, we observed an intensity increase in the series of impurity bands $O_2^+ A\,^2\Pi_u \rightarrow X\,^2\Pi_g$ in the 3600–4700 Å region having a characteristic matrix shift of $\Delta E \approx 2$ with respect to the gas. Another circumstance favoring the

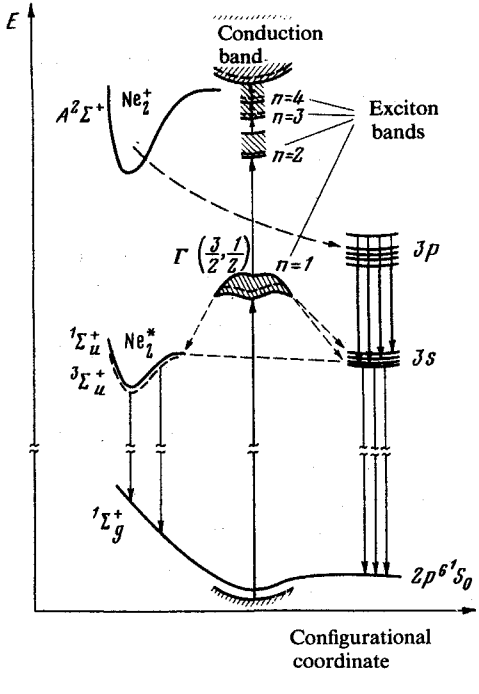

FIG. 3. General scheme of filling and luminescence processes of autolocalized states in neon crystals.

fact that the observed narrow bands belong to the solid phase is that each narrow line has a long-wavelength wing.

As seen from Fig. 1 the long-wavelength wing is observed for nearly all lines. The intensity and shape of the wings, as well as their structure, are strongly dependent on the temperature and energy of the stimulating electrons (see Fig. 2). With a decrease in T and the energy of the electrons the long-wavelength wing becomes less intense, and its maximum approaches the narrow line. The ratio of the integrated intensities of the narrow lines and the wings for the transitions from the lowest $3p$-state into the lower $3s$-levels amounts to 10^{-1}; it is even smaller for the other transitions. When the neon samples are heated, most commonly a maximum in the structure of the long-wavelength wing is separated at a distance of 40–50 cm^{-1}. The temperature variations of the wings, as well as the matching of the maximum of its structure to the frequency of the Debye phonons of solid Ne ($\omega_D = 52$ cm^{-1}) make it possible to assume a phonon origin for the wings.

If we recognize that the observed emission occurs from the excited states of the solid phase, then it is necessary to consider the following: 1) the mechanism for formation and for selective filling of the local $3p$ levels in solid Ne compared with the other excited states; 2) the reason for the agreement of the frequencies in the solid and gaseous phases. The arrangement scheme of the bands and localized quasiatomic and quasimolecular states in solid Ne is shown in Fig. 3. During the excitation by electrons, in addition to the direct excitation of exciton states, a formation of Ne^+ ions occurs which are easily localized in the lattice into a molecular ion Ne_2^+. During the dissociative recombination of the molecular ions $Ne_2^+ + e \rightarrow (Ne_2^*) \rightarrow Ne^* + Ne$ it is precisely the $3p$-states of neon that are effectively populated.[3] It has recently been established that in liquid Ar, Kr and Xe a considerably fraction of the excitations in the lower exciton bands arise precisely as the result of dissociative recombination.[4] It can be assumed that in the easily deformed Ne lattice, unlike in Kr and Xe, localized quasiatomic $3p$-states arise directly as the result of dissociative recombination. In fact, the exciton band of these states is located above the localized molecular ion level, and the $\Gamma(3/2,1/2)$ band is narrow and does not overlap the local $3p$-levels. The quasiatomic neon centers in the lattice form a microcavity around themselves.[1] Since the interaction of the $3p$- and $3s$-states with the surroundings does not significantly differ form each other, the atomic transitions within the microcavity occur with the frequencies of the free atom. The mechanism for the appearance of the quasiatomic $3p$-states in the neon lattice and its visible luminescence make it possible to explain the cause of such intense emission from the $3s$-states into the ground state in the far UV.[1]

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