

Defect formation in self-trapping of excitons in solid neon

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New features have been found in the cathodoluminescence spectra of solid neon and of argon, krypton, and xenon impurities in neon. A detailed analysis reveals the mechanism for defect formation in the neon lattice in the stage of the formation of single-site self-trapping states.

The self-trapping of excitons in single-site and two-site states in crystals of inert elements has been demonstrated by numerous experiments.¹ A single-site self-trapping occurs in crystals of light, inert elements and is predominant in neon. The structure of the single-site states is described by a model of a center formed by an excited atom in a microscopic cavity (an *A* center).^{1,2} The nature of the relaxation of the lattice in the course of self-trapping is reflected in the large Stokes shifts *S* of the emission bands and their approximate agreement with those corresponding to transitions in the gas. In contrast with alkali halide crystals, where defects form during the stage of the decay of the self-trapping states,^{3,4} the theory for crystals of inert elements predicts a mechanism in which defects are formed during the formation of the self-trapping states.⁵ In the present letter we report an experimental demonstration of this mechanism for defect formation.

We studied the effect of the excitation conditions, the temperature, and the structure of the samples on the intensity distribution in the spectra of the intrinsic luminescence and impurity (Ar, Kr, Xe) luminescence of *A* centers in solid neon. The experimental procedure is described in Refs. 1–6. The basis for the use of solutions of inert elements as model systems is the similarity in the dynamics of the electronic excitations in pure and impure crystals.¹ The optical spectra of the impurity and intrinsic *A* centers in neon are similar (Figs. 1–3). They contain series of bands which correlate with electronic transitions in the free atom, from the 3P_2 , 3P_1 , and 1P_1 states to the 1S_0

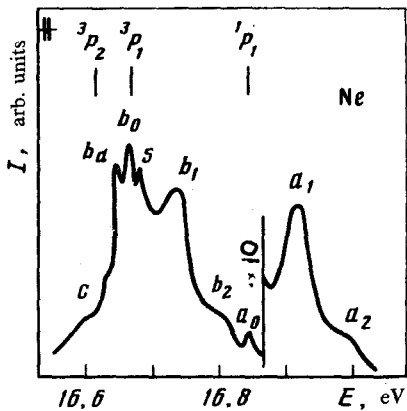


FIG. 1. Luminescence spectrum of pure neon at 5 K (s is a surface band).

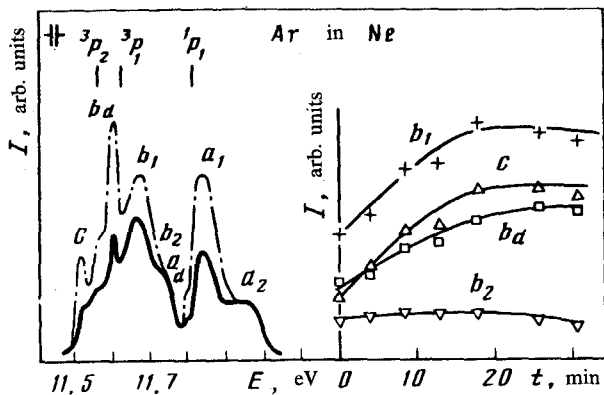


FIG. 2. Luminescence spectrum of impurity centers (0.01% Ar) in Ne. Solid line—Excitation energy of 500 eV; dot-dashed line—2000 eV. Shown at the right are the intensities of the various components of the spectrum versus the bombardment dose.

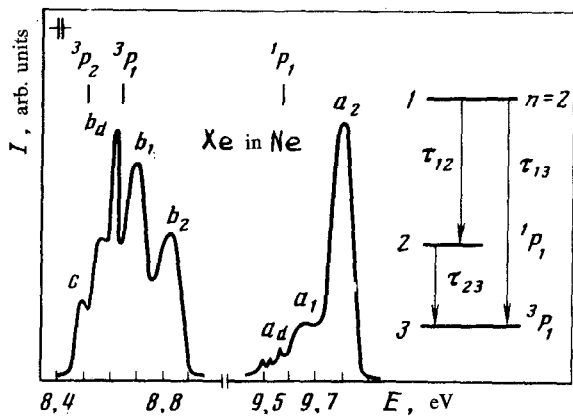


FIG. 3. Luminescence spectrum of impurity centers (0.01% Xe) in Ne; relaxation scheme.

state. The positions of the centers of gravity of the measured bands agree with experimental results on photoexcitation⁷ and x-ray excitation.⁸ The high resolution in the present experiments has made it possible to observe a fine structure of the bands and to detect some new emission peaks. On the basis of an analysis of the spectra of neon and the solutions, we propose new assignments for all the measured bands.

The spectra of the solid phase are richer than those of the gas phase, so it is not possible to identify each component of the fine structure with a transition in the free atom, as has been assumed elsewhere.^{7,8} Each transition in the luminescence spectrum of A centers in the volume of a sample corresponds to a characteristic doublet, with components specified by the subscripts 1 and 2. These components are significantly narrower than the corresponding absorption peaks, and their half-width δ increases from $\delta = 0.05$ eV for intrinsic A centers in neon to $\delta = 0.09$ eV for Xe in neon. The matrix shifts D of the doublets are small, and for component 1 we have $D \ll S$. The doublets have satellites a_d and b_d , which we attribute to the emission of A centers near defects. In contrast with the d lines, the 1 and 2 components are distinguished by the stability of their behavior in the spectrum. They are intense in the low-temperature spectra during excitation by low-energy electrons, i.e., under conditions such that the defects are frozen, and the energies of the electrons are insufficient to directly knock a neon atom out of a lattice site. An isothermal annealing of the samples at 10 K has essentially no effect on the intensity of the doublet I_1, I_2 . These facts are evidence that the two components of the doublets correspond to intrinsic electron excitations of A centers in the lattice. The "radiative" behavior of these components, on the other hand, is different. For component 2 the transition from excitation energies below the threshold to the regime of defect generation does not affect the intensity (I_2 ; Fig. 2). Furthermore, there is no intensification of I_2 with increasing irradiation dose; this result demonstrates that the centers responsible for the emission of component 2 do not include defects. The components 1 intensify during electron bombardment under conditions corresponding to the creation of Frenkel's pairs; with increasing irradiation dose, their intensities increase and eventually reach saturation (Fig. 2). This behavior is typical of defect lines (a_d, b_d , and c). These results indicate a relationship between components 1 and point defects.

All of these facts can be explained in a natural way by a mechanism proposed in Ref. 5 for defect formation during self-trapping. We believe that the doublet structure of the emission bands is due to the existence of two different configurations of the self-trapping state, separated by a barrier: a defect-free configuration and one containing a defect, formed in the course of the self-trapping. The components 2 reflect the initial stage of the self-trapping, which corresponds to the appearance of an elastic stress around the cavity formed by the excitation. In pure neon, the positions of the components 2 coincide with those predicted theoretically.^{9,10} Components 1 correspond to the final stage of self-trapping, in which there is a relaxation of the elastic stress due to a plastic expansion of the cavity through the intrusion of interstitial atoms into the crystalline surroundings of the A centers. Here an increase in the size of the cavity leads to a shift of the 1 peaks downward along the energy scale, toward the positions corresponding to transitions in the gas. The probability for the formation of defects is high, since the energy gain during self-trapping is far greater than the binding energy,

and it is distributed among a small number of atoms in the first few coordination spheres. Since the plastic deformation involves a surmounting of potential barriers by atoms, the self-trapping states involving defects form over a time $\tau_f \gg \omega_D^{-1}$, where ω_D is the Debye frequency.

We would naturally expect that the number of centers near which the lattice manages to undergo a deformation, incorporating interstitial atoms, will depend on the lifetime of the excitation, increasing with increasing lifetime. The time evolution of the formation of defects can be seen by comparing the ratio of the intensities of components 1 and 2 in the sequence of electronic transitions at A centers. Under conditions corresponding to the cascade filling of states, the deformation of the lattice can occur during a relaxation among electronic levels. The different states separated by radiationless relaxation serve as probes of a sort, which reflect the state of the system at various times. The validity of this mechanism is supported by the correlation between the scale times for the radiationless filling of the given label, τ_p , and the ratio I_1/I_2 . According to Ref. 7, most of the delay during the relaxation occurs in the stage of the filling of the 1P_1 and 3P_1 levels. Working from a simple three-level scheme, we can estimate the rates at which the 1P_1 (2) and 3P_1 (3) states are filled: They are proportional to $\{\tau_p^{(2)}\}^{-1} \sim (\tau_{12})^{-1}$ and $\{\tau_p^{(3)}\}^{-1} \sim (\tau_{13})^{-1} + (\tau_{12})^{-1}\tau_{20}(\tau_{23})^{-1}$, respectively. According to our assumption, we would have $I_1/I_2 \sim \tau_p$, and the following relation should hold for transitions from levels 2 and 3:

$$\frac{I_2^{(2)}}{I_1^{(2)}} : \frac{I_2^{(3)}}{I_1^{(3)}} = \frac{(\tau_{12})^{-1}}{(\tau_{13})^{-1} + (\tau_{12})^{-1}\tau_{20}(\tau_{23})^{-1}} \quad (1)$$

The ratio $I_2^{(2)}/I_1^{(2)} : I_2^{(3)}/I_1^{(3)}$ measured in the present experiments in the Ar/Ne system is $\cong 0.8$, in good agreement with the estimate $\tau_p^{(3)}/\tau_p^{(2)} \cong 0.87$ based on the data of Ref. 7. This suggestion is supported by the fact that relation (1) holds as τ_p is varied with a transition to another system. For example, for the Xe/Ne system, with $\tau_{13}, \tau_{23} \gg \tau_{12}$ (Ref. 7), an estimate yields $\tau_p^{(3)}/\tau_p^{(2)} \cong 22$. The ratio found in our experiments, $I_2^{(2)}/I_1^{(2)} : I_2^{(3)}/I_1^{(3)} \cong 20$, agrees with this value. Convincing evidence that τ_p has a governing effect on I_1/I_2 comes from experiments on the changes in the relaxation rate of an electronic excitation. A sharp increase in the relaxation rate during a "local phase transition" near 10.5 K in neon (Ref. 11), equivalent to a decrease in τ_p , involves a decrease in I_1/I_2 .

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