Singularities of the emission spectrum of solid argon

I. Ya. Fugol', E. V. Savchenko, A. G. Belov, and Yu. B. Poltoratskii

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences
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New bands have been observed in the emission spectrum of solid argon: the quasiatomic transition $^3P_1$–$^1W_0$, split in the crystal field, and a band ascribed to transitions from high vibrational levels of the state $^1\Sigma_u^+$ to the Van der Waals minimum of the term $^1\Sigma_g^+$. The existence of a barrier on the potential curve of the term $^1\Sigma_u^+$ is proposed.

Until recently, it was regarded as established that the luminescence of crystals of solidified gases stems from states of self-captured excitons, corresponding to the production of excited molecules of the type Ar_2^* in the lattice.[1–3] The shortest-wavelength band of the emission spectrum was identified with transitions from the lowest vibrational state of the terms $^1\sum_u^+$ and $^3\sum_u^+$ to the repulsion branch of the ground state of $^1\sum_g^+$. Figure 1 shows the exciton-band scheme of solid argon, with account taken of the parameters of the exciton absorption[4] and the potential curves of the Ar_2 molecules.[5] The occupation of the lowest vibrational state of the terms $^1\sum_u^+$ and $3^3\sum_u^+$ proceeds either by recombination from the states of the self-captured hole Ar_2^+ (in the case of excitation to the conduction band) or as the result of relaxation from excitonic states. The states of the free excitons in the inert-gas lattice correspond to the case of strong exciton-phonon coupling. In view of the smallness of the energy of the polarization interaction in inert-gas lattices, it is easily seen that lattice deformation can occur around a site with electronic excitation. Indeed, the lifetime of the excitation ($\tau_b \approx 10^{-9}$ sec) is long enough for relaxation to take place to a new stationary state of a local exciton of the molecular type ($\tau_{loc} \approx 10^{-11}$ sec).

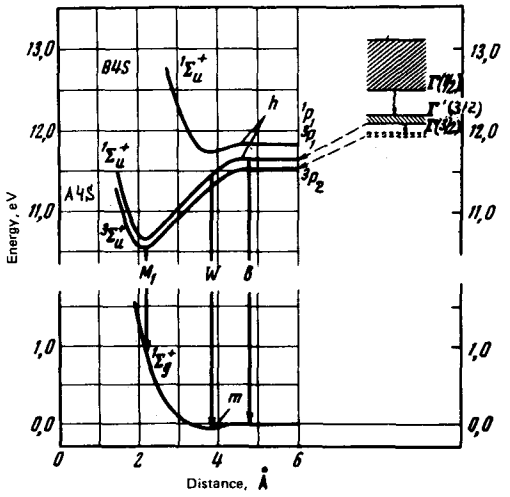

FIG. 1. Scheme of lowest exciton states of solid argon and of the potential curves of the diatomic molecule Ar_2.

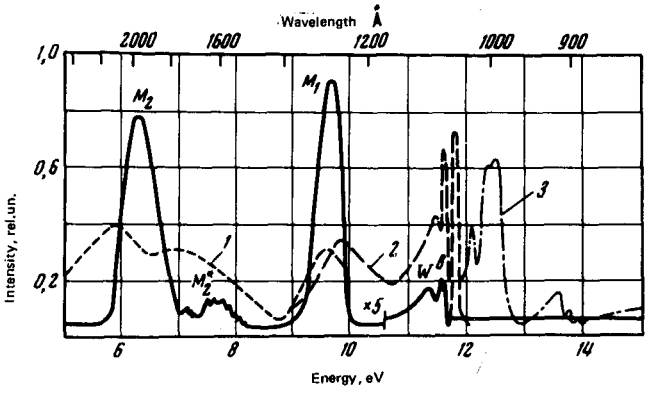

FIG. 2. Emission spectra of argon crystals at 4°K (solid line). The dashed curves 1 and 2 show the emission spectrum of gaseous Ar,[8,9] and the dash-dot line shows the absorption spectrum of solid Ar[10] (curve 3).

A somewhat different situation was observed in solid neon.[6,2] Experiments performed with high resolution have made it possible to establish uniquely the origin of the luminescence in neon crystals.[2] It turned out that the relaxation of the excitonic excitation in the neon lattice is to centers of the atomic type. No molecular bands typical of the luminescence of heavy inert gases could be observed. Only on the long-wave side of the quasiatomic transition $^3P_2 - {}^1S_0$ was there noted a band in the form of an asymmetrical prominence with intensity lower by one order of magnitude than the intensity of the quasiatomic bands (see Fig. 2 of[2]).

The luminescence of all crystals of inert gases exhibits a feature that is surprising at first glance: the emission frequencies of the atomic-type bands in neon, as well as the molecular-type bands in xenon, krypton, and argon, are very close to the frequencies of the corresponding transition in the free atom or molecule.[2] This indicates that the relaxation produced around the excitation a lattice deformation that led to an appreciable decrease of the resonant exchange interaction. In other words, the atoms are pushed asunder around the relaxation center, and a microcavity is produced.[2,3,7] We note that the effects of the resonant interaction are quite clearly pronounced in the absorption spectra of the inert crystals.[4]

Using an improved registration technique, we have recently investigated again the cathode-luminescence spectra of pure argon crystals. The measurements were made in a wide temperature interval from 2 to 25°K. Temperature annealing of the samples was carried out. Other details of the procedure are described in[2,7]. In these experiments, we observed new emission bands of solid argon in the region of the atomic transitions. Figure 2 shows the emission spectrum of argon crystal. The spectrum contains, first, intense maxima of the quasimolecular type, M_1, M_2, and M_2^*, analogous to the bands of solid xenon and krypton, and second, several new bands, designated b^1, b^0, and W, with intensity almost one-thirtieth of the intensity of the band M_1 at 9.63 eV. The narrow bands b^1 and b^0 correspond to emission energies 11.64 eV (1065 Å) and 11.58 eV (1070 Å). The maximum of the band W is at 11.37 eV (1090 Å).

To establish the correlation of the narrow bands b^1 and b^0 with the atomic argon levels, we investigated the impurity states of Ar in a Ne lattice, varying the concentration from 0.1 to 80 mol.% Ar. At low concentrations one can see intense $P-S$ transition components, $^1P_1 - {}^1S_0$ and $^3P_1 - {}^1S_0$, each of which is split in the neon lattice into two components. With increasing argon concentration, the intensities of both components of the term $^1P_1$ decrease, and at concentrations above 30 mol.% only the components of the $^3P_1$ terms can be seen in practice. With further increase of the Ar concentration in the Ne lattice, the components of the $^3P_1$ term go over into the bands b^1 and b^0 of pure argon. Since the transition $^3P_1 - {}^1S_0$ in the gas phase corresponds to an energy 11.62 eV, the shift of the bands in the crystal relative to the gas is quite small and is equal to +0.02 and −0.02 eV for the components b^1 and b^0, respectively. The identification of the bands b^1 and b^0 as components of the quasiatomic local transition $^3P_1 - {}^1S_0$ in the argon lattice leads to the following conclusion: a) a nonradiative transition from the exciton states $\Gamma(1/2)$ to the lowest band of the series $\Gamma(3/2)$ takes place in the argon lattice (unlike in neon); b) the observed emission is from the relaxed state of a local exciton of the quasiatomic type ($^3P_1$), and the Stokes shift relative to exciton absorption is $E = 0.5$ eV; c) the effect of the crystalline environment is manifest in a splitting of the quasiatomic transition into two components; d) the small shift of the $^3P_1 - {}^1S_1$ transition in the radiation, in comparison with the atomic line, indicates that lattice deformation, with a decrease of the resonant exchange interaction, has taken place around the local excitation center.

The band W, which begins immediately after the $^3P_1 - {}^1S_0$ transition, can be ascribed in our opinion to transitions from higher vibrational states of the $^1\Sigma_u^+$ term to the Van der Waals minimum of the ground state (see Fig. 1). Figure 3 shows the temperature dependences of the bands b^1, b^0, and W. With increasing temperature, the intensities of bands b^1 and b^0 decrease noticeably in comparison with the intensity of the band W. This can serve as proof of the existence of an ac-

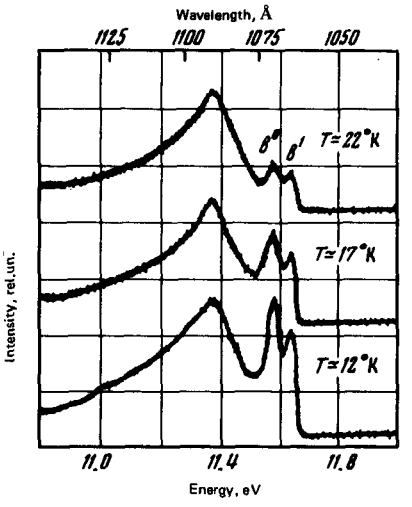

FIG. 3. Intensity of luminescence bands of argon crystals in the region of the atomic transition $^3P_1 - {}^1S_0$ at different temperatures.

tivation barrier between the atomic level $^3P_1$ and the molecular term $^1\sum_u^+$ in the argon lattice. *A* rough estimate shows that the height of the barrier on the potential curve of the term $^1\sum_u^+$ is not less than 30°K (0.003 eV). Our estimate does not contradict the analysis of the molecular system $^1\sum_u^+$ in the gas phase in accord with the data of[5]. A detailed discussion of the mechanism of de-excitation of the *W* band will be presented in a later article.

We note in conclusion that the spectrum of solid argon represents the first reliable observation of the possibility of simultaneous existence of local exciton states of several types, namely self-captured excitons of molecular centers (M_1 band) and relaxed states of atomic centers (the *b* bands).

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