USSR Acad. Sci., Moscow, 1978.

[12]B. S. Azimov, A. P. Sukhorukov, and A. K. Sukhorukova, Abstracts, 9th All-Union Conf. on Coherent and Nonlinear Optics, Leningrad, Vol. 2, p. 105, 1978.

[13]Kafi el Haj, Candidate's dissertation, Moscow State Univ., 1976.

Translated by J. G. Adashko

Exciton luminescence on anthracene-gold boundary

V. V. Bondar and M. V. Kurik

Physics Institute, Ukrainian Academy of Sciences

(Submitted 13 July 1979)
Zh. Eksp. Teor. Fiz. **78**, 94–99 (January 1980)

The luminescence spectra of thin anthracene single crystals in optical contact with quartz and gold were measured for the first time ever at low temperatures (1.7–100 K). It is shown that the presence of the metal layer leads to metallic quenching of the Frenkel excitons on the interface. Questions involved in the quenching of coherent and noncoherent excitons are discussed, as well as the peculiarities of the influence of a metallic substrate on the processes of exciton-phonon interaction in anthracene crystals.

PACS numbers: 71.35. + z, 78.60. – b, 63.20. – e

INTRODUCTION

A number of recent studies are devoted to the peculiarities in the behavior of excitons near the surface of the crystal, especially if the latter is in contact with another medium. For molecular crystals, such as anthracene, these investigations were carried out in Refs. 1–6. In addition to the singularities of exciton reflection and luminescence spectra, studies are made also of luminescence quenching, which is important for the determination of the behavior of Frenkel excitons on a free surface or in the case of contact between the crystal and another medium. The quenching of excitonic luminescence of a single crystal of anthracene was measured in Refs. 3 and 4 at room temperature as a function of the thickness of the dielectric interlayer between the crystal and the metal. It was concluded that the quenching is due to annihilation of the excitons into electrons and holes on the separation boundary.

Theoretical investigations of the behavior of Frenkel excitons on a boundary with a metal[1,5,6] show that the phenomena depend substantially on whether the excitons that come into play are coherent or noncoherent. Thus, for example, if the excitons are noncoherent then the presence of a metal can produce forces that drag the excitons to or from the metal, and metallic quenching of the excitons should be observed. To identify the type of excitons that manifest themselves in the spectra, it is necessary to carry out the measurements at various temperatures, especially at low temperatures, when the excitons can be coherent.[7] There are still no published reports of investigations of Frenkel-exciton quenching on an interface with a metal at low temperatures.

We report here the results of investigations of the characteristics of the luminescence spectra of thin anthracene single crystals which are freely mounted and in optical contact with quartz and gold, as functions of the temperature in the interval from 1.7 to 100 K. We prove experimentally, for the first time ever, the existence of metallic quenching of excitons on the anthracene-gold interface, and that the quenching depends substantially on the temperature, An analysis of the dependence of the parameters of the electron band of the exciton luminescence (position and half-width) on the temperature and on the type of the substrate has made it possible to identify the different effects of metallic and dielectric substrates on the exciton-phonon interaction in anthracene.

EXPERIMENT

The investigated anthracene single crystals were less than 1 μm thick and were grown by sublimation in an inert atmosphere from zone-purified (~100 zones) of material. No impurity bands whatever were observed in the luminescence spectra of these crystals at low temperatures. One part of the anthracene crystal was in optical contact with fused quartz and the other with a semitransparent gold electrode. For comparison, we investigated also freely supported single crystals of anthracene approximately 10 μm, with a gold semitransparent layer evaporated on half of their surface.

The luminescence spectra were measured in the temperature interval 1.7–100 K. Stabilization and monitoring of the temperature were by means of two germanium thermoresistors of the KGG type (which measured the temperature in the range from room to helium and below). The accuracy of the temperature determination was 0.05° in the interval 1.7–4.2 K and 0.1° in the interval 4.2–100 K. The spectra of the exciton luminescence of the anthracene were measured with a DFS-12 spectrometer. The luminescence was excited at an angle <10° to the crystal by a DRSh-250-2 mercury lamp through a UFS-6 filter ($\lambda_m = 365$ nm). The anthracene emission spectra were registered from the side of the free surface of the crystal, with account taken of the light lost in the various substrates on the other side of the crystal. Since the crystal thickness was less than

1 μm, we disregarded the reabsorption of the luminescence. The quenching of the singlet excitons was estimated from the relative change of the integrated intensity of the exciton luminescence in the spectral range 397–407 nm when the same crystal was placed on a gold electrode and on quartz, under perfectly identical spectrum-registration conditions. The contribution of the exciton luminescence reflected from the interface with the subtrate in the direction of the free surface of the crystal was taken into account by converting it into a coefficient of reflection from the substrate. The reflection standard was a quartz plate 1 mm thick.

EXPERIMENTAL RESULTS

We measured in the experiment such characteristics of exciton luminescence as the change of the integrated intensity, the shift of the maximum of the band of the purely electronic transition, and the increase of its half-width with increasing temperature, for crystals that are freely supported and those in optical contact with gold and quartz.

Figure 1 shows the exciton-luminescence spectra of freely supported anthracene single crystals (curves 1 and 1′) and of crystals in optical contact with fused quartz (curve 2) and with a gold electrode (curve 3), all at 1.7 K. The emission spectrum of the free anthracene crystal reveals at low temperature a fine structure of the band in the region 398–401 nm (purely electronic transition, 00 band) and a separate band at 404.75 nm, resulting from the 396 cm^{-1} intramolecular vibration.[8-10] The fine structure of the 00 band is due to intracombination scattering of polaritons by the phonons of the anthracene lattice.[9] The presence of optical contact between the thin anthracene single crystal and the substrate leads to a substantial change of the spectrum of the exciton luminescence of the crystal measured at the same temperature. The fine structure of the spectrum vanishes and the electronic band broadens, while the position of the maximum of the band shifts towards the shorter wavelengths compared with its position for the free crystal. In addition, the intensity of the electron-vibrational band decreases and an additional band appears in the spectrum at 401.7 nm (24,877 cm^{-1}), whose intensity depends on the number of defects and on the magnitude of the crystal deformation, and varies with the type of substrate. It is customarily assumed[11] that this band is of strain origin.

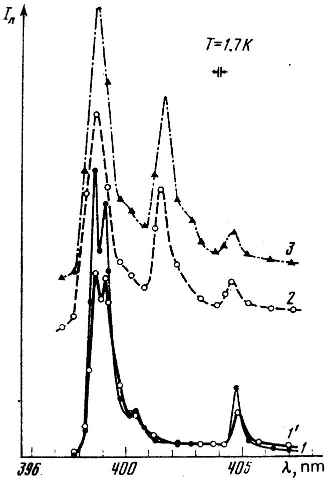

FIG. 1. Luminescence spectra of anthracene single crystals (the figure shows the spectral width of the slit used to register the spectra): 1, 1′—freely supported crystal; 2—crystal placed on quartz; 3—crystal placed on a gold layer.

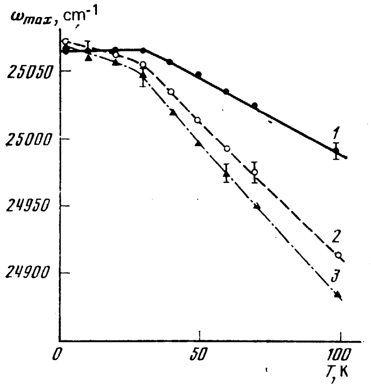

FIG. 2. Temperature dependence of the position of the maximum of 00 band of the exciton luminescence of anthracene: 1—freely supported crystal; 2—crystal in a contact with quartz; 3—crystal in contact with a gold layer.

Raising the temperature from 1.7 to 30 K causes a redistribution of intensity in the fine structure of the electronic band of the free standing single crystal anthracene without changing its position or its half-width (Figs. 2 and 3, curve 1), and leads to an appreciable decrease of the integral intensity of the exciton luminescence. The emission spectra of an anthracene crystal located on a gold electrode and on quartz, a negligible shift of the maximum of the electron band towards longer wavelengths is observed (Fig. 2, curves 2 and 3), as well as an increase of the half-width (Fig. 3, curves 2 and 3), a decrease of the intensity of the electronic and defect bands, and a slight increase of the intensity of the vibronic band. Further raising of the temperature from 30 to 100 K causes considerable changes in the emission spectra of both the free anthracene single crystal and on those in contact. The fine structure vanishes, the purely electronic band shifts towards longer wavelengths and its half-width increases (the largest shift and broadening are observed for a crystal placed

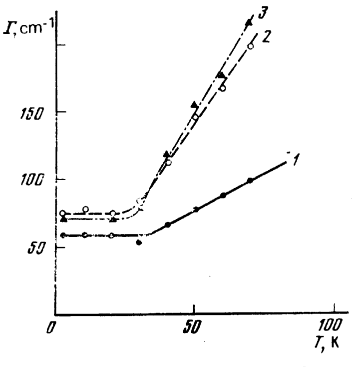

FIG. 3. Temperature dependence of the half-width Γ(*T*) of the 00 band of the exciton luminescence of anthracene: 1—freely supported crystal; 2—crystal on quartz; 3—crystal on gold.

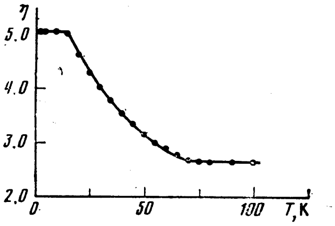

FIG. 4. Temperature dependence of metallic quenching of Frenkel excitons.

on a gold electrode). For a crystal placed on an optical contact, the intensity of the deformation band decreases and vanishes at a temperature close to 50 K. The temperature at which the defect band vanishes varies from sample to sample, depends on the crystal strain due to optical contact of the crystal with the substrate. In the same temperature interval, the asymmetry of the electron energy bands of all the crystals decreases.

The metallic quenching of the Frenkel excitons were determined experimentally from the formula

$$\eta=I_{\mathrm{qu}}/(I_{\mathrm{qu}}-I_{\mathrm{met}}), \tag{1}$$

where I_{qu} and I_{met} are the integrated luminescence intensities of the same anthracene single crystal placed respectively on quartz and on gold. The temperature dependence of η for the anthracene-gold system on a quartz plate is shown in Fig. 4.

DISCUSSION OF RESULTS

Metallic quenching. Before we discuss the plot shown in Fig. 4, we must examine the influence of inhomogeneous strains in the single crystal on a contact with a substrate on the process of the exciton quenching. These strains are produced at low temperatures because of the difference in the coefficients of the linear expansion of the crystal and the substrate. At 100 K the coefficient of thermal expansion of anthracene is 20×10^{-6} deg^{-1},[12] while for gold and quartz the respective values are 11.5×10^{-6} and 6.1×10^{-7} deg^{-1}.[13] To produce a relative decrease of the contribution of the strains to the exciton quenching, the same single crystal was simultaneously placed in optical contact with gold and fused quartz. It was assumed that the character of the strains in the anthracene on the quartz and on the gold is the same.

A control experiment was also performed and demonstrated the presence of metallic quenching of the excitons. To this end, a dispersed film of gold (thickness ~100 Å) was sputtered on an anthracene single crystal (thickness ~10 μm). The luminescence of this crystal was excited and registered through the gold film. Curve 1′ of Fig. 1 shows the result. It is seen that the luminescence spectrum is similar to the spectrum of the free anthracene single crystal, although the integral intensity is substantially decreased. The emission spectrum of the crystal with the sputtered gold film has no deformation band. This result, in our opinion, confirms the existence of metallic quenching of the Frenkel electrons on the boundary of the anthracene with the gold, and the plots shown in Fig. 4 reflects qualitatively the change of the magnitude of this quenching with temperature.

We examine first quenching of noncoherent excitons, i.e., we discuss the results of the measurements at high temperatures (60–100 K). In the diffusion approximation of the description of the exciton motion, the expression for the exciton quenching is of the form[1]

$$\eta=\frac{l_a+L}{L}\left(1+\frac{L}{v\tau}\right), \tag{2}$$

where $L=(D\tau)^{1/2}$ is the diffusion displacement of the excitons, τ is their lifetime, D is the diffusion coefficient, v is the rate of quenching of the excitons, and $l_a=1/K_a$ is the depth of penetration of the light exciting the excitons in the crystal.

If we assume for anthracene[1] $l_a=1000$ Å, $L=420$ Å, $\tau=5\times10^{-9}$ sec, and $v=4\times10^{4}$ cm/sec, we obtain $\eta=3.45$— a value close to the experimental one (Fig. 4). From this we can conclude that quenching of noncoherent excitons takes place in the temperature region in question. In the case of noncoherent excitons, in accordance with Ref. 1, the presence of the metal leads to the appearance of forces that contribute to exciton diffusion directed towards the substrate. This circumstance can be regarded as an additional exciton-annihilation channel.

When the temperature is lowered to 1.7 K, the motion of the excitons in the anthracene becomes coherent. This fact should influence the function $\eta(T)$. It seems to us that the growth of η in the region of low temperatures and the saturation of this growth are due to the influence of the coherence of the Frenkel excitons on their metallic quenching. Unfortunately it is difficult to speak of good coherence of excitons, since the crystal is deformed. It is qualitatively seen, however, that the values of the exciton quenching in the low-temperature and in the high-temperature regions are different. If we assume that expression (2) can be used for the low-temperature region, then the increase of η with decreasing temperature is due to the increase of L and v. At low temperatures the increase of the rate of surface annihilation of the excitons can also produce surface states of the crystal.

Exciton-phonon interaction. The processes of interaction of excitons with phonons can be assessed from the dependence of the half-width and the position of the electronic luminescence band on the temperature. The results of measurements of these dependences are shown in Figs. 2 and 3.

An analysis of the relations obtained for a freely supported single crystal shows that the main contribution to the broadening and the displacement of the 00 band of the exciton luminescence with temperature (up to 100 K) is made by phonons with energy 45 cm^{-1}. This agrees with the published data.[9,10]

Substantial changes of the plots of $\Gamma(T)$ and $\omega(T)$ are observed for crystals in contact with quartz and gold. The temperature-independent sections of the quantities $\Gamma(0)$ and $\omega(0)$ decrease, and the plots of $\Gamma(T)$ and $\omega(T)$ become much steeper with increasing temperature. The observed changes are apparently due to two circumstances, to the influence of the inhomogeneous strains of the crystal and to the appearance of interaction of excitons with the metal. Thus, from the different behaviors of $\Gamma(T)$ and $\omega(T)$ of an anthracene crystal placed on a contact with a gold layer and with quartz one can conclude only qualitatively that the metal exerts an influence on the exciton-phonon interaction in the anthracene. It is of interest to obtain theoretical relations for $\Gamma(T)$ and $\omega(T)$ with account taken of the influence of the considered metallic quenching of the excitons.

Thus, the measurements of the luminescence spectra of single crystals of anthracene on a contact with gold at low temperatures have made it possible to observe experimentally, for the first time ever, metallic quenching of Frenkel excitons in the low-temperature region. It is concluded that the coherent and noncoherent excitons are differently quenched. Finally, it is shown that metallic quenching of excitons influences the exciton-phonon interaction in crystals.

In conclusion, the authors thank A. F. Prikhot'ko for support and V. G. Litovchenko for a discussion of the results.

[1] V. M. Agranovich and M. D. Galanin, Perenos energii élektronnogo vozbuzhdeniya v kondensirovannykh sredakh (Electronic Excitation Energy Transport in Condensed Media), Nauka, 1978, Chaps. 7, 8.
[2] V. I. Sugakov and V. N. Khotyantsev, Zh. Eksp. Teor. Fiz. **70**, 1566 (1976) [Sov. Phys. JETP **43**, 817 (1976)].
[3] H. Kallmann, G. Vaubel, and H. Baessler, Phys. Stat. Sol. (b) **44**, 813 (1971). G. Vaubel, H. Baessler, and D. Mobius, Chem. Phys. Lett. **10**, 334 (1971).
[4] J. Singh and H. Baessler, Phys. Stat. Sol. (b) **62**, 147 (1974). H. Baessler and H. Kurczewska, J. Luminesc. **15**, 261 (1977).
[5] V. M. Agranovich, Yu. V. Konobeev, and M. A. Mekhtiev, Fiz. Tverd. Tela (Leningrad) **10**, 1754 (1968) [Sov. Phys. Solid State **10**, 1383 (1968)].
[6] N. A. Efremov and A. G. Mal'shukov, *ibid.* **17**, 2239 (1975) [**17**, 1482 (1975)].
[7] A. Hammer and H. C. Wolf, Mol. Cryst. **4**, 191 (1968).
[8] M. D. Galanin, Sh. D. Khan-Magometova, and E. A. Chizhikova, Izv. AN SSSR ser. fiz. **39**, 1807 (1975).
[9] M. S. Brodin and M. A. Dudinskii, S. V. Marisova, and É. N. Myasnikov, Ukr. Fiz. Zh. **20**, 1217 (1975). A. S. Davydov and É. N. Myasnikov, *ibid.* **23**, 705 (1978).
[10] A. R. Lacey and L. E. Lyons, J. Chem. Soc. No. 12, 5393 (1964).
[11] V. A. Lisovenko and M. T. Shpak, Izv. AN SSSR ser. fiz. **39**, 2226 (1975).
[12] A. I. Ryzhenkov, V. M. Kozhin, and P. M. Myasnikova, Kristallografiya **13**, 1028 (1968) [Sov. Phys. Crystallogr. **13**, 896 (1969)].
[13] S. I. Novikova, Teplovoe rasshirenie tverdykh tel (Thermal Expansion of Solids), Nauka, 1974, pp. 204 and 265.

Translated by J. G. Adashko

Coherent excitation of inversion of nuclei by a modulated beam of randomly distributed relativistic electrons

V. I. Vysotskiĭ, V. I. Vorontsov, and R. N. Kuz'min

Kiev State University
and Moscow State University

(Submitted 13 July 1979)
Zh. Eksp. Teor. Fiz. **78**, 100–104 (January 1980)

The possibilities are analyzed of obtaining a coherent flux of resonant pseudophotons for the excitation of an inversion state in Mössbauer nuclei. The spectral composition of radiation accompanying the motion of a modulated beam of superrelativistic electrons whose space-time distribution is described by Poisson statistics is considered. The emission spectrum has coherent and noncoherent components at the beam-modulation frequency. The flux density of the coherent component of the radiation, at realistic parameters of the beam, of the modulator, and of the accelerator, satisfies the γ-amplification threshold condition.

PACS numbers: 76.80. + y, 23.20.Lv, 41.80.Dd

The continuing active discussion of the problem of developing a gamma laser stimulates the search for optimal mechanisms of excitation of the inversion in such devices. In view of the considerable principal difficulties in the realization of a system of long-lived gamma transitions, due to the need of eliminating vanishingly small perturbations and stimulated narrowing of the line width by 5–8 orders of magnitude, a search is being made for more realistic results on the basis of another system, which makes use of different variants of a system based on short-lived Mössbauer nuclei with natural line width. As a result of the high spectral pump density $P(\omega)$ needed to realize such a model, the source must satisfy a number of conditions, one of which, for the case of radiation pumping, reduces to the requirement that the pump spectrum band be narrow $\Delta\omega \lesssim \Gamma\hbar$ ($\Gamma/\hbar$ is the width of the activation level of the excited nuclei). If the inverse inequality $\Delta\omega \gg \Gamma/\hbar$ is satisfied, the possible strong heating and destruction of the working medium make the use of the Mössbauer effect practically impossible, and without this effect the problem cannot be solved. From this point of view [as well as with

0038-5646/80/010049-03$02.40