previously observed and identified as a second-order Doppler shift resulting from the thermal motion of the atoms. See R. V. Pound and G. A. Rebka, Jr., Phys. Rev. Letters 4, 274 (1960).

[6]I. Solomon, Compt. rend. 250, 3828 (1960). Apart from the numerical constant which was not given in this reference, our Eq. (1) is the same as the result given there.

[7]R. E. Watson and A. J. Freeman, Phys. Rev. 120, 1125 (1960).

[8]C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Govern-

ment Printing Office, Washington, D. C. 1952), Vol. 2.

[9]R. E. Watson, Phys. Rev. 119, 1934 (1960). An estimate of the charge $|\psi_0(0)|^2$ for the inner s electron was made from this reference in which the configurations $3d^{n-2}4s^2$ are considered.

[10]J. S. Van Wieringen, Discussions Faraday Soc. No. 19, 118 (1955).

[11]The effect of covalency on the occupation of d orbitals is neglected.

[12]M. Goldhaber (private communication).

[13]J. Eisinger and V. Jaccarino, Revs. Modern Phys. 30, 528 (1958).

EVIDENCE FOR THE EXISTENCE OF SURFACE EXCITONS IN TETRACENE MICROCRYSTALS*

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During the past few years there have been a number of predictions of new types of excitons in molecular crystals.[1]

Selivanenko[2] predicted the existence of surface excitons in molecular crystals with a high heat of fusion. Ferguson and Schneider[3] observed a b-polarized shoulder in a 0.2μ anthracene film which was not observed in thicker films. These authors believed that it was unlikely that this band be due to a surface exciton. However, McClure[1] interpreted this 25100-cm^{-1} band as the b-polarized factor group component of the pure electronic transition occurring in these surface molecules.

We have observed two absorption bands in thin tetracene (microcrystalline) films prepared by rapid sublimation under conditions which produce a high surface-to-volume ratio. Rapid sublimation is essential[2] to increase the density of surface states.

No absorption above 5200 A was observed in thick crystals grown from the vapor under vacuum. However, when these same crystals were sublimed rapidly, under vacuum, onto a quartz disk forming a highly imperfect surface, a band at about 5400 A was observed. The two bands in the range 530-600 mμ could not be observed in the solutions made by dissolving the films in suitable solvents. This proves that these bands were not due to an impurity produced during the preparation.

Films were prepared under a pressure of 30 μ, but with different rates of sublimation. No absorption in the range 520-600 mμ occurred in

slowly sublimed films. However, films prepared by rapid sublimation (at 130°C) exhibited one strong band when the film was about 0.5 μ and two strong bands at a thickness of 1 - 1.5 μ. The 1 μ need not be the thickness of the microcrystals involved. This observation of a critical thickness is an indication that the 5330A band (I) involves either a minimum crystalline length or a crystalline structure that can exist in stable form only above a certain thickness. Below such a thickness either the strains or the large number of imperfections, due to the high (surface/volume) ratio, make such a crystalline structure unstable. Table I summarizes sample data on the positions and extinction coefficients. Band II at 5350 A shifts continuously to about 6000 A with increasing thickness. Band I is very sharp

Table I. Dependence of the position and intensity of the surface excitons on thickness.

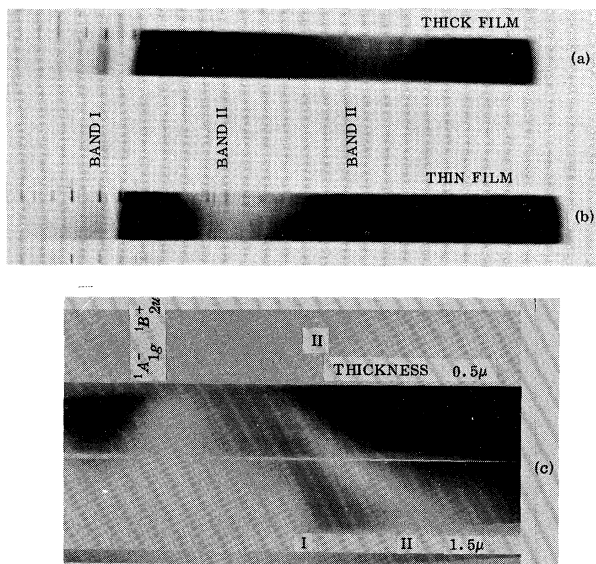| Wavelength (A)	Thickness (μ)	$\epsilon \times 10^{-3}$ (cm^{-1})	Bandwidth (cm^{-1})
5344 (I)	1 - 2	. . .	25 - 75 (80°K)
5650 (II)	0.4 - 2	. . .	100 - 300 (300°K)
5340 (II)	0.4	4.2	. . .
5410 (II)	1	4.4	. . .
5540 (II)	1.3	4.9	. . .
5680 (II)	1.5	4.4	. . .

FIG. 1. In (a) and (b), bands I and II are clearly seen at 80°K. The thickness of the film in (a) is about 1.5 μ and in (b) it is about 0.5 μ. Note the shifts of I and II with thickness. In (c) the continuous shift of II with thickness is seen clearly at 300°K. Note that I appears suddenly at a critical thickness (see text). The 0-0' of the molecular $^1A_{1g}{}^- \rightarrow {}^1B_{2u}{}^+$ transition is shown for comparison. A large Hilger spectrograph with glass optics was used throughout.

and shifts with thickness (see Fig. 1) about 100 A over the range 1 - 2 μ. The critical thickness depends on temperature. At 80°K, I is observed in a thinner film that at 300°K.

Besides the shift in the position of band II with thickness, its intensity may increase or decrease as it shifts to longer wavelength. We do not report oscillator strength, and due to variations in bandwidth with thickness, the intensity of the band is not linearly proportional to the extinction coefficient.

Heating in air up to 130°C for 3 hours did not induce any absorption in films where the bands are absent. Furthermore, a similar heat treatment did not change the bands when these were present. Tetracene is extremely sensitive to oxidation in solution but stable in the solid state. The lack of sensitivity of these bands to oxidation means that these states involve several "crystalline" layers of tetracene, and due to the packing in a crystal, the oxygen molecules cannot penetrate deep enough to produce observable damage.

Using a 10^3 magnification and polarized light, a difference between films that do not display "surface states" and those that do was observed: The nonabsorbing films consisted of microcrystals whose linear dimensions were of the order of 5 microns, about 1 micron thick, and appeared to be of the flaky type. As for the "absorbing" films, their dimensions were just at the limit of visibility and must be less than a micron. It was not possible to determine the shape, or dimensions, of these microcrystals. Furthermore, a large number of needle-like crystals were observed along with these microcrystals. Thus two different crystalline forms exist in these films. I and II might then arise in the same crystal or in two different types of crystalline structure.

Two arguments in favor of surface states rather than surface imperfections are the shift of the energy with thickness and the sharpness of the bands. The shift in the energy is of the order of 10%, i.e., 0.2 ev, from the thin to the thick edge of a film. It has been pointed out[3] that surface imperfections could lead to new states but theoretical and experimental proofs do not exist to support this hypothesis. Surface imperfections are, however, important perturbations of surface states. Since such imperfections act to decrease the degree of surface order they also act to raise the energy levels. This might account for the observed shift with thickness—it being assumed that film thickness determines approximately the size of the microcrystals.

Since there should be a large variety of surface imperfections, there should be an equally broad distribution in the energy levels. This would lead to broad absorption bands, whereas we observe a very sharp band I and band II is still sharper than the molecular $^1A_{1g}{}^- \rightarrow {}^1B_{2u}{}^+$ bands (these bands have half-widths of 480, 340, 480, 780 cm^{-1}) in the solid state at 90°K.

[1] D. S. McClure, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1959), Vol. 8, p. 1.

[2] A. S. Selivanenko, J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 75 (1957) [translation: Soviet Phys.- JETP 5, 79 (1957)].

[3] J. Ferguson and W. A. Schneider, J. Chem. Phys. 28, 761 (1958).
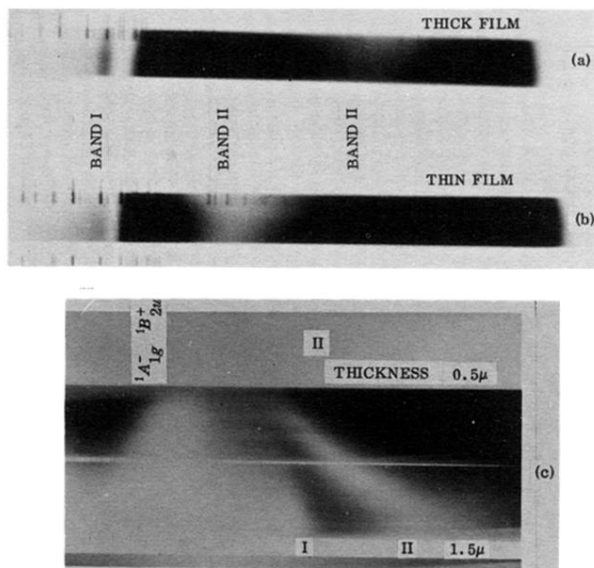
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