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# Pressure-Induced Phase Transition in Pentacene-Doped Tetracene Single Crystals†

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From the pressure dependence of the spatial anisotropy of the magnetic field effect on the guest fluorescence of pentacene-doped tetracene single crystals it is concluded that a phase transition occurs near 3 kbar.

The result is briefly discussed in comparison with a similar phenomenon in neat tetracene crystals.

The spatial anisotropy of the effect of the magnetic field on singlet exciton fission can be utilized to infer about changes in the crystal structure.

The angular separation between the high field pair state resonances in tetracene crystals under normal conditions is approximately 53° in the ab-plane.[1-5]

The introduction of large amounts ($>9\%$) of 2,3-benzocarbazole was found to reduce this separation for the host fluorescence down to about 37°.[4] In contrast, at pressures greater than ~3 kbar the neat tetracene high field resonance directions are separated by a greater angular distance of 58°.[5]

These experimental results are interpreted as indicating that tetracene crystals undergo a crystallographic phase transition.

As in the case of homofission, exciton heterofission in pentacene-doped tetracene crystals was found to be magnetic field sensitive.[6-8]

From the positions of the level crossing resonances for the guest fluorescence and known spin—Hamiltonian parameters conclusions concerning the guest molecule orientation in the host crystal can be inferred. It is usually assumed

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that pentacene molecules enter substitutionally into lattice sites in the tetracene crystals without significantly distorting the lattice.[6,8]

Since undoped tetracene crystal undergoes a pressure-induced phase transition at the pressure $p \approx 3$ kbar[5,9] and since the new high-pressure crystal structure reveals a different behaviour under hydrostatic pressure one would expect a suitable change in the orientation of the guest molecules embedded in the crystal lattice and as a result a change in the anisotropy of the magnetic field effect on guest fluorescence.

We have therefore measured the angular dependences of the red pentacene fluorescence from a pentacene-doped tetracene crystal* for rotation of the magnetic field in the ab-plane at various pressures (from 1 Atm to ~5 kbar).

For the measurements, a gaseous high-pressure system consisting of an optical cell, pressure intensifier and pressure conducting paths was assembled. The experimental details have been described elsewhere.[5,9] Figure 1 shows a schematic drawing of the measuring cell placing between the poles of the rotating magnet.

The anisotropy of the magnetic field dependence of both green tetracene and red pentacene fluorescence in a pentacene-doped tetracene crystal (thickness 32 μm) is shown in Figure 2.

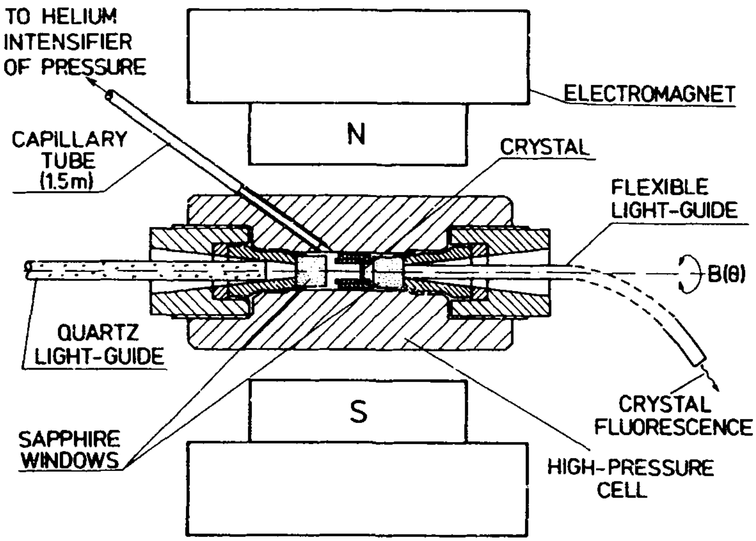

FIGURE 1 Diagram illustrating the high pressure cell placing between the poles of the rotating electromagnet used for measurements of the high-field anisotropy in the magnetic field effect on the crystal fluorescence.

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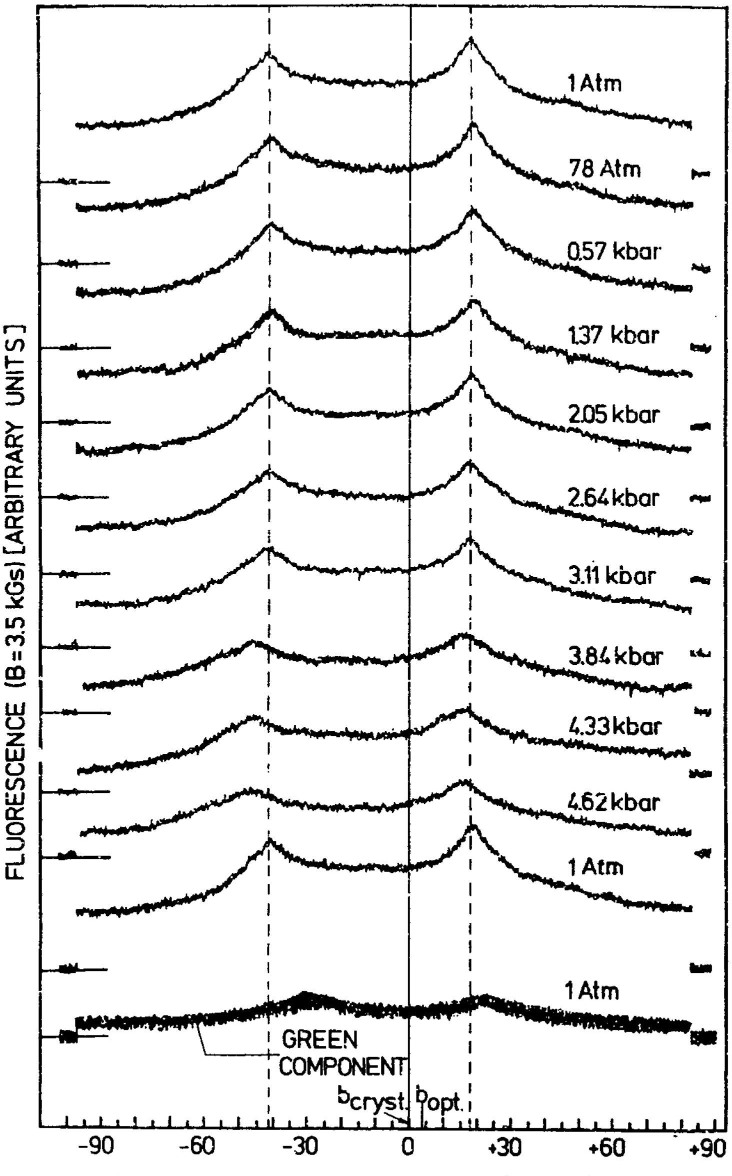

FIGURE 2 The fluorescence intensity in a magnetic field of 3.5 kGs rotating in the ab-plane of a pentacene-doped tetracene crystal (thickness 32 $\mu$m; pentacene concentration: $10^3$ ppm) under various pressures. All of the curves, except the lo-west one (green component), obtained for the red pentacene fluorescene.

The first curve above that for the green component, was obtained afterwards when the pressure in the cell was reduced to $p = 1$ Atm. The short horizontal lines in the left of the figure indicate fluorescence levels before the application of a magnetic field. The maximal percentage of the field enhancement (at 1 Atm before the pressure run) is ~32% for the red and ~10% for green fluorescence. Excitation with (430 ± 10 nm) wavelength light.

The green fluorescence exhibits the two peaks at −30° and +22° with respect to the crystallographic $b$-axis ($b_{\text{cryst}}$) in reasonable agreement with the results of undoped crystals and after corrections on location of the optically determined extinction direction for the $b$-axis ($b_{\text{opt}}$), with those found in Refs. 1, 3, 4, and 7. The maximal percentage of the magnetic field enhancement however, is only 10% for the doped crystal as compared to 35%[1,3,4,8] and 25%[5,10] in neat tetracene.

The experimentally observed red fluorescence at atmospheric pressure exhibits two prominent resonances at −42° and +18° in addition to two very weak peaks at approximately +46° and −11°. The theoretical calculated orientations for these maxima are −42° and +20° according to Ref. 6, −47° and +13° according to Ref. 8 for pentacene site I and −12° and +44° Ref. 6, −18° and +42° Ref. 8 for pentacene site II (the site designations are those of Campbell *et al.*[11]).

Our experimental results are in good agreement with the calculated data of Geacintov *et al.*[6] and show differences as compared with the data of Burgos *et al.*[8]

In light of these comparisons and because of the difficulties of locating the crystallographic axes and then aligning the crystal in a holder, the hypothesis of the substitutional entering of pentacene molecules into tetracene crystal at atmospheric pressure[6,8] still requires verification.

In constrast, the measurements of the resonance peaks separation and particularly a relative change in their position measured with the same crystal in the same holder can be performed with a much better accuracy of about 0.5°.

With increasing pressure, fluorescence intensity of both components increases gradually† and there is a concomitant decrease in the magnetic field enhancement of the prompt fluorescence. Above 1 kbar, the magnetic field enhancement for the green component was beyond the experimental detectability.

For the red component, within experimental error, the orientations of the magnetic field where resonances occur remain unchanged up to 3.11 kbar. At higher pressures ($\gtrsim 3$ kbar) both the position and separation of the prominent resonance peaks have been found to change discontinuously. The new orientations of the resonance maxima are −46.5° and +16.5°. They are 63° apart and remain constant up to the maximum pressure applied 4.62 kbar (see Figure 2). The new angular separation shows 3°-difference as compared to the low pressure case.

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† A discussion of the pressure-induced fluorescence increase in neat tetracene is given in Ref. 12.

We note that this difference in the high field pair state resonances in neat tetracene for low- and high-pressure modifications equals 6 ± 1°.[5]

This change is reversible, after the pressure in the cell is returned to atmospheric pressure the resonance peaks return to their previous positions (Figure 2—the first curve above that for the green component).

If we assume that the observed discontinuity in the spatial anisotropy of the magnetic field effect on the red fluorescence component is due to the same pressure-induced phase transition as that found in undoped tetracene crystals[5,9] then the difference observed in the pressure-induced shift in the positions and separations of the resenonace peaks in these two (doped and undoped) crystals can be ascribed to the difference in the guest and host molecular zero field splitting parameters[6] and/or to a new orientation of the pentacene molecules deviated from that of an unperturbed host molecule. Thus it may not be excluded that the observed difference in the magnitude of the pressure shift of the guest resonance positions as compared to that in neat tetracene could be due to a different incorporation of the pentacene molecules, at least, into site I of the tetracene crystal lattice in its high-pressure modification.

This supposition requires, however, independent verification which could be done if the high-pressure structure of tetracene crystal is determined.

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