

# Critical point of isostructural phase transition in photomodified anthracene

I. L. Aptekar' and A. E. Galashin

*Institute of Solid State Physics, Academy of Sciences of the USSR, Moscow*

(Submitted 19 August 1982)

*Pis'ma Zh. Eksp. Teor. Fiz.* **36**, No. 7, 256–259 (5 October 1982)

An isostructural phase transition (IPT) is observed under certain temperatures and UV radiation intensities in a photomodified anthracene (dianthracene) crystal. The IPT curve, which ends at the critical point, and the coordinates of this point ( $T_c = 620 \pm 20$  K,  $I_c = 70^{19.5 \pm 0.3}$  photons/cm<sup>2</sup>·s) are calculated from the experimental data.

PACS numbers: 64.70.Kb, 61.65. + d

Isostructural phase transitions in the solid state are very rare and have heretofore been observed only in cerium, samarium sulfide and their alloys.<sup>1</sup> These substances are pseudobinary solutions of rare-earth metal ions with different valency. The concentration  $X$  of pseudobinary solutions is not an external, fixed parameter, as for the usual solutions, but an internal parameter corresponding to minimum thermodynamic potential. For this reason, they behave as single-component systems and undergo an isostructural phase transition instead of stratification into phases with different composition. The equilibrium curve for two crystalline isomorphic phases in the  $P$ - $T$  diagram terminates at the critical point.<sup>2</sup>

In a UV-stabilized, photomodified anthracene crystal, a stationary concentration  $X$  of sandwich-like pairs of anthracene molecules  $A \cdot A$  is established; this represents a pair of molecules arranged in parallel, one above the other. For all  $X$  up to  $X \cong 1$ , the photomodified anthracene lattice retains the crystallographic dianthracene, i.e., orthorhombic syngony and spatial group  $P_{bca}$ . Without visible changes in the lattice, dianthracene molecules (dimer)  $A_2$  decompose into pairs  $A \cdot A$ , and after absorbing a photon, the latter again dimerize: chemical bonds form between two molecules in  $A \cdot A$ .<sup>3</sup> In its shape and dimensions, the dimer  $A_2$  is close to  $A \cdot A$ , but its volume is  $\sim 2.7\%$  smaller. The transformations  $A_2 \rightleftharpoons A \cdot A$  in photomodified anthracene are similar to the transformations  $\text{Sm}^{2+} \rightleftharpoons \text{Sm}^{3+}$  in SmS crystals, which suggests an analogous isostructural phase transition in these compounds, which differ in their nature.

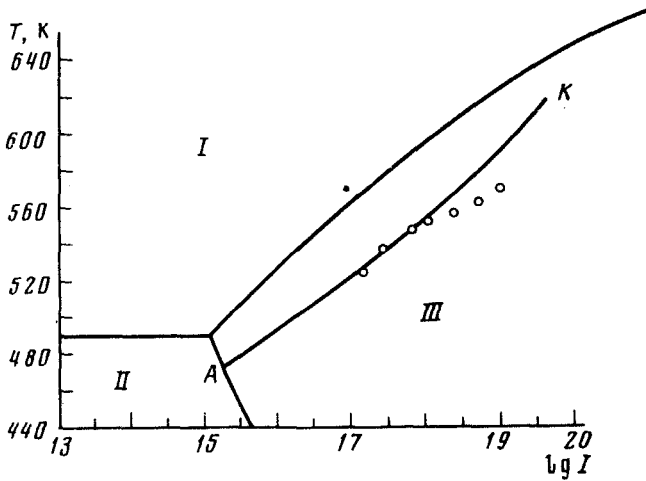


FIG. 1. The phase  $T$ - $\log I$  diagram of anthracene. I) Liquid; II) anthracene crystal; III) photomodified anthracene crystal;  $AK$  is the IPT curve, and the points indicate the fracturing temperature of the crystals.

The pseudobinary solutions formed under the action of light correspond to stationary states rather than equilibrium states. Nevertheless, their phase transitions (photocondensation and photocrystallization,<sup>3,4</sup> photostimulated decrease in the melting temperature of molecular crystals<sup>5</sup>) are phenomenologically indistinguishable from the usual phase transitions. An analogous situation can be expected for photophase transitions in the solid state. In fact, when photomodified anthracene crystals are heated under conditions  $I = \text{const}$ , they seem to decompose, and this process occurs simultaneously throughout the entire volume at a temperature, reproducible to within 2 K, similar to the explosive atomization of single crystals, which is accompanied by IPT in compounds based on SmS.<sup>1</sup> The dependence of the temperature of such breakdown on the light intensity for photomodified anthracene is shown in Fig. 1. The decomposition, i.e., the IPT, is recorded visually with the help of a setup described in Ref. 4.

In order to confirm the fact that the IPT occurs in photomodified anthracene crystals and to find the position of the critical point, it is necessary to know the dependence  $X(T, I)$ . The entire set of experimental data can be analyzed within the framework of the model of pseudobinary solutions.<sup>2,3</sup>

We determined the composition of the photomodified anthracene crystal by measuring its optical density at a wavelength of 337 nm (light with  $\lambda > 300$  nm is not absorbed by dimers) in an evacuated cell with a gap thickness  $\sim 1 \mu\text{m}$  made of optical quality quartz. The probing was performed with a laser light beam ( $\lambda = 337$  nm,  $\nu_{\text{pulse}} = 10$  Hz,  $\tau_{\text{pulse}} = 10$  ns,  $N_{\text{pulse}} = 10^7$ - $10^8$  photons/pulse), which was focused at the center of the crystal up to  $\phi 0.3$  mm. The crystal was stabilized by a light from a point mercury lamp ( $\lambda = 365$  nm). The optical-density dependences  $D(T)$  obtained with different  $I$  and the kinetic curves of accumulation of  $A \cdot A$  with the IPT under dark conditions are presented in Figs. 2 and 3.

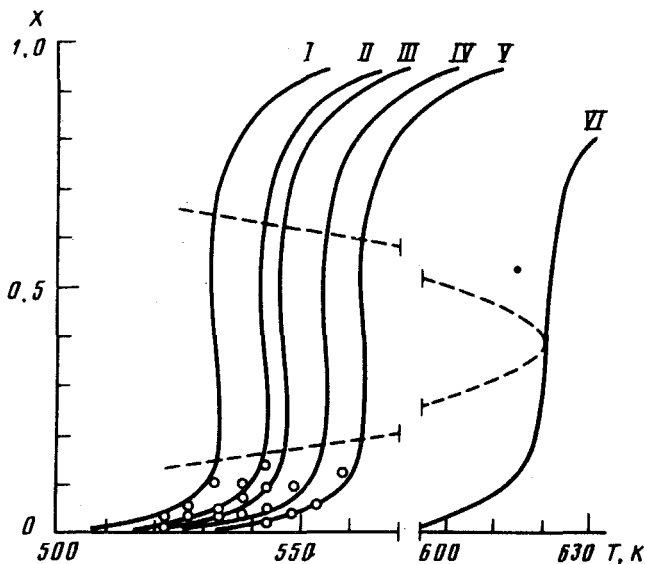


FIG. 2. Computed temperature dependences of stationary concentrations of sandwich pairs of anthracene molecules in a photomodified anthracene crystal. I— $I = 1.4 \times 10^{17}$ , II— $I = 2.7 \times 10^{17}$ , III— $I = 3.6 \times 10^{17}$ , IV— $I = 6.2 \times 10^{17}$ , V— $I = 10^{18}$ , VI— $I = 4 \times 10^{19}$  photon/cm<sup>2</sup>·s; the points indicate experimental values.

The condition for a stationary state in photomodified anthracene crystals is the equality of the rates of photodimerization of pairs  $A \cdot A$

$$v_p = \left. \frac{dX}{dt} \right|_{I=0} = (1-X) A_p \exp \left[ - \left( U_p^0 + K_p^1 X + K_p^2 X^2 \right) / T \right] \quad (1)$$

and decomposition of dimers  $A_2$

$$v_d = I X A_d \exp \left[ - \left( U_d^0 + K_d^1 X + K_d^2 X^2 \right) / T \right]. \quad (2)$$

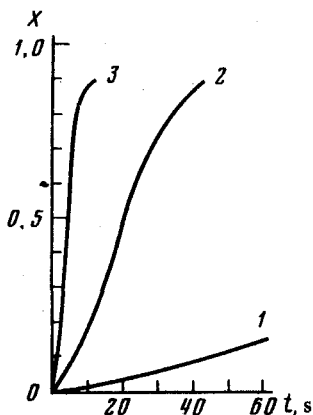


FIG. 3. Kinetics of decomposition of anthracene dimers in a photomodified anthracene crystal after switching-off the stabilizing UV radiation. 1)  $T = 503$  K; 2)  $T = 523$  K; 3)  $T = 543$  K; the experimental curve almost coincides with the computed curve.

TABLE I. Values of the coefficients in the equation of state of photomodified anthracene.<sup>1)</sup>

$A_p/A_d$ cm <sup>2</sup> /s/photon	$U_p^0$ , K	$k_p^1$ , K	$k_p^2$ , K	$U_d^0$ , K	$k_d^1$ , K	$k_d^2$ , K
$1.5 \times 10^{-23}$	$2.4 \times 10^4$	$-2.6 \times 10^3$	$2 \times 10^3$	$3 \times 10^3$	$2.6 \times 10^3$	$-2 \times 10^3$

From this condition we obtained the equation of state of photomodified anthracene in a UV field

$$(1 - X) / X = I (A_d / A_p) \exp \{ [ U_p^0 - U_d^0 + (k_p^1 - k_d^1) X + (k_p^2 - k_d^2) X^2 ] / T \}. \quad (3)$$

Since the optical densities were measured in the experiments, and  $X = D/D_0$ , where  $D_0$  is the optical density of the crystal consisting only of  $A \cdot A$ , the results were analyzed using Eqs. (1)–(3) that contain  $D$ .

The coefficients in the equation of state (3) were determined from the conditions that they give the best description of all of the experimental data (see Table I). The observed dependence of the activation energy of the decomposition of dimers and their formation in the photomodified anthracene crystal proves the possibility of the occurrence of IPT. For  $T < T_c$ , Eq. (3) has three roots, two of which correspond to stable isomorphous phases in a UV field with different compositions, while for  $T > T_c$ , they have a single root. Therefore, in the supercritical region, when the external factors ( $T$  and  $I$ ) vary, the composition of the photomodified anthracene can change continuously, while for  $T < T_c$ , an IPT is observed (see Fig. 2). Applying a Maxwell construction to the equation of state (3), we obtain the IPT curve (Fig. 1), which terminates at the point  $T_c = 620 \pm 20$  K,  $I_c = 10^{19.5 \pm 0.3}$  photons/cm<sup>2</sup>·s. The points in Fig. 1, which correspond to visually recorded decomposition of photomodified anthracene crystals, are close to the computed IPT boundary. Their deviations toward lower values of  $T$  can be attributed to a short-time decrease of  $I$  due to the instability of the arc of the mercury lamp, which leads to premature (relative to the average value of  $I$ ) fracturing of the crystals due to the high  $\nu_p$  at high values of  $T$ .

It was not possible to observe the behavior of the crystals directly near the critical point and in the supercritical region due to the great experimental difficulties. Nevertheless, all of the observed properties of the behavior of photomodified anthracene in a light field, as well as the analysis performed indicate the presence of a critical point of IPT in photomodified anthracene crystals on the  $T$ - $I$  state diagram and, correspondingly, the critical curve of this transformation on the  $P$ - $T$ - $I$  state diagram of anthracene.

<sup>1)</sup>The equalities  $k_p^i = k_d^i$  indicate that the same factor increases the activation energy for decomposition of dimers and decreases it with their formation. There is a basis for assuming that stresses arising due to the difference in the sizes of  $A_2$  and  $A \cdot A$  are such a factor.

<sup>1)</sup>I. A. Smirnov and V. S. Oskotskii, Usp. Fiz. Nauk **124**, 241 (1978) [Sov. Phys. Usp. **21**, 117 (1978)].

<sup>2)</sup>I. L. Aptekar' and E. G. Ponyatovskii, Dokl. Akad. Nauk SSSR **173**, 851 (1967).

<sup>3)</sup>I. L. Aptekar' and A. E. Galashin, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 421 (1978) [JETP Lett. **28**, 389 (1978)].

<sup>4</sup>A. E. Galashin and E. A. Galashin, Dokl. Akad. Nauk SSSR 225, 345 (1975).

<sup>5</sup>I. L. Aptekar', A. E. Galashin, E. A. Galashin, and V. B. Yakovlev, Khim. Vys. Énerg. 13, 453 (1979).

Translated by M. E. Alferieff

Edited by S. J. Amoretty