

Kinetics of intercalation

V.Koshkin, N.Tkachenko, O.Yurchenko, Yu.Dolzhenko, V.Glushko

Kharkiv State Polytechnical University,
21 Frunze St., 310002 Kharkiv, Ukraine

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The process rate has been first directly measured for penetration of molecules into a layered crystal matrix resulting in formation of equilibrium intercalation compounds. Taking piperidine penetration into thin textured PbI_2 films as an example, the penetration speed has been shown to be from 10^{-4} to 10^{-3} cm/s, thus exceeding any typical diffusion rates. The intercalant penetration process has been shown to consist in the phase front motion along the matrix layers at a speed depending logarithmically on the intercalant vapor pressure. It is shown that layered crystals can be used to purify air from organic contaminants, in first turn, from those having pronounced electron-donating molecular properties.

Впервые осуществлено прямое измерение скорости процесса проникновения молекул в слоистую кристаллическую матрицу, результатом которого является образование равновесных интеркаляционных соединений. На примере тонких текстурированных пленок PbI_2 показано, что скорость этого процесса составляет 10^{-3} – 10^{-4} см/с, которая превышает любые характерные скорости диффузии. Показано, что процесс внедрения интеркалянта представляет собой движение фронта вдоль слоев матрицы, скорость которого зависит от давления паров интеркалирующих молекул. Показано, что слоистые кристаллы могут быть использованы для эффективной очистки от органических загрязнений, в первую очередь, от молекул с выраженными электродонорными свойствами.

Intercalation is the penetration of foreign atoms, ions or molecules into interlayer gaps of crystals having layered lattices. This process results in formation of equilibrium intercalation compounds [1, 2].

The intercalation becomes an important line in the functional materials technology. It allows to obtain high-capacity electrochemical accumulators [3] and solid catalysts [1], to modify parameters of superconductors [4], to produce equilibrium composites with miniband electron energy spectra [2, 5, 6], to detect small amounts of amines in gaseous and liquid media [7, 8], etc.

While thermodynamics of intercalation has been studied in sufficient detail both by theoretical and experimental methods [1, 2, 6, 9, 10], its kinetics is known only scantily. Works in this field, though few in number, have shown that the process goes

not by diffusion of individual molecules but as a frontal displacement of the intercalation phase accompanied by the dispersion of the initial matrix [11–13].

The purpose of this work is to investigate the first of above-mentioned features in detail. This process was studied in [11] on the qualitative level using massive single crystals. The intercalant penetration (in the form of intercalation phase) was shown to occur exceptionally along the crystal matrix layers. In this work, the phase front displacement is studied quantitatively using thin textured films as the matrix. This offers principally new possibilities for the process study.

Lead diiodide, a wide-band semiconductor with layered lattice, was used in experiments. The films were produced by vacuum evaporation onto glass substrates. The film

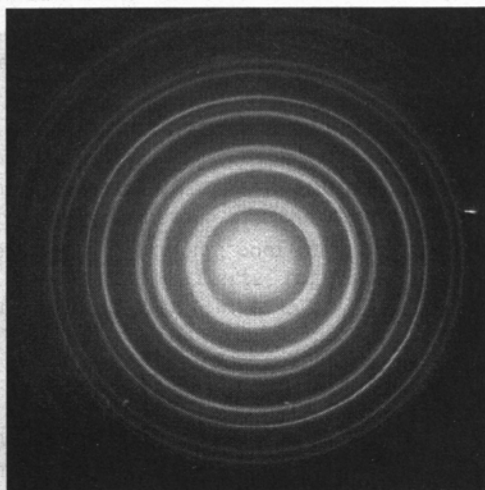


Fig.1. Electron diffraction pattern for a textured PbI_2 film at normal incidence of the electron beam.

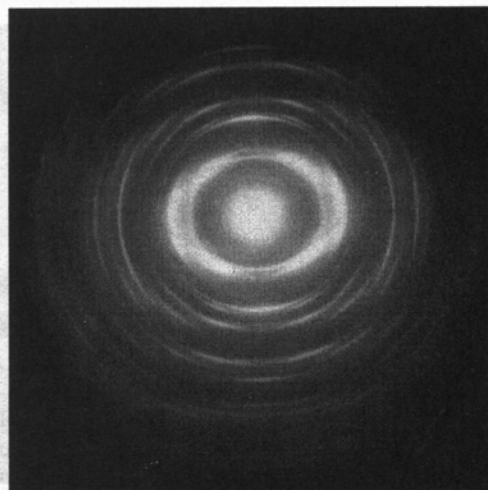


Fig.2. Electron diffraction pattern for a textured PbI_2 film at the incidence angle of electron beam 45° .

thickness was varied from 100 to 1500 Å. Films of thicknesses up to 1000 Å obtained at specific deposition conditions (which Prof. V.K.Miloslavsky had kindly reported to us) exhibit a well-pronounced texture confirmed specially by electron diffraction measurements. The films are oriented so that the layer planes are parallel to the substrate surface. Films of thickness less than 1500 Å are mirror-reflecting while thicker ones show an opalescence in reflected light, thus evidencing the texture deterioration and appearance of morphology nonuniformities on the surface.

Piperidine ($\text{C}_5\text{H}_{11}\text{N}$) was used as the intercalant. Its molecules were shown before [2] to form intercalation phases with PbI_2 .

To measure the intercalation phase penetration speed, the enlarged film image was projected on a screen and the video shooting was used, since the process is very fast. The formed intercalation compound shows the energy gap wider than that of the initial matrix [2, 5], therefore, the displacing intercalation phase is easy to distinguish (the intercalated film becomes colorless).

The intercalation was performed in a closed vessel from the vapor phase of piperidine. To study the process rate dependence on the piperidine concentration, solutions of piperidine in benzene were prepared (benzene was specially confirmed to be inert with respect to intercalation). The vapor-phase piperidine concentration calculated using the Raoult equation was varied from p_{pp} 2.7 Torr to 25 Torr.

The intercalation compound formation is accompanied obviously by the intercalant molecules removal from the vapor phase. To maintain its constant concentration, a vapor source in the form of liquid piperidine or its benzenic solution was placed into the sealed vessel where the samples were treated.

The film texturization is of fundamental importance, since the penetration of molecules into the layered matrix is defined by their motion along these layers, so the presence of texture ensures the process mechanism remains the same in through the whole film. Fig.1 presents the electron diffraction pattern (EDP) for the initial PbI_2 film taken at the electron beam normal to the film surface. The presence of a pronounced texture with the axis directed approximately along to [001] of PbI_2 hexagonal lattice is evidenced by very high intensities of all diffraction reflexes observed at rather small angles. This points that crystallites in the film are oriented so that at least planes corresponding to small indices are similar to the film surface in their orientation. As to the azimuthal direction, the reflex intensity varies at 60-degree period, thus reflecting the hexagonal lattice symmetry and confirming the pronounced texture. The picture becomes more complex when the electron beam is inclined to the film surface (Fig.2), since the coaxial structure gives reflexes in cross-sections inclined to [001] axis; but the periodicity in azimuthal direction along each reflex evidences also the texture.

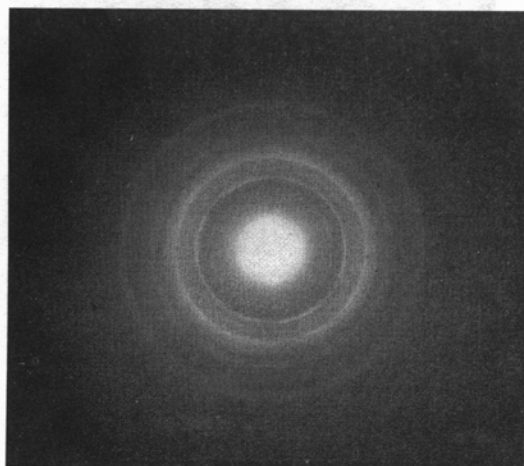


Fig.3. Electron diffraction pattern for a piperidine-intercalated PbI_2 film at normal incidence of the electron beam.

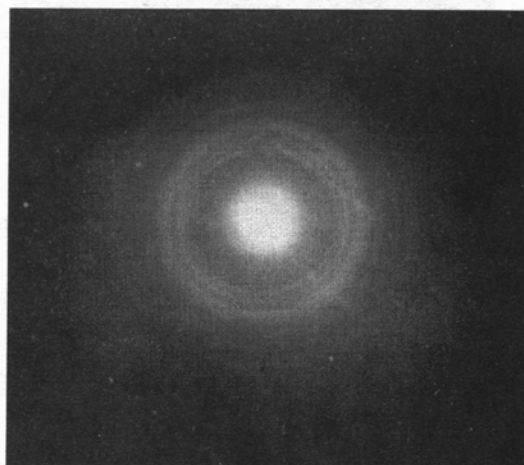


Fig.4. Electron diffraction pattern for a piperidine-intercalated PbI_2 film at the electron beam incidence angle 45° .

All signs of the film texture are retained after intercalation (Figs.3 and 4). The reflex intensity reduction is associated, in particular, with the film fragments breakdown (see below), but a rather insignificant reflex broadening after intercalation points that characteristic fragment size is not less than 1500 \AA . Reflex angles in electron diffraction patterns of intercalated samples differ obviously from those typical for initial PbI_2 films due to formation of the intercalated compound retaining the initial lattice symmetry as well as the texture but having a larger c parameter along the hexagonal axis and perhaps along directions perpendicular to the 6th order axis that results from formation of planar superlattices [2].

Qualitative observations. During first few seconds of experiment, the phase front is observed to move only from the film edges towards its center. The fronts pass in this time distances of the order of one millimeter remaining therewith very contrast. Further transformations of the film observable visually include the intercalated phase appearance on the whole film surface along with the front displacement. Examination by optical microscopy has shown that the intercalated phase arises in the form of islands which then grow at a rate of the same order as the front displacement speed from the film edges. The participation of an additional reaction channel acting on the whole film surface is sure to accelerate the process. It is concluded from this observation that the intercalated phase generation away from the film edges is defined by

macroscale defects—grain boundaries giving way to penetration of vapor phase molecules into the matrix interlayer gaps.

To avoid the intercalant penetration across the film surface defects, the film was covered by glass plates. In this case, the intercalated phase was observed to move only from the film edges on. In what follows, such experiments will be referred to as those made in sandwich geometry.

The films subjected to intercalation become dim and opaque. This confirms that the process is accompanied by the sample dispersion [11].

Using the projection at high magnification and the video shooting, we have revealed that the front of intercalation phase transparent in the visible spectral range is preceded by a "rainbow" one where the leading violet band is followed by green one while the band nearest to the intercalation phase front is red. This phenomenon will be explained in what follows.

Experiments were performed at two film orientations with respect to the vapor source, namely, the film was positioned either horizontally above the liquid surface or uprightly; in the last case, one sample edge was closer to the source surface than another. It turned out that in the horizontal film the intercalation phase fronts move symmetrically from all four film edges on, while if it is in upright position, the phase front is generated and moves more fastly at the side closest to the source. This fact is rather surprising, since characteristic times necessary to establish the equilibrium pres-

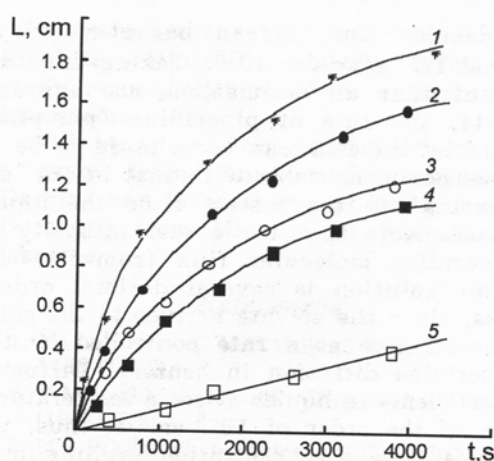


Fig. 5. Time dependence of the distance, L , passed by the intercalated phase at the piperidine partial pressure 8.4 Torr for films of different thicknesses d (Angstrom units): 100 (1), 200 (2), 450 (3), 1000 (4), 1500 (5).

sure in gas media are very short so that any process in condensed media is hardly able to compete with those. The intercalation seems to be just such a process. This phenomenon will be considered in what follows.

Quantitative results. Fig. 5 presents the dependence of distance, L , passed by the intercalation phase front on the exposure time, t , in piperidine vapor at its partial pressure 8.4 Torr for lead diiodide films of different thicknesses. The corresponding dependence for the front movement speed obtained by differentiation of curves shown in Fig. 5 is presented in Fig. 6. The speed values amounting typically 10^{-3} to 10^{-4} cm/s are many decimal orders higher than any typical diffusion rates in solids. Accounting for the above-mentioned fact that the intercalation phase front is sharply defined, it is to believe that the intercalation is not a diffusion-controlled process but resembles more closely the surface phase propagation in spreading effects [14].

It is seen from data of Figs. 5 and 6 that for the film thicknesses not exceeding 500 Å, the front displacement speed at the initial intercalation stage depends on the film thickness and becomes stabilized away from the film edges. These results are in agreement with the model [11] which states that the front of penetrating molecules causes high elastic stresses in the mouth of the crack developing according to the Griffith-Rebinder mechanism. It is just these stresses that hinder the penetration of intercalating molecules into interlayer gaps

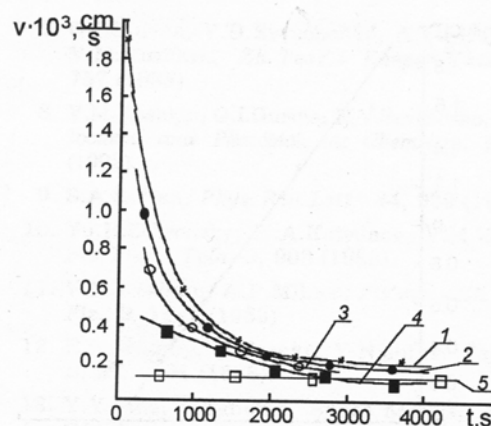


Fig. 6. Time dependence of the intercalation phase front speed, V , for films of different thicknesses d (Angstrom units): 100 (1), 200 (2), 450 (3), 1000 (4), 1500 (5).

nearest to that being filled. The characteristic size of the region where the mentioned stresses are of importance seems to be of several hundreds of Angstrom units. At larger distances between forming microcracks the intercalant penetrates into each interlayer gap independently of the process in other ones.

It was mentioned above that the intercalation front is preceded by a "rainbow" band. This fact confirms qualitatively the intercalation kinetics model [11] where the intercalant penetration results in cracks formation along cleavage planes similar to those studied by Obreimov and Landau [15]. No interference in the visible wavelength range is of course observed in a film having thickness of several hundreds of Å. However, if the sample is wedged out immediately before the intercalation front, the effective film thickness increases and an interference picture is formed where the color sequence reflects exactly the diminution of the crack width when passing from the phase front to the crack mouth.

The dependence of the intercalation phase front speed on the piperidine vapor pressure turned out to be logarithmical one (Fig. 7) as would be expected, since, no matter what is the migration mechanism, its motive force is the difference between chemical potentials of piperidine in vapor phase and in layered matrix. The latter is independent of the vapor pressure while the former is defined by the known equation $\mu = \mu_0 + RT \ln p$ where μ_0 is the standard chemical potential of piperidine and the dimensionless pressure p is normalized to the

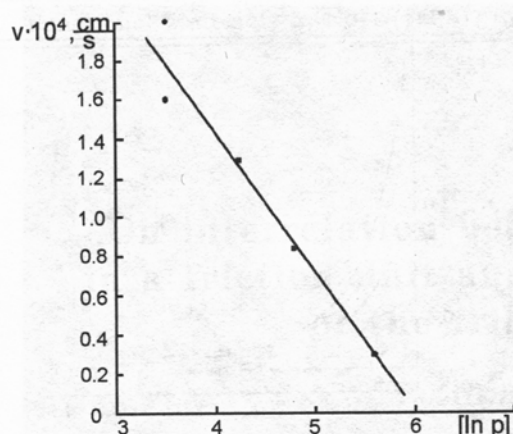


Fig. 7. Dependence of the intercalation speed, V , on the dimensionless pressure of piperidine vapor for 1500 Å thick films.

atmospheric one ($p = p_{pp}/p_{atm}$) where p_{pp} is the partial pressure of piperidine saturated vapor.

At last, let us consider the surprising fact that the intercalation front speed in layered films is different depending on the film arrangement with respect to the vapor source. The concentration levelling process in gas phase turns out to be not too fast. Estimations of the diffusion time in gaseous media in the absence of convection (what is unambiguously the case in our experiments) at the diffusion coefficient $D = 10^{-1} \text{ cm}^2/\text{s}$ typical for gases give the characteristic diffusion time $t = x^2/D = 1 \text{ s}$ for distances about 1 cm. If the intercalation front speed is about 10^{-4} cm/s , the film thickness about 10^{-5} cm and its side length about 1 cm, the film volume where the intercalant is absorbed has the order of $10^{-9} \text{ cm}^3/\text{s}$. The mean volume falling for each intercalated molecule can be assumed to be 10^{-22} cm^3 [1, 2, 4]: thus, the number of molecules absorbed during 1 s has the order of 10^{13} . The piperidine partial pressure is varied from 2.7 to 25 Torr corresponding to the molecular concentration above the liquid surface $C_0 = 10^{15} \text{ cm}^{-3}$ (the concentration in the liquid phase being e.g. $10^{-3} \text{ mol.}\%$).

Considering the most unfavorable case when the piperidine concentration near the absorbing sample is zero, we obtain the concentration gradient in the gas phase $dC/dX = C_0/X_0 = 10^{15}$ where X_0 is the typical distance from the liquid phase (piperidine source) to the edge of the film being subjected to intercalation. If the liquid phase surface, S , is about 1 cm^2 , the

molecular flux, j , can be estimated as $j = D \cdot S \cdot dC/dX = 10^{15}$. Taking into account that all estimations are approximate, the rate of piperidine "pumping-out" by the film can be believed to be at least commensurable with that of its "delivering" to the system from the liquid phase. Note that the actual intensity of piperidine molecular flux from its benzenic solution is several decimal orders less, since the solvate arrives to the solution surface at a rate controlled by the piperidine diffusion in benzene. Diffusion coefficients in liquids at room temperatures are of the order of $10^{-5} \text{ cm}^2/\text{s}$, thus, the typical time of concentration levelling in an about 10^{-1} cm thick liquid layer in the source is about 10^3 s . The "intercalation pump" turns out to be of a higher power. At very low piperidine concentrations in the solution, it is just the piperidine diffusion to the liquid surface that can be supposed to become the limiting stage of the whole process. Passing from the lower film edge to the upper one, the vapor contacts with the side film edges absorbing the intercalant at the same intensity that the lower one. Therefore, a considerably smaller number of intercalant molecules attain the upper edge than the lower. If an open-surface film is used in the experiment, its surface defects act also as intercalation channels, thus, the molecular flux attaining the upper edge is still less intense. This defines the concentration lowering near the upper film edge and thus a smaller intercalation front displacement speed as compared to that near the lower edge.

The above evidences that film type intercalation pumps as well as those based on disperse powders can be used with success to purify air in production areas where any substances with electron-donor type molecules are used in production processes, in particular, amines, e.g. ammonia. Basing on ideas presented in [2, 16], similar selective molecular pumps can be developed to eliminate impurities having electron-accepting molecules.

To conclude, it should be noted that penetration of molecules into a layered matrix is a very fast non-diffusion process of the ordered intercalation phase motion along interlayer gaps of layered crystals; its rate depends on the concentration of intercalable molecules in the medium surrounding the crystal. The process is accompanied by microcracks formation along cleavage planes and the matrix dispersion.

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Кінетика інтеркаляції

В.Кошкін, Н.Ткаченко, О.Юрченко, Ю.Долженко, В.Глушко

Вперше здійснено безпосереднє вимірювання швидкості процесу впровадження молекул у міжшарові простори шаруватої кристалічної матриці, що результатом його є утворення рівноважних інтеркаляційних сполук. На прикладі тонких текстурованих плівок PbI_2 продемонстровано, що швидкість процесу становить 10^{-3} – 10^{-4} см/с, що перевищує будь-які характерні швидкості дифузії. Продemonстровано, що процес впровадження інтеркалянту є просуванням фронту фази вздовж шарів матриці, що його швидкість логарифмічно залежить від тиску пара інтеркалюючих молекул. Продemonстровано, що шаруваті кристали можуть бути використані для ефективної очистки від органічних забруднень, в першу чергу, від молекул з електродонорними властивостями.