Stability of Manganese(II) Phthalocyanine Films in Ambient Air

Pavel A. Yunin,[a,b@] Yury I. Sachkov,[a,c] Vladislav V. Travkin,[a,c] and Georgy L. Pakhomov[a,c]

[a]*Institute for Physics of Microstructures of the Russian Academy of Sciences, 603087 Nizhny Novgorod, Russian Federation*
[b]*Lobachevsky State University of Nizhny Novgorod, 603022 Nizhny Novgorod, Russian Federation*
[c]*Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russian Federation*
[@]*Corresponding author E-mail: yunin@ipmras.ru*

Manganese phthalocyanine (PcMn) stands out among the well-known paramagnetic molecules for being both an extraordinary and unsteady complex. These characteristics are likely interrelated, which complicates interpretation of the experimental data. Notably, that conclusion on the PcMn instability follows from the coordination activity and redox-behavior of molecules in solutions, whereas the 'extraordinary' magnetic and electric properties are measured in solid samples. In this paper we consider PcMn films that for a month were kept in inert atmosphere as well as in regular laboratory conditions and studied by the optical spectroscopy, X-ray diffraction, secondary ion mass spectroscopy and surface control methods. It is shown that ageing of solid-state PcMn samples affects the molecular packing and microstructure of crystals and causes changes in their surface morphology and impurity concentration. However, these changes are reversible and unrelated to bulk heterogeneous chemical reactions, oxidation in particular.

Keywords: Manganese phthalocyanine, molecular magnets, films, microstructure, crystallinity, ageing, oxidation.

Стабильность плёнок фталоцианина марганца(II) на воздухе

П. А. Юнин,[a,b@] Ю. И. Сачков,[a,c] В. В. Травкин,[a,c] Г. Л. Пахомов[a,c]

[a] *Институт физики микроструктур РАН, 603087, Н.Новгород, Российская Федерация*
[b] *ННГУ им. Н.И. Лобачевского, 603022, Н.Новгород, Российская Федерация*
[c] *Ивановский государственный химико-технологический университет, 153000, г. Иваново, Российская Федерация*
[@]*E-mail: yunin@ipmras.ru*

Фталоцианинат марганца (PcMn) выделяется среди известных парамагнитных молекул тем, что он является одновременно необычным и неустойчивым комплексом. Вероятно, эти характеристики взаимосвязаны, что затрудняет интерпретацию экспериментальных данных. Примечательно, что вывод о нестабильности PcMn следует из координационной активности и окислительно-восстановительного поведения молекул в растворах, тогда как «необычные» магнитные и электрические свойства измеряются в твердой фазе. В данной работе рассматриваются пленки PcMn, которые в течение месяца выдерживались в инертной атмосфере, а также в обычных лабораторных условиях и исследовались методами оптической спектроскопии, рентгеновской дифрактометрии, масс-спектроскопии вторичных ионов и методами контроля поверхностной морфологии. Показано, что старение твердофазных образцов PcMn влияет на молекулярную упаковку и микроструктуру кристаллов, вызывает изменение рельефа поверхности и концентрации примесей. Однако эти изменения обратимы и не связаны с объемными гетерогенными химическими реакциями, в частности с окислением.

Ключевые слова: Фталоцианинат марганца, молекулярные магниты, пленки, микроструктура, кристалличность, старение, окисление.

Introduction

Manganese phthalocyanine (PcMn) is a rather interesting material for molecular electronics and spintronics research. A flat molecule of PcMn is paramagnetic due to the presence of manganese atom in the centre of heterocyclic ligand (spin 3/2) and in a solid phase can have several polymorphous modifications that practically do not differ in structure from phthalocyanines of other transition metals, such as copper, cobalt or iron.[1,2] However, the conductivity of polycrystalline PcMn films is by orders of magnitude superior to those above and is strongly dependent on a sample history.[3,4] We have shown recently[5] that the presence of even weak magnetic fields in the zone of vacuum growth of PcMn films induces noticeable changes in their microcrystal structure. Morphology is known to determine not only the conducting and magnetic properties of phthalocyanine films, but, to a certain extent, their optical and absorption characteristics as well.[2,6-9]

It is commonly known that PcMn films degrade in air under the influence of oxygen[3,6,7,10,11] and/or possible moisture.[6,7,13,14]. This interaction is believed to proceed easier than in the case with other phthalocyanines due to the presence of a polyvalent manganese atom. The latter can exist in several stable oxidized forms, depending on the amount and nature of other ligands attached axially with respect to the flat heterocycle. In this work we show that oxidation is not the only, let alone dominating, process that governs the changes in PcMn films subjected to long-term exposure to air in laboratory conditions.

General considerations

From general considerations, the interaction of gases including atmospheric oxygen with films can be viewed as physisorption and chemisorption. Since real samples have a complex morphology, physisorption should actively proceed on multiple intergrain boundaries, defects, dislocations, *etc*., with most likely an impact on electrical measurements.[15] This is a purely van-der-Waals interaction, the process heat <<10 kJ/mol or ~0.1 eV/particle.[16] A physisorption is fully reversible: at balance bias induced, say, by heating or prolonged pumping of sample to high vacuum (as is the case in many analytical measurements), gas molecules will desorb from the surface. Chemisorption is generally an exothermic reaction with the process heat >100 kJ/mol or ~1 eV/particle, it is irreversible and site-specific (for organics, specific functional group or atom in a molecule). A typical example of chemisorption is oxide film formation on a metal surface. Chemisorption may proceed from surface into bulk, ending up in a conventional heterogeneous chemical reaction with a precise stoichiometry and redox mechanism. These two forms of interaction can coexist, if the physical adsorption is a stage of a surface-activated chemical reaction.
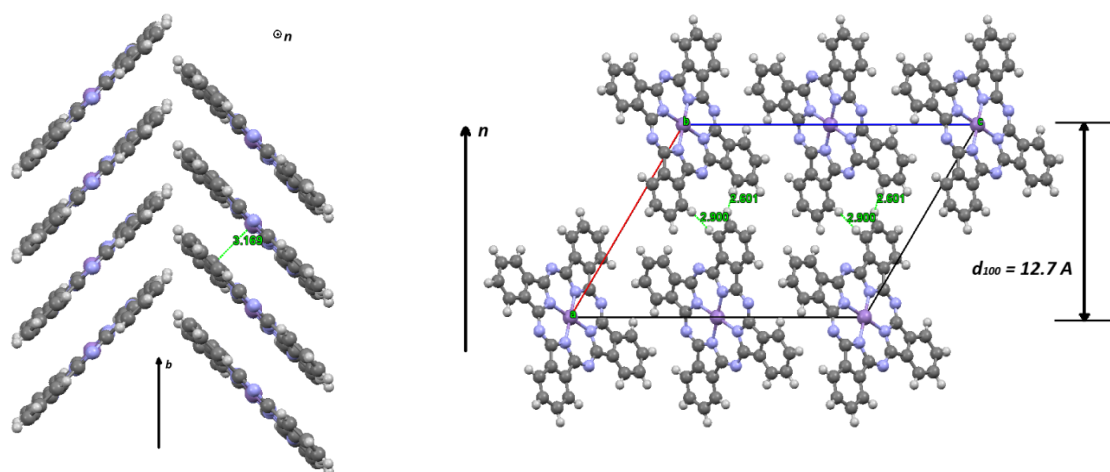

Figure 1. Views of PcMn molecules packing in β-phase: (a) View of β-PcMn molecules in stack: shown in green is the distance between Mn and N atoms of the adjacent molecules; vertical arrow is the direction of crystallographic axis *b* [010], *n* is the normal to the film surface; (b) Lateral view of the molecular stacks: vertical arrow is the direction of normal *n* to the surface of β-PcMn film; shortest intermolecular distances in the adjacent stacks are shown in green.

Labile phthalocyanine metal complexes are known to interact with air oxygen under the impact of white light (its UV component being most important to trigger this interaction), yielding phthalimide and a metal oxide as the end products.[13,17,18] However, the situation is not so simple with PcMn: the experiments on solutions have revealed a molecule to feature an intricate chemistry of photo-oxidizing processes involving both the π-system of macroligand and the central atom of metal.[3,12,13,19,20] Stable Mn^{II}, Mn^{III} and Mn^{IV} forms can (co-)exist. Depending on an oxidizer/solvent nature, they can be, for example, μ-oxodimers, where two molecular fragments are bonded by an O-bridge as Mn-O-Mn, or oxygen may attach to metal in the form of superoxide-ion O_2^-. PcMn:O_2 (1:1) adduct appearing in a solution purged with oxygen is quite

stable and can be isolated as a solid.[21] Bonding occurs through interaction between the π*-orbital of an oxygen atom and the corresponding d-orbital of manganese.

However, a direct bonding of molecular oxygen to a solid-phase metal atom can be spatially difficult. PcMn molecules in a crystal are arranged as slipping stacks ('herringbone'): in a certain direction the central atoms are inside a slanting column of molecules shifted as to one another (Figure 1a). The distance between the close-lying molecular planes is about 3.4 Å,[1,2,14,22-25] without account for the van-der-Waals radii of molecules. Moreover, monoclinic β–phase features a specific type of intermolecular interaction in a stack, which results in the manganese atom being in a pseudo-octahedral environment due to coordination with the azamethine atoms of nitrogen in the upper- and lower-lying molecules. Axial contacts N'…Mn…N'' are 3.1-3.2 A. However, the equilibrium van-der-Waals radius of oxygen equals 1.71 Å.[26] This suggests that for an O_2 molecule to take up an axial position with respect to the manganese atom the motif of molecules packing in a crystal has to be changed.[7,27] To this effect, as per the data in [25], it is necessary to overcome the energy of the existing interaction Mn…π(N'') of ~10 kJ/mol. For the α-phase, the metal atom is even less approachable because of the larger tilt angle of molecule planes with respect to the stack axis.[1,9,14,23-25,28] A more advantageous octahedron cannot be achieved here, so the phase is metastable. Equilibrium van-der-Waals radii of the macroligand-forming atoms are C = 1.96 Å, N = 1.79 Å[26] (Mn = 2.25 Å).

In another projection the crystal exhibits interstack channels or voids formed by azamethine bays between the benzene rings of the phthalocyanine ligand.[22,29] They can be available for oxygen molecules[27] (Figure 1b). Therefore in a crystal, oxidation through the Pc-ligand is spatially more probable than through the metal.

A redox reaction in the PcMn+O_2 system would result in a compound containing either a Mn…O bond (in the form of an oxide or hydroxide), or C…O, or N…O in similar forms, considering the composition of phthalocyanine ligand. There is a little probability that any of these bonds will break down by such a soft treatment like annealing (it would sooner need a strong donor[21]) to the extent that will make these forms reverse to the unoxidized PcMn. For comparison, the dissociation energy for MnO→Mn+O is 403 kJ/mol, for MnOH→Mn+OH – 305 kJ/mol (values for the ideal gas in the ground state at 0 °C); the dissociation energy for C…O and C…OH is still higher ($CH_2CO→C_2H_2+O$ = 535 kJ/mol and $C_6H_5OH→C_6H_5+OH$ = 456 kJ/mol[30]). For all the roughness of this estimation, these values by about two orders of magnitude exceed the energies put in a sample by conventional resistive heating.

This leads us to a conclusion that any degradation processes in crystals or thin films of PcMn in air, reversible due to thermal annealing in vacuum or recrystallization (temperatures ranging as 250-550 °C), can hardly be related to genuine chemosorption.

Experimental

Manganese phthalocyanine powder (Sigma Aldrich) was stored in supplier's packaging in a dark dry aired place (humidity of not more than 20 %) at temperatures within the range of 23-25 °C. Prior to use it was purified by evaporating impurities in a vacuum chamber at the crucible temperature of about 500 °C and residual pressure of not more than $5 \cdot 10^{-6}$ Torr, $i.e.$ recrystallization. Films were deposited on (001) oriented 20×20×0.5 mm silicon substrates and 10×20×1 mm substrates from optical quartz. PcMn films were deposited on (001) oriented 20×20×0.5 mm silicon substrates and 10×20×1 mm substrates from optical quartz. The substrates were first cleaned mechanically with cotton and acetone and then subjected to 5-minute cleaning in ultrasonic bath using acetone and isopropanol, and finally dried in Ar flow. The films were deposited by thermal evaporation in vacuum at the temperature of crucible 520 °C and substrate temperatures of either 25 or 200 °C set by a heating of the substrate holder. The temperature was controlled with a Pt-1000 thermal resistor attached to a holder. The film growth rate was less than 0.01 nm/s according to a quartz piezo-resonator.

X-Ray diffraction measurements on PcMn powders and 300 nm thick films on Si(001) substrates were performed with a Bruker D8 Discover diffractometer (Cu Kα radiation). A LynxEye linear PSD detector was used. The films surface was studied by both a semi-contact AFM (Proton-MIET SMM2000, probe NSG 30) on scales to 2×2 mcm, and by a white light interferometry technique, WLI (TalySurf CCI 2000, Taylor & Hobson) on scales to 1×1 mm. The films chemical composition was investigated by the time-of-flight secondary ion mass spectrometry (SIMS) with a depth profiling on a ToF.SIMS-5, IONTOF GmbH facility. For a probe beam the Bi_3^+ ions of 25 keV were used, and for a profiling beam – Cs^+ ions of 1 keV. More details on the analytical methods and regimes are given in [17,31-33]. The electronic spin resonance measurements were carried out at T=295 K and T=120 K on an EMX X-band continuous-wave (CW) ESR spectrometer, Bruker. The PcMn films were deposited on the ESR glass tubes under conditions identical to film deposition on silicon or quartz substrates and underwent the same treatment.

Results and Discussion

The PcMn powder diffraction patterns in Figure 2 reveal that degradation of the diffraction pattern that had been observed over a long-term storage period is fully reversible. Thus, the lower pattern (black line) was obtained for the powder acquired from Aldrich several months prior to the beginning of measurements and stored in laboratory conditions. Then the powder was purified or, rather, recrystallized by vacuum annealing at 500 °C and instantly measured (red line). This pattern fully coincides with the picture published by Knupfer et $al.$ in [7] for commercial PcMn powder heated to 420 °C for 2 h in Ar atmosphere. The authors[7] did not find any difference between this pattern and the one for the annealed PcMn powder exposed to air for 3 days, because no changes could yet have taken place in the morphology, and there apparently were no reactions with oxygen, that would yield a new product. Even if reaction did occur, the amount of PcMn involved is very small, being adequate, for example, just for the surface layer of molecules in crystallites.[3,7]

As shown by identity with the diffraction pattern calculated from the data in CIF-file CCDC#1212698,[22] the PcMn powder upon recrystallization is essentially a phase of untextured polycrystalline β-PcMn (see Supplement 1 in $Supporting$

Information). The experimental peak at the smallest angle of 6.3° appears in the calculated diffraction pattern of the β-phase in the form of a shoulder due to partial overlap with the most intensive (100) peak.

The XRD-pattern exhibits first noticeable changes for the recrystallized powder that has been kept in air for more than 10 days (blue line), and after one month storage the intensity of all peaks drops drastically (green line). At storage periods exceeding 6 months (for example, 8 months – purple line) the pattern is the same as for the original, unprocessed powder (black line). The diffraction patterns of the original raw powder, as well as the recrystallized powder aged for more than one month, show additional diffraction peak at 7.7°, which cannot be related to β-PcMn. It is important to note that the (100) peak of the β-PcMn phase at 7.05° does not disappear or shift to smaller angles. It can be assumed that during long-term storage of the PcMn powder, recrystallization and partial rearrangement of the crystal structure associated with the formation of α-PcMn crystallites occur. This can occur, presumably, for very small PcMn grains,[23] while the structure of the β-phase is retained for the other part of the grains. Importantly, the aged powder can be recrystallized again so that we obtain, with the quantitative yield, a product featuring the same pattern as in Figure 2, red line.
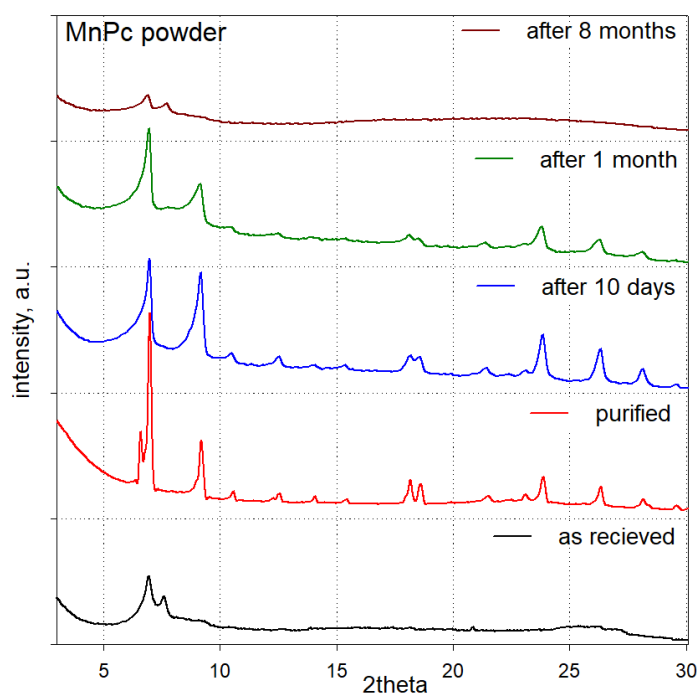

Figure 2. XRD patterns of PcMn powders

We went on with the subject of research started in[5] in order to compare the changes taking place in PcMn films grown by deposition on a strongly heated substrate (T_g=200°C) with the changes in films deposited on a room-temperature substrate (T_g=25 °C). The films grown in this temperature range are commonly used for electrophysical and magnetic measurements. In Figure 3a there is a XRD pattern for PcMn films of 300 nm thickness grown on a silicon substrate. The top panel pattern was taken immediately from the as-grown films, the two lower panels present the pattern from the films stored in air or Ar for a month. Considering the practical experience of handling laboratory samples and severity of changes in Figure 2, measurements after a month-long storage of samples seem to be most advisable.

In vacuum-deposited PcMn films the diffraction pattern is much poorer than in powders: there is generally a single peak near 7°. As-grown film on a heated substrate has (100) peak at 7.01° and a weak peak at 14.04°, which is close to the (200) reflection of β-PcMn.[5] Small differences from single crystal data for β-PcMn (7.05° and 14.11° correspondingly for (100) and (200) reflections) can be attributed to the structural features of thin films, which, as a rule, differ from bulk crystals. Thus, the β-PcMn (100) interplanar distance is 12.7 Å, which corresponds to the projection of the distance between Mn atoms in molecules of the adjacent stacks on vector *n* in Figure 1b. The energy estimated in[25,34] shows that the interaction between PcMetal stacks is second-strong after the intermolecular interaction within the stacks. Obviously, this determines a needle-like shape of the crystallites both in grains of powder and in thin films β-PcMn (see Supplement 3). According to the calculations in [34], the aspect ratios and faceting of the PcCu and PcH₂ crystallites, which determine their needle-like shape, largely depend on growth conditions. Qualitatively, the same would hold for isostructural crystals of β-PcMn.

Thus, as-deposited film with T_g=200 °C is basically a pure β-PcMn phase strongly textured by the (100) plane parallel to the substrate surface. The φ-scans of the asymmetric reflections reveal an isotropic angular distribution of intensity, which points to the absence of fixed directions for crystallites in the substrate plane, *i.e.* the film is essentially an axial texture. Analysis of the (100) reflection rocking curves shows that the texture scattering angle for as-grown β-PcMn films is no more than 0.1°. The established fact of film texturing and comparison between the powder diffraction results and the data from the XRD analysis of a single crystal[22] allows one to unambiguously define the molecular packing motif in β-PcMn films as "standing molecules" (Supplement 2).

Stability of manganese(II) phthalocyanine films in ambient air

As is known,[2,9,14,23,28] deposition of flat-square phthalocyanines on unheated substrates proceeds with formation of a metastable α-phase. Temperature polymorphs can coexist, so a phthalocyanine layer may contain domains of two phases, their dimensionality and ratios being dependent on the conditions (progress) of a polymorph α→β transition. However, F. Iwatsu[23] has shown theoretically that with the surface energy taken into account the small-size α-phase crystallites gain better stability than those corresponding to the formally stable β-phase. In large needle crystals the β-phase is always stable, unless they are not ground up or somehow diminished in size, as that would lead to a β→α transition.

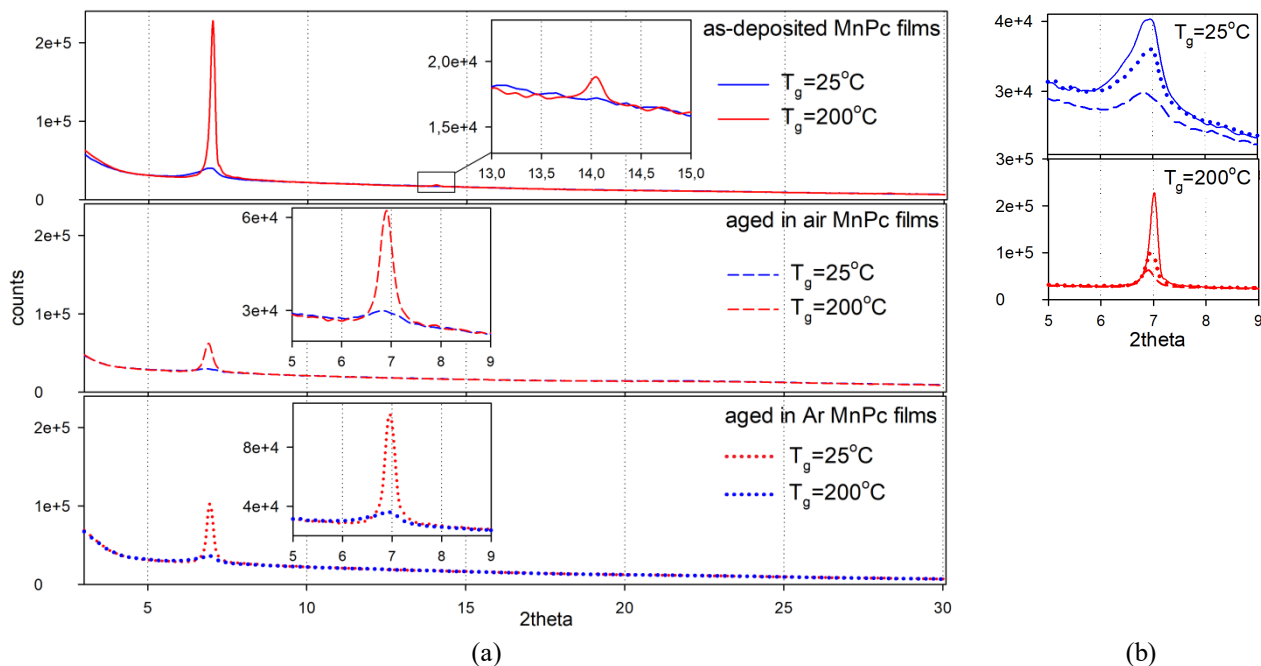

(a)   (b)

Figure 3. XRD patterns of 300 nm thick PcMn films deposited on silicon substrates

The changes taking place at α→β polymorph transition mostly pertain to the angle and distance between the molecules in stacks along the [010] direction rather than the distance between the adjacent stacks perpendicular to (100). Hence, there would be very little difference in the diffraction patterns from thin textured layers of α-PcMn and β-PcMn. In literature we failed to find any results on decoding of the atomic structure of α-phase for the manganese phthalocyanine complex. It is believed that its molecular packing should be similar to the α-phases of other phthalocyanines of transition metals, yet this analogy is not quite evident, considering, for instance, the strength of intermolecular interactions in PcMn. Important, that no diffraction peak at 7.7° was observed in the X-ray diffraction pattern of the low-temperature film, in contrast to the pattern of the aged powder. Therefore, we do not relate PcMn films with T_g=25 °C to a pure α-phase. As mentioned above, the texture scattering angle for β-PcMn films as-deposited on a heated substrate is of order 0.1°. There is no way to accurately measure the scattering angle for films grown on an unheated substrate, as it exceeds 10°, which implies a much weaker texturing. One can see in Figure 3b that the peak from the initial low-temperature phase is not only more diffuse, but also shifted towards smaller angles with respect to the peak from the initial film with T_g=200 °C. A similar effect was described earlier in [14] for stable α-PcCu crystals, and it possibly reflects the contribution of the α-phase PcMn in films deposited on an unheated substrate.

In aged films we observe a considerable decrease in the intensity and a broadening of the 7° peak with a shift towards the smaller angles side. Estimation of the crystallite sizes from the diffraction peak width in an as-grown film at 200 °C shows them to decrease from 50 nm to 33 nm, and down to 25 nm after storage in Ar and in air, respectively. In a film grown on an unheated substrate the crystallites are reduced in size from 14 nm to 12 nm, and to 10 nm after storage in Ar and in air, respectively. Besides, ageing high-temperature films feature an increase in the angular width of the (100) reflection rocking curve from fractions to units degree, which indicates a substantial texture weakening. The shift of the β-PcMn peak towards smaller angles suggests that as the crystallites degrade into smaller fragments and the texture weakens, the distance between the molecular stacks slightly decreases in the n direction (Figure 1b). This process is likely to be related with loosening of the molecular packing due to impurities accumulation in the inter-stack voids, and/or with a change in the surface energy due to adsorption of the impurities at the external facets of crystallites or at the intergrain borders.

Interestingly, the intensity of the (100) peak near 7° in samples long stored in Ar is higher and its FWHM value is smaller, than after storage in air (Figure 3b). This fact points to a difference in the degradation dynamics in different media. And this is exactly where it is appropriate to mention the chemical activity of O_2 molecules and of other possible components in the air mixture (H_2O, CO_2, CO, NO_x).[15,23] Their presence may affect the degradation rate due to, for instance, changing surface forces in the layer-forming PcMn grains (Figure 6). However, no changes of bulk periodicity are observed in the molecular packing, at least in the direction perpendicular to (100), which fully coincides with the data obtained for powders.

Absorption spectra

The absorption spectra of 40 nm thick PcMn films deposited on quartz substrate are presented in Figure 4. The top panel spectra were measured instantly on as-grown films, the two lower panel curves are for the films that within a month were stored in air or argon. The films are colored dark-green without metal glitter;[25] the color varies insignificantly at storage (Supplement 4).

Although the PcMn complex proper has long been synthesized and structurally characterized, unambiguous interpretation of the bands in its optical spectrum still is incomplete.[10,35,36] Enhancing the problem, the structure of the crystalline-state electronic transitions, in vacuum-deposited films also, is perturbed by the strong intermolecular interactions,[10,12,20,25,35] partly described above (see Figure 1).
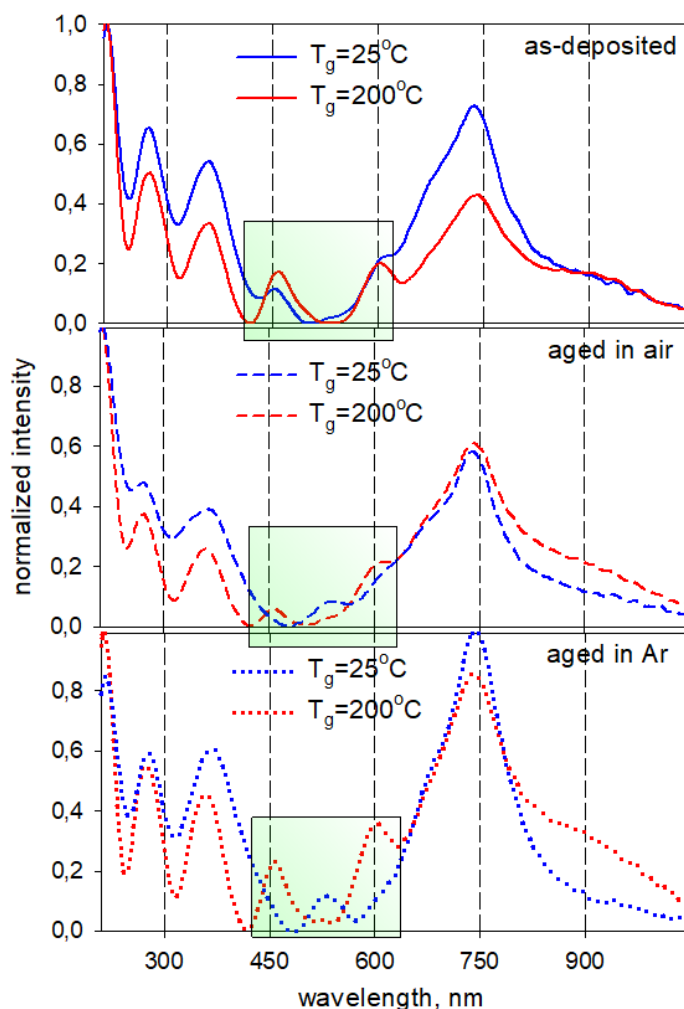

Figure 4. Absorption spectra of 40 nm thick PcMn films deposited on quartz substrate

The bands of higher intensity have maxima at 212, 275, 360 and 740 nm (= 5.84, 4.51, 3.44, 1.68 eV), which closely resemble the spectral pattern from other works, *e.g.*[11,12] Possible attribution of bands to the electron transitions in a PcMn molecule was referred to in our previous paper.[5] It should be stressed here that these bands remain practically unchanged in position and relative intensity for films stored in any environment, except for increase in the absorption in the near-IR region in films with T_g=200 °C stored in Ar (Figure 4). Moreover, there is no fundamental difference in the patterns of these bands in films grown at various temperatures. This indirectly confirms the conclusion made from the XRD results about the absence of the α-phase in a pure low-temperature film, as the electron absorption spectra of the α- and β−phases of phthalocyanines must have distinctive features.[8,9,20,24,37] As in the XRD-patterns, the bands of aged films in the low-temperature phase become broader than in the high-temperature one.

Much more interesting is the situation with the peaks of medium and lower intensity in the region 450-630 nm with the maxima around 456, 534 and 602 nm (= 2.72, 2.32 and 2.06 eV) highlighted by square in Figure 4. It is the region where the bands undergo a noticeable change in amplitude, when they are discernible. In literature we have failed to find any clearly stated reference to the origin of the bands highlighted in Figure 4. According to Schlettwein *et al.*,[3] the band at 534 nm should best be assigned to the adduct $PcMn(III)O_2^-$ which, in their opinion, is bound to form even in as-grown samples. Watching the intensity of this band increase during a lengthy storage of the samples in air, the authors came to a conclusion that eventually the film becomes fully oxidized, containing a metal in the form of Mn^{III}. Stabilization of manganese by a higher degree of oxidation proved so favorable that both the stored vacuum-deposited films and the original powder were

thought to consist mostly of PcMn(III)O_2^-.[3] It is curious that in their earlier work[12] the same authors admitted Mn^{IV} to be the most stable form, also noting that the 534 nm band disappears in films that have been stored in air for half a year.

The hypotheses put forward in [3] do not quite coincide with the findings by Zahn, Knupfer *et al.* [7,11] who did a thorough study into the behavior of PcMn films in air, with account for the influence of other components, such as H_2O and CO. According to their reported data, the spectra of films assumingly containing a PcMn-O_2 complex either had a very weak peak around 534 nm,[7] or there was no peak at all.[11] The changes in other absorption bands occur only in their relative intensities rather than positions. The calculations in [7] suggested that only one of the two oxygen atoms in an O_2 molecule is bonded to manganese in the putative PcMn-O_2 complex, the other hangs freely, as in the Lever's model.[21] The authors[7,11] and Lever[21] believe that the planarity of phthalocyanine macrocycle is disrupted when a superoxide-ion is attached to the central metal ion. If so, then the D_{4h} symmetry breaking should lead to a shift of the bands, as in the case with extraligated complexes like PcVO. But this has never been observed experimentally.

The theoretical predictions are rather contradictory, too. Thus, the PcMn-O_2 bond energy of 0.5 eV calculated in[7] was assessed as very small, while the bond energy of 7 meV for PcMn-N_2 as extremely small. However, theoretical modeling of an O_2 molecule adsorption on a PcMn complex made in[37] yielded absolutely different results: the energy of ~0.8 eV and a triangle-shaped configuration of the Mn+O_2 adduct, in which both atoms of oxygen form bonds at an equal distance from the Mn atom, thus increasing its valency.

The values obtained in[7,38] correspond to a firm donor-acceptor bond.[16] They are higher than the experimentally estimated bond energy for, say, PcFe-CO complex: 0.3 eV,[39] and much higher than the energy of thermal desorption of the oxygen molecules from various surfaces, *i.e.* 0.1-0.2 eV.[40] Despite this, the same authors[10] are confident that oxygen completely desorbs from PcMn films during vacuum annealing to 87 °C for 3 h, or to 197 °C within an hour. The peak at 534 nm in Ref.[10] appears only in the spectra of individual (non-interacting) PcMn molecules dissolved in an inert coronene matrix, and the authors claimed that vacuum annealing removes the oxygen, but not this band.

If, according to Knupfer,[10] the 534 nm peak should be considered the attribute of an individual PcMn molecule weakly- or non-interacting with other molecules, then it follows from Figure 4 that the disordering in films increases during storage, all the more so in low-temperature samples.[20]

In a word, the history of thin-film PcMn samples formation is reflected on the fine structure of their optical spectra, but still there are no indisputable data on how the position or intensity of the absorption bands are related with a content of oxygen in a sample. The 'oxidation' nature of changes occurring in the absorption spectra is not confirmed in Figure 4 either. Firstly, despite a long-term exposure of the films to air, no transformations that could be indicative of the presence of an redox-reaction take place in the basic bands profiles, whereas it is the electron absorption spectra that are considered to be the main metric of this process.[19-21,41] We do not observe a highly intensive line at 708 nm, which indicates the formation of PcMn(III)O_2^- adduct. Another sign is the behavior of the weak bands around 450-630 nm highlighted in Figure 4. If, as mentioned above, the 534 nm band was related to formation of some product {PcMn+O}, it would show up much more clearly for samples stored in air than in Ar, but this is not the case (Figure 4). The two other bands, 456 and 602 nm, become weaker in films stored in air, although their intensity should increase if they are associated with products of the {PcMn+O} type. In the low-T phase these bands practically disappear in the spectra of samples stored both in air and in Ar, while in the high-T phase of the films stored in Ar we observe an increasing intensity of these bands. Meanwhile, the SIMS analysis (Figure 5) shows that films grown on a heated substrate have a lower oxygen content in spite of a more developed surface (Figure 6 below). Besides, as seen in Figure 6, the high-T films surface roughness changes with time on a wavelength scale, which may affect the relation between the absorbed, reflected and scattered light in spectral measurements.

None of the above-cited papers attempts to explain the appearance/disappearance of this and other peaks by the peculiarities of intermolecular interactions in the solid phase of PcMn, although the data on such a dependence are available, for example, in Refs.[20,36] And none of these works mention the external light being/not being used during the experiments. However, photo-activated oxidation of metal-phthalocyanines is a much more likely redox-process than the dark reaction. We verified this point by comparing the absorption spectra of PcMn films deposited on a hot substrate, that were directly illuminated by sunlight simulator within 12 hours in air or argon (Supplement 5). Despite the anticipated intensive photo-oxidation in air, there is no appreciable difference in the spectral profiles between the original and degraded PcMn films. (interestingly, A.B.P. Lever[21] noted back in 1981 that the PcMn(O_2) adduct is breaking up into the original PcMn form and free molecular oxygen slowly by degassing, and rapidly when a solution is intensively irradiated by white light). On the contrary, accelerated ageing of a sample in high-purity argon leads to much more appreciable difference, the resulting spectrum resembles that of a low-temperature PcMn film after a month-long storage in Ar (Supplement 5). All of these facts point to the morphological (microstructural) rather than chemical processes behind the changes in the absorption spectra of PcMn films.

A film structure and, consequently, its spectrum image can also be influenced by other growth parameters, such as deposition rate and substrate material.[9,14,28,29] In Supplement 5 we compare the spectra of PcMn films grown on quartz and on ITO-coated glass kept at room temperature. Further, Supplement 6 provides AFM images of the surface of 40 nm thick PcMn films deposited on quartz. The films deposited on an unheated quartz substrate show no perceptible difference from those grown on unheated silicon. Films grown on a heated quartz have crystallites of a smaller size for the same aspect ratio of the facets (100-200 nm length) and a lower density of the vertically growing whiskers (0.4/mcm^2 versus 1/mcm^2). Storage in air facilitates a reduction of crystallites in size and enhances isotropy of their form. The thermodynamics and kinetics issues of the phthalocyanine films growth on various substrates are considered in the overview.[9]

Secondary ion mass-spectrometry (SIMS) with depth profiling

We addressed the problem of space distribution of oxygen in PcMn films stored in air and argon by analyzing the chemical composition using the SIMS depth profiling technique. Prior to measurements the samples were kept for about 24 h inside an ultra-high vacuum analytical chamber of the spectrometer for degassing, and, obviously, part of the weakly bonded oxygen molecules could leave the PcMn film. However, the samples in two batches were measured simultaneously in identical conditions, hence, their quantitative comparison is correct.
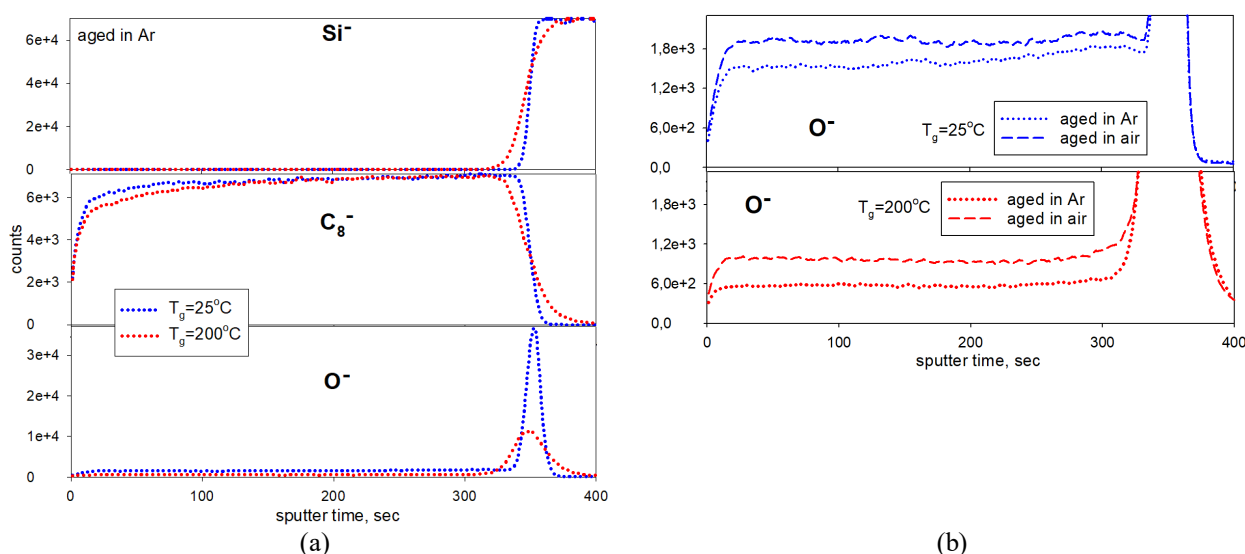

(a)   (b)

Figure 5. ToF-SIMS profiles of characteristic secondary ions in 300 nm thick PcMn films deposited on silicon substrate, the same samples as in Figure 2.

Figure 5a shows the SIMS profiles for a film stored in argon. It takes about 350 sec. for a sputtering cesium beam to reach a substrate, which is readily seen from a sharp increase in the yield of secondary ions Si^-. This time is the same for all of the samples under study. A secondary ion C_8^- is characteristic of the phthalocyanine molecules; most likely, it originates from a carbon skeleton of one of the four benzopyrrole fragments of a ligand formed by ion impact. The internal interface 'PcMn/Si' looks less diffuse in films deposited on an unheated substrate, whatever secondary ion is traced. This effect is associated with the physical (interface morphology) rather than chemical reasons (diffusion or reactions of the components). The silicon surface underneath the PcMn film remains just as smooth for films deposited on a hot substrate, too, but the adherence to it of the elongated grains of β-PcMn is different. Therefore, the interface broadens, similarly to what is shown, for example, in Ref.[24] We controlled the surface relief of all samples before SIMS analysis by WLI technique, followed by measurements of the crater bottom profiles, on scales coinciding with the raster area of the sputtering beam (Supplement 7). Neither a difference in the surface roughness (the outer interface 'vacuum/PcMn'), nor the roughness of Si wafer in a SIMS crater can contribute in 'blurring' of the profiles in Figure 5.

The peak of oxygen concentration in the interface area has several possible assignments. First, it is the presence of an ultrathin layer of natural oxide on the surface of intact Si wafer before deposition of PcMn layer (Supplement 8). Secondly, it can be a purely interface effect, that is a rise of absolute yield of the oxygen secondary ions from the inhomogeneous matrix 'PcMn/Si'. Third, one can assume that some amount of the deeply diffused oxygen or water molecules had accumulated in the interface area before the samples got into vacuum and was not removed by pumping.

After storage in argon the films with T_g=200 °C contain approximately 2.5 times less oxygen than the films grown at room temperature and stored for the same period of time (Figure 5b). Also note the absence of a marked gradient of oxygen concentration from surface to substrate and *vice versa* (Figure 5 and Supplement 8).

The samples stored in air feature an almost similar picture of the internal interface 'PcMn/Si': in hot-deposited films the interface is diffused, and the oxygen content is 2.1 times lower than in films deposited on an unheated substrate. However, the profiles in Figure 5b show that during storage in air the PcMn films in any phase absorb roughly 1.2-1.5 times larger amount of oxygen, which cannot be removed by a pump-down to ultra-high vacuum. This oxygen is uniformly distributed throughout the depth of the PcMn layer (Figure 5). Presumably, it can be bound due to a rather strong physisorption of O_2 molecules (desorption needs heating) along the intergrain boundaries, packaging defects, *etc*. Although it is impossible to give a quantitative estimate of the PcMn:O ratio from the SIMS data, the oxygen content must be quite high. If we assume that oxygen exists in the form of $PcMn(III)O_2^-$, this complex is certain to show up somehow in the optical, XRD spectra or ESR, which is not observed in the experiment.

Unfortunately, it is hard to judge what form the oxygen takes from SIMS. The presence of O_2 secondary ions in the spectra does not mean that the film contains molecular oxygen; the yield of MnO cluster ions is very small in the film bulk, and yet we cannot assert that there are no such chemical forms in it. Secondary ion O_2^- appears in the SIMS spectra in detectable amounts only in the area of internal interface PcMn/Si, being, obviously, related with the presence of a SiO_2 layer on the substrate surface (Supplement 8). However, its yield in this region nearly doubles in hot-deposited films that were stored in air, with the peak maximum being on the PcMn side, which cannot be explained by the presence of SiO_2 alone. This tendency is also seen in the profiles of secondary ions O^- and OH^-. With a great deal of caution we may assume that the

internal ("blurred" in SIMS-profiles) interface of films grown at T_g=200 °C contains multiple voids, active facets, *etc*. This facilitates adsorption of the oxygen-containing impurities in it.

Static SIMS data, *i.e.*, only surface spectra without depth profiling, do not provide any more unambiguity. In the negative mode there is no correlation of storage conditions or film growth temperature with an yield of oxygen-containing cluster ions, such as MnO, MnO_2, MnOH . The yield of H_2O^- and H_2O^+ ions over the entire depth of the layer is insignificant. We noticed a more than twice increase in the yield of secondary ions NO_2^- from the surface of films stored in air. In the positive mode the spectra show intensive lines for manganese-containing ions, MnN and MnCN. In both modes there is a clearly seen fragment at m/z = 133, where the signal intensity is 1.5-2 times higher for the samples stored in air. This could be some oxidized form of the isoindole fragment of a ligand, which is structurally close to phthalimide rather than phthalodinitrile whose molecular mass is smaller.
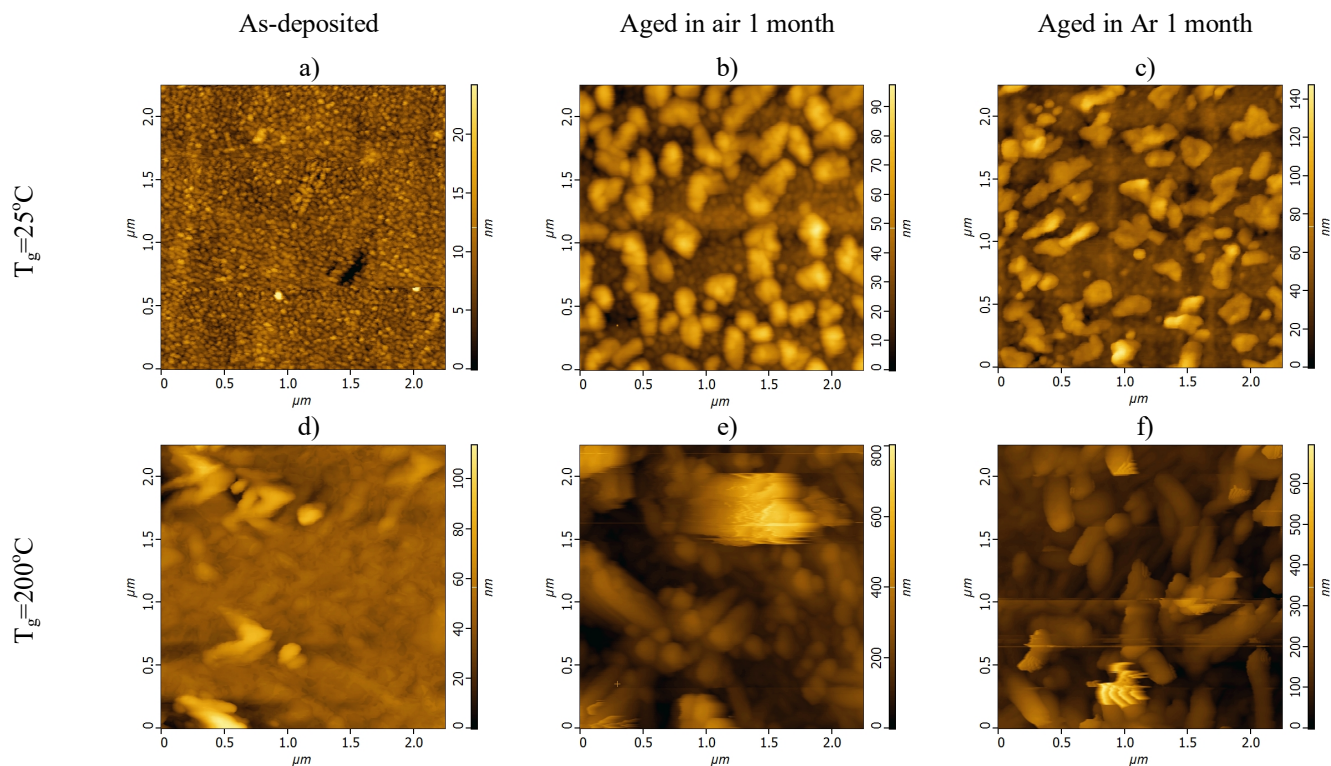

Figure 6. AFM-images of the surface of 40 nm thick PcMn films deposited on silicon substrates. Failures on panels (d), (e), (f) come from the oscillating probe touching a soft surface object. The oscillation frequency of the former estimated from its motion speed and a spatial period of oscillation is roughly 10 Hz.

Atomic force microscopy

AFM surface images of 40 nm thick PcMn films deposited on (001) silicon wafers are shown in Figure 6. The films grown at room temperature have a typically phthalocyanine relief of the surface,[9,15] consisting of fused grains about 50 nm in diameter. When the films are stored in high-purity argon or air, the surface objects lying on a sublayer of smaller gains of under 80-100 nm increase in size up to 100-300 nm. There are no obvious facets in these objects, nor other regularities. We did not find any noticeable difference in the morphology of the films stored in air and argon, either.

The surface of high-temperature samples is formed by parallel-to-substrate oblong crystallites of about 300 nm length, 100 nm width and to 50 nm height, the characteristic dimensions of the transition metal phthalocyanines.[9,15] At long-term storage the crystallites bend and fracture, there is a rise in a relative amount of crystallites oriented non-parallel to the substrate. The crystallites packing density reduces.

We were able to observe faceting of a single crystallite on the AFM image (Figure 7). Comparison between the facet angles and the angles formed by the crystallographic planes of β-phase by analogy with [34] confirms the inner molecular structure of whisker β-PcMn crystals, which was experimentally established for other isostructural phthalocyanine complexes:[9,15,34] the crystals are extended lengthwise along molecular stacks in the [010] direction, whereas the whisker side facets are formed by the (100) and (101) planes.

Sorption/diffusion processes in phthalocyanine films with thicknesses of several hundred nanometers are quite fast, so gas molecules are equally distributed within such a small depth/volume,[6,7,27] intrastack $\{PcMn+O_2\}$ interactions disregarding (see above). Polymorph transitions in the crystals of aromatic molecules can take a very long time.[42] For example, the orthorhombic phase transition to a more stable monoclinic phase of trinitrotoluene (transition heat 0.92 kJ/mol, ~0.01 eV) at room temperature takes two months. Schlettwein *et al*.[3,12] noted repeatedly that the changes in the absorption spectra of 100 nm PcMn films occur on a time scale of a few months to half-a-year to year and a half. Generally, the energies of polymorphous transitions in molecular crystals are in the range of 10 kJ/mol or ~0.05-0.07 eV,[42] which is close to thermo-induced processes. By the theoretical calculations of F. Iwatsu,[23] the difference between the lattice potentials of

α- and β-polymorphs of metal-free phthalocyanine is 5.7 kJ/mol. In PcMn this value should be apparently higher, as, according to the data,[25] in the series PcH$_2$ < PcNi < PcFe < PcCu < PcCo < PcZn < PcMn the energy of intermolecular interactions doubles, reaching a maximum for the manganese complex (estimations were made on the basis of the bond critical points for a hypothetical dimer in a crystal).
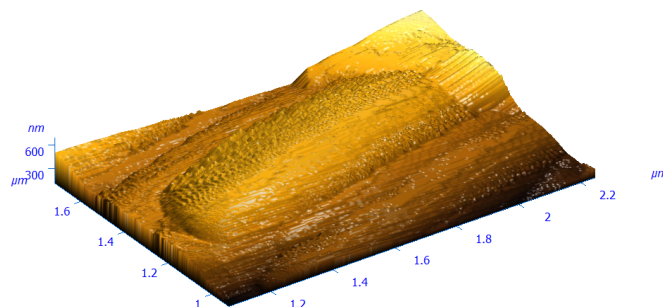

Figure 7. AFM image of a single β-PcMn whisker crystal in a high-T film on a silicon substrate. One can clearly see the outer facets formed by the (100) and (101) planes.

The changes observed in PcMn powders and films can be interpreted as follows. In normal conditions PcMn crystals are characterized by a certain equilibrium length/thickness aspect ratio (form-factor), which corresponds to the minimum free energy in a crystal.[34] The elongated crystal morphology (Supplement 3) is due to a strong anisotropy of the intermolecular forces inside and between the stacks. This anisotropy of shape leads to texturing of polycrystal grains simply by the force of gravity, which in the original powder pattern shows up through dominating intensity of the diffraction peaks that correspond to the inter-plane distances between the adjacent stacks (Figure 2, black line).

Critical heating in vacuum (purification) of powder creates the conditions for recrystallization, by which the aspect ratio decreases and the crystallites become less elongated. The powder diffraction pattern now resembles that of a non-textured polycrystal with a complete set of diffraction peaks (Figure 2, red line). With time, during storage in air the PcMn slowly recrystallizes back to the equilibrium morphology, which is manifested by broadening of the peaks on the diffraction pattern. There is a decrease in size and amount of crystallites with the unfavorable orientations and aspect ratios (Figure 2, blue and green lines), until the diffraction pattern becomes identical to that of the original powder (Figure 2, purple line).

Similar processes are expected to run in high-temperature β-PcMn films, the only difference being the whisker aspect ratio that in this film is initially above equilibrium. For this reason, the film texture degrades through breaking down into shorter whiskers and their bending.[15] This manifests itself in a shift, a decrease in the intensity, and a broadening of the (100) diffraction peak in Figure 3b, as well as in a broadening of the rocking curves. In low-temperature films, the changes in XRD-patterns are less pronounced due to the absence of β-phase whisker crystals. The (100) peak shift towards smaller angles is appreciable enough in comparison with the films grown on a high-T substrate, so any further peak shifting that might occur with the aging of films is imperceptible (Figure 3b).

The powders and films after storage feature no peaks that would indicate the presence of a new crystalline phase formed through the chemical reactions of PcMn with atmospheric gases, neither in the XRD-, nor in electron spectra. Electron spin resonance (ESR) can be used to detect {PcMn+O$_2$} adducts in solutions or solid phases.[21] However, we failed to detect an ESR-signal in β-PcMn films at room temperature. Both the reference and aged samples remained ESR-silent at temperatures down to 120 K. Therefore, in PcMn samples being stored within a few weeks to a few months period the dominating degradation process is a rearrangement of morphology and microstructure, possibly stimulated/accompanied by the surface phenomena, like a PcMn+adsorbate interaction.

Conclusions

However, we believe that the role of atmospheric oxygen in changing the chemical and phase composition of films and crystals of PcMn, which is frequently acknowledged in the literature, is exaggerated. Indeed, the PcMn molecule can more easily enter into charge transfer reactions than other metal phthalocyanines do;[19,41] its ionization potential is by 0.5 eV less than that of copper phthalocyanine.[36] Therefore, sample storage and testing conditions should be rigidly maintained and thoroughly described in every experiment. Interpretation of the results of electrophysical measurements on thin-film samples[3,7,12,14] does not rule out a likelihood of the PcMn+O$_2$ or PcMn+H$_2$O interactions. However, in this study we focus on a contribution of simultaneously occurring morphological changes in samples exposed to long-term storage, in oxygen-free conditions as well. None the less important than storage conditions is the role of the original microstructure of the PcMn film, in this work it was set by the substrate temperature during growth.

The results obtained through this study can be useful to researchers in the area of molecular (semi)conductors and magnets based on phthalocyanine complexes with transition metals. The next logical step, from the 'physical' point of view, could be an attempt at advancing down the temperature scale both in growth process and measurements of structure-dependent phenomena. On the "chemical" side, it seems worthwhile to use the closest analogues of phthalocyanine ligand (tetraphenylporphine, etioporphyrin), complexation with which leads to changes in both the spin state of the central atom and packing design of molecules in a crystal.

References

1. Bartolomé J., Monton C., Schuller I.K. In: *Molecular Magnets,* Ch. 9, Magnetism of Metal Phthalocyanines. Berlin: Springer-Verlag **2014**, p. 221-245.
2. Yamada H., T Shimada., Koma A. *J. Chem. Phys.* **1998**, *108*, 10256.
3. Schlettwein D., Meyer J.P., Jaeger N.I. *J. Porphyrins Phthalocyanines* **2000**, *4*, 23.
4. Rajesh K.R., Menon C.S. *Eur. Phys. J., B* **2005**, *47*, 171.
5. Yunin P.A., Sachkov Y.I., Travkin V.V., Skorokhodov E.V., Pakhomov G.L. *Vacuum* **2021**, *194*, 110584.
6. van Faassen E., Kerp H. *Sensor Actuat B-Chem* **2003**, *88*, 329.
7. Friedrich R., Hahn T., Kortus J., Fronk M., Haidu F., Salvan G., Zahn D.R.T., Schlesinger M., Mehring M., Roth F., Mahns B., Knupfer M. *J. Chem. Phys.* **2012**, *136*, 064704.
8. Nguyen A., Cosue C., Gredig T. *FWS16 Meeting of The American Physical Society* **2016**, S2.00002
9. Cranston R.R., Lessard B.H. *Rsc Adv* **2021**, *11*, 21716.
10. Pagenkopf F., Müller E., Knupfer M. *J. Chem. Phys.* **2018**, *148*, 044701.
11. Haidu F., Fechner A., Salvan G., Gordan O.D., Fronk M., Lehmann D., Mahns B., Knupfer M., Zahn D.R.T. *AIP Advances* **2013**, *3*, 062124.
12. Meyer J.P., Schlettwein D. *Adv. Mater. Opt. Electron.* **1996**, *6*, 239.
13. Mousazade Y., Najafpour M.M., Bagheri R., Jaglicic Z., Singh J.P., Chae K.H., Song Z.L., Rodionova M.V., Voloshin R.A., Shen J.R., Ramakrishna S., Allakhverdiev S.I. *Dalton Trans.* **2019**, *48*, 12147.
14. Berger O., Fischer W.J., Adolphi B., Tierbach S., Melev V., Schreiber J. *J. Mater. Sci.-Mater. Electron.* **2000**, *11*, 331.
15. Kumar P., Sharma A., Yadav S., Ghosh S. *Org. Electron.* **2013**, *14*, 1663.
16. *Electronic Processes in Organic Molecular Crystals: The Phenomenon of Polarization and Localization* (Silinsh E., Ed.), Zinatne: Riga, **1988**. 329 p. [Электронные процессы в органических молекулярных кристаллах: Явление поляризации и локализации (Силиньш Э., ред.), Зинатне: Рига, **1988**. 329 с.].
17. Pakhomov G.L., Travkin V.V., Drozdov M.N., Sachkov Y.I., Yunin P.A. *Appl. Surf. Sci.* **2022**, *578*, 152084.
18. Slota R., Dyrda G. *Inorg. Chem.* **2003**, *42*, 5743.
19. Dolotova O.V., Bundina N.I., Kaliya O.L., Lukyanets E.A. *J. Porphyrins Phthalocyanines* **1997**, *1*, 355.
20. Williamson B.E., Vancott T.C., Boyle M.E., Misener G.C., Stillman M.J., Schatz P.N. *J. Am. Chem. Soc.* **1992**, *114*, 2412.
21. Lever A.B.P., Wilshire J.P., Quan S.K. *Inorg. Chem.* **1981**, *20*, 761.
22. Mason R., Williams G.A., Fielding P.E. *J. Chem. Soc., Dalton Trans.* **1979**, 676-683.
23. Iwatsu F. *J. Phys. Chem.* **1988**, *92*, 1678.
24. Yim S., Heutz S., Jones T.S. *J. Appl. Phys.* **2002**, *91*, 3632.
25. Jiang H., Hu P., Ye J., Ganguly R., Li Y.X., Long Y., Fichou D., Hu W.P., Kloc C. *Angew. Chem. Int. Ed.* **2018**, *57*, 10112.
26. Batsanov S.S. *Inorg. Mater.* **2001**, *37*, 871.
27. Muckley E.S., Miller N., Jacobs C.B., Gredig T., Ivanov I.N. *J. of Photonics for Energy* **2016**, *6*, 045501.
28. Heutz S., Mitra C., Wu W., Fisher A.J., Kerridge A., Stoneham M., Harker A.H., Gardener J., Tseng H.H., Jones T.S., Renner C., Aeppli G. *Adv. Mater.* **2007**, *19*, 3618.
29. Rochford L.A., Keeble D.S., Holmes O.J., Clarkson G.J., Jones T.S. *J. Mater. Chem., C* **2014**, *2*, 6056.
30. Gurvich L.V., Karachevtsev G.V., Kondratyev V.N., Lebedev Yu.A., Medvedev V.A., Potapov V.K., Khodeev Yu.S. The *Energy of Chemical Bonds Breaking. Ionization Potentials and Electron Affinity,* Moscow: Nauka, **1974**, p. 351 [Гурвич Л.В., Карачевцев Г.В., Кондратьев В.Н., Лебедев Ю.А., Медведев В.А., Потапов В.К., Ходеев Ю.С. *Энергии разрыва химических связей. Потенциалы ионизации и сродство к электрону*, Москва: Наука, **1974**. 351 с.].
31. Travkin V., Yunin P., Stuzhin P., Pakhomov G. *Materials Today: Proceedings* **2020**, *20*, 12.
32. Drozdov M.N., Yunin P.A., Travkin V.V., Koptyaev A.I., Pakhomov G.L. *Adv. Mater. Interfaces* **2019**, *6*, 1900364.
33. Travkin V.V., Luk'yanov A.Y., Drozdov M N., Vopilkin E A., Yunin P A., Pakhomov G L, *Appl. Surf. Sci.* **2016**, *390*, 703.
34. Panina N., van de Ven R., Janssen F.F.B.J., Meekes H., Vlieg E., Deroover G. *Cryst. Growth Des.* **2009**, *9*, 840.
35. Brumboiu I.E., Totani R., de Simone M., Coreno M., Grazioli C., Lozzi L., Herper H.C., Sanyal B., Eriksson O., Puglia C., Brena B. *J. Phys. Chem. A* **2014**, *118*, 927.
36. Rückerl F., Waas D., Büchner B., Knupfer M., Zahn D.R.T., Haidu F., Hahn T., Kortus J. *Beilstein J. Nanotechnol.* **2017**, *8*, 1601.
37. Meng L., Wang K., Han Y.Y., Yao Y., Gao P., Huang C., Zhang W.H., Xu F.Q. *Prog. Nat. Sci.-Mater.* **2017**, *27*, 329.
38. Liu K., Lei Y., Wang G. *J. Chem. Phys.* **2013**, *139*, 204306.
39. Vesselli E. *J. Phys. Mater.* **2020**, *3*, 329-332.
40. Bagsican F.R., Winchester A., Ghosh S., Zhang X., Ma L.L., Wang M.J., Murakami H., Talapatra S., Vajtai R., Ajayan P.M., Kono J., Tonouchi M., Kawayama I. *Sci. Rep.* **2017**, *7*, 1774.
41. Dolotova O., Konarev A., Volkov K., Negrimovsky V., Kaliya O.L. *J. Porphyrins Phthalocyanines* **2012**, *16*, 946.
42. Bernstein J. *Polymorphism in Molecular Crystals,* Oxford: Clarendopress, **2002**, p. 574.