Subphtalocyanine molecules ordering on Ag(111)

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To find an appropriate candidate for single-molecule memory devices, self-assembly of different organic supramolecules on metal surfaces was extensively studied by the STM. Very interesting patterns of two ordered superstructures (honeycomb and hexagonal closed packed (hcp)) in co-existence with 2D lattice-gas phase were found by room temperature STM during adsorption of chloro(subphtalocyaninato)boron(III) (SubPc) molecules on Ag(111) [1,2]. The SubPc molecule is very large to compare with Ag lattice period and have the form of three-lobed mushroom, SubPc/Ag(111) system has interesting rotational symmetry, and the ordering depends on mutual arrangement of neighboring molecules. Intermolecular interactions of polar SubPc molecules on Ag(111) depend on distance and are caused by complicated mixing of direct Coulomb, dipole-dipole and van der Waals interactions and indirect SubPc interactions via Ag substrate.

Here we present the model describing the ordering of SubPc molecules on Ag(111) into honeycomb and hcp patterns. Assuming that the position of the molecule in the intersite of triangular lattice of Ag(111) depends on its interaction with Ag atoms closest to the intersite, we can explain why the molecules possessing three-fold symmetry have diffent arrangements with respect to each other. Summarizing known experimental data [2,3], we proposed complex intermolecular potential with exclusion part at closer distances, attraction at intermediate distances and decaying repulsion of dipole-dipole origin at further distances. To cope with computational problems due to large size of the molecules compared to the substrate lattice period, we introduce the rescaling of Ag(111) lattice and took into account an infinite exclusion of first, second and third neighbors, attraction - of fourth and fifth, and repulsion - of sixth and seventh. The minimum of intermolecular potential corresponds to the intermolecular distance obtained for the honeycomb structure Lattice-gas model on triangular lattice of Ag(111) intersites, Metropolis algorithm and Glauber dynamics were used to simulate numerically phase diagrams of SubPc ordering. In agreement with STM experiments [2,3], we obtained phase co-existence between honeycomb and disordered as well as between hcp and disordered phases. The co-existence was manifested by. very strong first order phase transitions between the phases and was observed in large limits of SubPc concentration. Pure honeycomb and hcp phases were found only at small intervals around the stoichiometric concentrations of both phases. In order to make some predictions for temperature STM studies, we also demonstrated how the phase diagram changes varying the interaction constants of the model.

References

1. S. Berner, M. Brunner, L. Ramoino, H. Suzuki, H.-J. Guentherodt, T. A. Jung, Chem. Phys. Lett. 348, 175 (2001).
2. S. Berner, M. de Wild, L. Ramoino, S. Ivan, A. Barratoff, H.-J. Guentherodt, H. Suzuki, D. Schlettwein, and T. A. Jung, Phys. Rev. B 68, 115410 (2003).

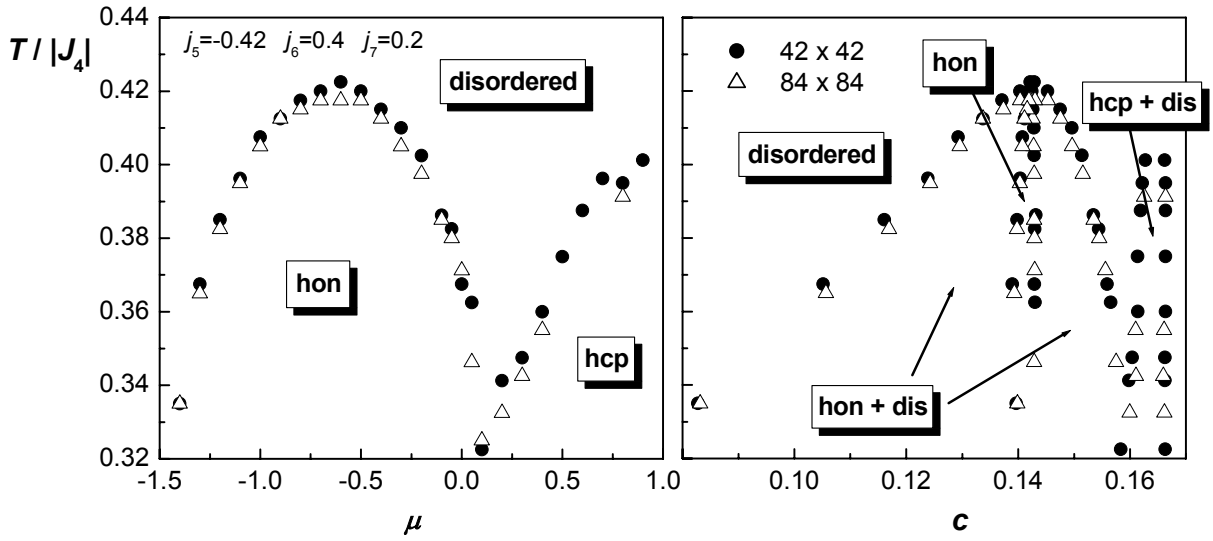

Fig. 1. Phase diagrams of SubPc ordering in temperature $T/|J_4|$ vs chemical potential μ (left) and temperature $T/|J_4|$ vs SubPc concentration c (right) coordinates. Here the temperature is normalized to the value of attractive interaction potential in fourth coordination sphere of Ag(111) lattice, $J_4 < 0$. The values of other interaction potentials are $J_1 = J_2 = J_3 = \infty$ (infinite repulsion (exclusion) due to large size of the SubPc molecules compared to Ag(111) lattice period), $J_5/|J_4| = -0.42$, $J_6/|J_4| = 0.4$, $J_7/|J_4| = 0.2$, $J_{8 \text{ and etc}} = 0$. The results are obtained for two lattices of 42x42 (circles) and 84x84 (triangles) Ag sites by Monte Carlo calculations. Performing calculations with even larger values of J_6 and J_7 and correspondingly increasing the repulsive forces of the system, we found some differences from the diagram of Fig. 1: (i) the values of the phase transition temperature T_c increase and especially prominent is the increase of T_c of disordered-to-hcp phase; (ii) the maximum of the honeycomb phase in $T/|J_4|$ vs μ dependence moves to higher values μ. The area, where the honeycomb and disordered phases co-exist at $c > 1/7$ in $T/|J_4|$ vs c diagram, correspondingly narrows and disappears for higher repulsive forces due to vicinity of the honeycomb-to-hcp phase boundary; (iii) the vanishing of this co-existence increases the area, where hcp and disordered phases co-exist, and this area starts to occur for coverages corresponding to 0.85 of full monolayer of the hcp structure. In STM experiment [2] this number is 0.6-0.9.