

Nucleation of “Hard” Crystals Directed by a “Soft” Template: *In Situ* X-ray Studies

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Introduction

Macromolecular substrates play a key role in many biomineralization processes, and many systems are characterized as being “organic-matrix-mediated” [1]. The organic surface acts as the nucleation catalyst; it lowers the activation energy for cluster formation. Furthermore, the matrix exerts powerful control over the size, structure, morphology, and crystallographic orientation of the nucleating mineral. The assembly of nuclei is often explained to proceed through the route of “interfacial molecular recognition.” The recognition process involves several molecular mechanisms: electrostatic interactions, geometrical complementarity, and stereochemical equivalence. Although widely accepted in explanations of the orientation phenomena, molecular recognition is a profound assumption that has so far been supported by only circumstantial evidence. For the first time, we present direct *in situ* evidence for the geometrical complementarity (epitaxy) between the organic matrix and the inorganic mineral at the interface.

Methods and Materials

We studied the influence of a heneicosanoic acid monolayer at zero pressure and 25°C on the nucleation of barium fluoride. We prepared a supersaturated aqueous solution of barium fluoride according to a method similar to that described in Ref. 2. We mixed appropriate stoichiometric amounts of barium chloride and ammonium fluoride to obtain metastable solutions of barium fluoride in several concentrations between 3 mM (saturated) and 12 mM (supersaturated).

Results and Discussion

Scans along Debye rings reveal intensity variations that confirm the preferential orientation of the crystals. An inspection of Fig. 1 clearly shows that the (100) face of barium fluoride lies parallel to the plane of the matrix.

When the epitaxy is being established, it is often assumed that the “hard” mineral has the same structure at the interface as it does in the bulk and that the “soft” matrix on pure water has the same lattice spacings as it does in the presence of ions in water (e.g., in Ref. 3). Such assumptions are misleading for two reasons: (1) the structure of the crystalline phase of Langmuir monolayers has recently been shown to change in the presence of various ions [4], and (2) at the initial stage of growth, the

mineral is expected to have a strained lattice. Analogous reorganization of atoms occurs in laterally strained structures of thin films grown in registry with a rigid lattice of a solid substrate. However, in the matrix-mineral system, neither of the lattices is rigid; they exert a mutual influence on each other. This mutual interplay makes *a priori* predictions of the geometrical relationship between the lattices virtually impossible. Any potential lattice match must be sought experimentally.

Because synchrotron x-rays can see both the organic and inorganic structures *in situ*, the geometrical relationship between lattices of these structures can easily be determined. Diffraction peaks from the heneicosanoic monolayer (“organic peaks”) are shown in Fig. 2, and a representative (200) peak from barium fluoride (“inorganic peak”) is shown in Fig. 3. The organic peaks are identified from “elongated” Bragg rods (not shown). In addition to the (200) inorganic peak, five other peaks have been observed and indexed with the barium fluoride structure, and they all shift to a higher reciprocal in-plane vector with increasing concentration. This shift indicates that the unit cell of the first few interfacial layers of the mineral is contracted (strained) in real space. The real-space organic and contracted inorganic lattices are drawn in Fig. 4, where the commensurate relationship between the lattices becomes apparent.

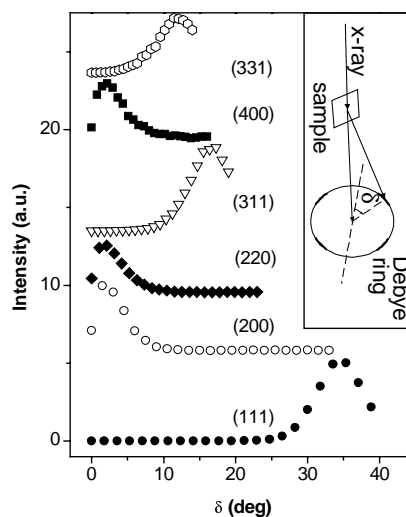


FIG. 1. Scans along Debye rings.

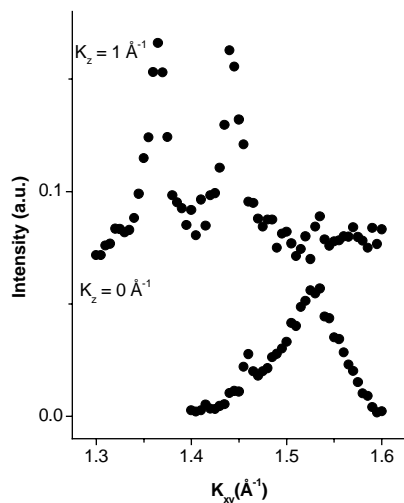


FIG. 2. Peaks from the organic matrix.

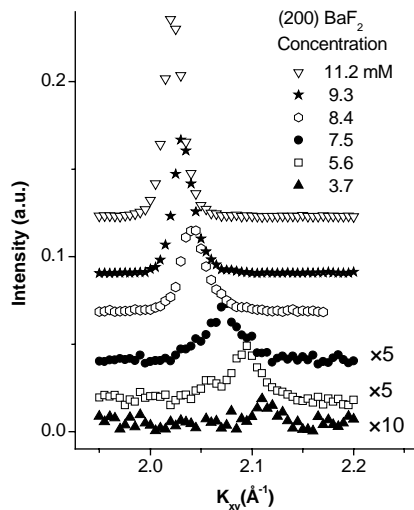


FIG. 3. Representative peak from barium fluoride.

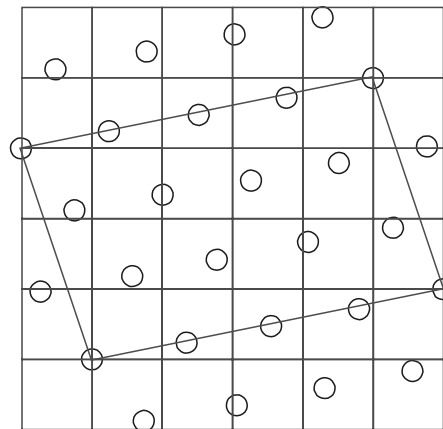


FIG. 4. The commensurate relationship between lattices of the organic head groups (blue) and the (100) face of BaF_2 (red).

The ratio of the area of the organic primitive unit cell to the area of the (100) face of the barium fluoride cubic unit cell is 1.5, a whole fraction pinpointing the commensurability. In conventional notation, the surface lattice of the (100) face of barium fluoride is related to the organic unit cell as $c(4\sqrt{2} \times 8\sqrt{2})$.

Acknowledgments

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References

- [1] S. Mann et. al., *Science* **261**, 1286 (1993).
- [2] J. B. A. Walker, B. R. Heywood, and S. Mann, *Mater. Chem. Comm.* **1**, 889 (1991).
- [3] L. Lu et. al., *Chem. Mater.* **13**, 325 (2001).
- [4] J. Kmetko et al., *J. Phys. Chem. B* **105**, 10818 (2001).