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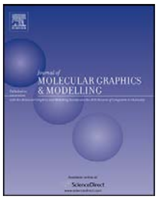

First principle study towards the influence of Cd^{2+} on the morphology of sodium chloride

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ABSTRACT

The influence of Cd^{2+} on the morphology of sodium chloride has been investigated with Density functional methods. The preferential interactions of Cd^{2+} ion with the {1 1 1} surface of NaCl support the observed octahedron morphology of NaCl. The calculations were performed both in the gas phase and aqueous phase using continuum model (COSMO). We have examined the interaction of Cd^{2+} with various surface sites of sodium chloride such as, flat face, steps and kinks. The stabilization of {1 1 1} NaCl surface by mixed Cd^{2+} ion and explicit water molecules in the ratio of (1:3) is in agreement with the SXRD results (Surf. Sci. 599 (2005) 196 [17]). The Cd^{2+} ion prefers to interact with {1 0 0} surface of NaCl by surrounding with water molecules, whereas, the mixed layer formation on {1 1 1} is not specific in nature. The interaction of $CdCl_2$ with the surface of sodium chloride is ineffective to induce this phenomenon.

1. Introduction

Surface chemistry and surface phenomena is always under debate, even more rigorous, if we talk about crystal habit. The nucleation, growth and morphology of crystals can be significantly altered by the presence of low concentrations of impurities. These impurities may be reaction by-products or impurities present in the reactants or they may be additives purposely added to alter the crystallization process. The effects of impurities and additives on crystallization are summarized in some recent reviews [1,2]. Additives can reduce crystal growth rate and alter morphology by binding to crystal faces and interfering with propagation steps [3,4]. The control of crystal morphology by use of additives is a subject of great interest which has been studied experimentally and theoretically employing molecular modeling techniques [5–7]. Rome de 1'Isle showed that octahedrons instead of normal cubes are formed, if rock salt is grown in the presence of urine [8]. Many authors have since reported the cube–octahedron shape transition under various experimental conditions. In this regard, earlier work reported that octahedron crystals can also be obtained from pure water solution [9–11]. A schematic diagram for the change in the shape of an alkali halide crystal from cubic to octahedron was shown in Scheme 1. The morphological changes appears in the crystals is due to the interaction of additives on a specific face which reduces the growth of that face, as a result, other fast growing surfaces disappear and eventually, the slow growing surface controls the morphology. Mathieu et al. have measured the adsorption isotherms of Cd^{2+} ions onto {1 0 0} and {1 1 1} faces of NaCl crystal in saturated solutions of sodium chloride [12]. This study concluded that the impurity adsorbs on the high energy kink sites instantaneously compared to steps and flat sites and hence the growth of surfaces would predominantly be governed by such kink sites [2]. Growth kinetics can be measured by adsorption isotherm of impurity onto the crystal faces under study or else by estimating the surface fee energies of the faces with incorporation of new solute units into the crystal lattice [13].

A significant effort in investigating the role of impurities on the occurrence of NaCl {1 1 1} faces during growth from aqueous solutions has been made by Kern [14], Boistelle [15] and Bienfait et al. [11]. Cd^{2+} shows the strongest effect, because even small concentration results in the appearance of {1 1 1} faces, which are not present in clean solutions. Boistelle and Simon proposed that the NaCl covered by an epitaxial layer consists of $CdCl_2 \cdot 2NaCl \cdot 3H_2O$ instead of $CdCl_2$, responsible for the morphological change of salt [16]. Recent study performed to understand the proposed model for the epitaxial layer interaction with NaCl concluded that the observed adsorption isotherm is negligibly small and may not be responsible for the change in the habit of NaCl. Further, it was concluded that the Cd^{2+} ion is in direct contact with the crystal surface and the polar {1 1 1} NaCl is stabilized by a

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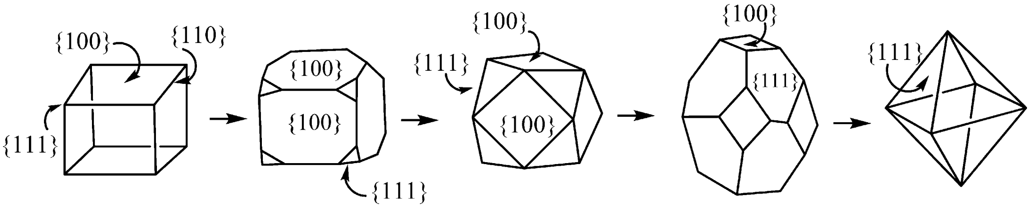


Scheme 1. A schematic diagram from cubic to octahedron for alkali halide crystals.

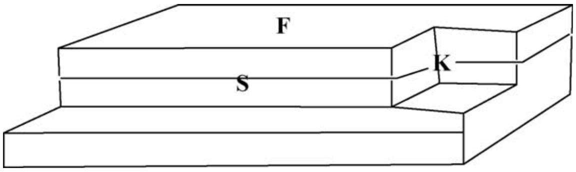
mixed monolayer of Cd^{2+} and water in a ratio of 1:3 based on SXRD results [17].

Cabrera and Vermilyea hypothesized that strongly adsorbing immobile impurities on terraces of crystal surfaces and steps drastically impede the movement relative to that expected without impurities present causing the morphological change in crystals [18]. The Cd^{2+} ions were also expected to retard the specific planes of sodium chloride and render the morphological change of this alkali halide [19]. Therefore, the models proposed for the adsorption of Cd^{2+} ions on sodium chloride planes with or without water molecules warranted a theoretical study.

In the present work, we have explored the interaction of Cd^{2+} with specific surfaces of NaCl in absence and presence of water molecules employing density functional theory calculations. An approach similar to surface docking developed to predict the influence of additives on the crystal morphology has been employed here [20–26]. The basis of this approach is to analyze the effect of additives on the individual crystal faces, which are cleaved from a crystal. If the additive has a preferred interaction on special face, the growth of this face will be slower, as a result, the other fast growing surfaces will disappear and eventually, the slow growing surface will control the morphology. In this way, the additive influences the morphology of crystals. The surface docking studies can, in principle, be undertaken both with the slab and cluster models [27]. In the cluster models, the crystals are mimicked with finite size representation whereas the slab models mimic the infinite surface of solids and are generally considered to be a better approach. Hence, we have employed the slab models for sodium chloride planes to study the interaction with cadmium ions using surface docking approach. A conventional array of these alkali halide ions has been employed in slab (constructed using periodic boundary conditions) using respective crystal data. The stable {1 0 0} surface of sodium chloride was modeled with alternating arrangement of Na^{+} and Cl^{-} ions. However, modeling the electrostatically polar {1 1 1} surfaces of these alkali halide crystal structure was considered a mystery in surface science, because it is difficult to investigate both experimentally and theoretically [28,29]. Since the bulk structure consists of alternating cationic and anionic sheets stacked along the {1 1 1} directions, the {1 1 1} polar surfaces must have a very high divergent electrostatic energy, which makes them theoretically highly unstable [30]. It has been shown in the earlier studies that the adsorption of negatively charged site of additives would be preferred with the positive ions on top of the surface of alkali halides. Recently, it was determined that the rock salt {1 1 1} surface is Na^{+} terminated in presence of aqueous solution and formamide [30]. However, the interaction with positive ions of additive would be preferred with the negative ions of rock salt on top of the surface, i.e. {1 1 1} surface of is Cl^{-} terminated [17]. Hence for this study, {1 1 1} NaCl surface was modeled with the Cl^{-} ions on top of the surface.

2. Computational procedure

Study of interactions of Cd^{2+} with 3D slabs of NaCl has been performed employing the density functional program $DMol^3$ in Material Studio (version 4.1) of Accelrys Inc., the electronic wave functions are expanded in atom-centered basis functions defined on a dense numerical grid [31–34]. We used DND and DNP double numerical basis sets which are comparable to 6-31G* and 6-31G** basis sets, respectively. The interaction of Cd^{2+} on surfaces of NaCl was optimized with local spin density approximation with Perdew–Wang correlational (LDA/PWC) [35]. The LDA is one of the earliest approximations in DFT. It includes correction for electron correlation effects. However, it is known that the LDA overestimates the binding energies. Generalized gradient approximations (GGA's) go beyond LDA descriptions by including density gradients, and improve the energies significantly [35–44]. The functional Vosko, Wilk, and Nusair–Becke and Perdew–Wang (VWN-BP) [37,38] was used to calculate the interaction energies of Cd^{2+} with NaCl surfaces [33]. Flat face (F), double step (S) and kink (K) were generated for {1 0 0} and {1 1 1} planes of sodium chloride (Scheme 2). All the three possible situations with these planes were considered in the study to determine the highly preferred sites of interaction of additive in each case. To generate the surfaces, the 3D models depend not only on number of layers in the slab, but also on the vacuum gap between the successive slabs. In each case, F, S and K, the slabs generated with periodic boundary conditions was electrically neutral. We have investigated this dependence by optimizing the numbers of layers in the slab as well as the vacuum gap thickness. We have optimized the supercell lattice by varying the number of layers in each case and keeping the sufficiently large vacuum thickness 20 Å fixed. Further, the vacuum thickness was varied from 8 to 20 Å in 2 Å steps with the previously optimized layers and considered the values when the total energy as a function of the vacuum thickness separations was minimum. Our optimized supercell lattice for NaCl was found to be consistent with Ermoshkin et al. results in that six layered slabs are large enough to reproduce surface states and bulk states of alkali halide crystals [45]. The k-points were generated by Monkhorst-Pack schemes [46]. This scheme produces a uniform grid of k-points along the three axes in reciprocal space. The k-points used in this study were 2 × 2 × 1 with separation from origin 0.30744, 0.0355 and 0.03955/Å respectively. The tolerances of energy, gradient, and displacement convergence were 2×10^{-5} Ha, 4×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively (1 Ha = 627.5095 kcal/mol). The SCF convergence criteria for all calculations were 1.0×10^{-5}. The electrical neutrality was maintained for the slabs, however, the bare cadmium ion was placed with charges on it and no counter-ion was used in these cases. The conductor-like screening model (COSMO) has been employed for implicit solvent calculations [47–52]. The LDA/PWC/DND optimized gas phase geometries of Cd^{2+}on the surface of slab models of



Scheme 2. .