Atomic-scale study of ion incorporation at calcite surface using synchrotron X-ray methods

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
for the degree

DOCTOR OF PHILOSOPHY

Field of Materials Science and Engineering

By

Likwan Cheng

EVANSTON, ILLINOIS
December 1998
ABSTRACT

Atomic-scale study of ion incorporation at calcite surface using synchrotron X-ray methods

Likwan Cheng

Understanding the structure of impurity ions incorporated at the surfaces of ionic crystals is of both fundamental and practical significance. The impurity acts as an atomic probe, and the structural perturbation it induces on a surface reveals the structural properties of the surface. The process of impurity ion incorporation from the aqueous phase is also directly related to such practical issues as the transport of trace elements at the water-solid interface.

With the first extensive applications of the combined experimental techniques of X-ray standing wave triangulation and surface extended X-ray absorption fine-structure spectroscopy, this thesis presents a survey on the atomic-scale structures of impurity ions incorporated at the calcite (10\(\bar{4}\)) cleavage surface by adsorption at the water-calcite interface. The three-dimensional surface lattice sites, and the in-plane first-neighbor coordination structure and distances, are determined for a series of divalent cations, including Zn, Co, Ni, Cu, and Pb. These cations substitute for Ca at the calcite surface. A model is proposed to interpret the common features in these surface impurity structures, by considering them as bulk impurity structures under the effect of the surface. In addition, a direct measurement of a surface impurity’s vibrational amplitude is made. The concept of using a Jahn-Teller ion as a probe for the surface impurity’s near-surface vertical location is proposed.

The surface incorporation structures of molecular anions of related symmetries to the host CO\(_3^2\) anion are investigated, including the pyramidal SeO\(_3\) and AsO\(_3\)
ions, and the tetrahedral CrO$_4$ ion. These anions are found to substitute for the CO$_3$ ion at the calcite surface.

These studies provide direct structural evidence of monoatomic and molecular ion surface incorporation by substitution.
Acknowledgments

I am grateful to my advisors, Professor Michael Bedzyk and Dr. Neil Sturchio, for their guidance and encouragement during this work.

I thank Drs. Paul Lyman, Ronald Chiarello and Paul Fenter, for instruction of experimental techniques; Drs. J.C. Woicik and Jörg Zegenhagen, for experimental collaborations; Dr. Guy Jennings, for advice in computer programming. I thank Professors David Seidman and Kenneth Shull for serving on my examination committee; Drs. Gordon Knapp, Mark Beno, Kenneth Kemner, John Hanchar and Zhong Zhong for consultation and assistance. I thank the former and current graduate students in our research group: Dr. Yonglin Qian, Holly Hutchason, David Marasco, William Rodrigues, Brad Tinkham and particularly Tien-Lin Lee, as well as Drs. Osami Sakata, Alexander Kozimirov and Don Walko, for their help and company. I thank the staff at the National Synchrotron Light Source.

I thank the Graduate School for the awards of a University Fellowship and a University Scholarship; Argonne National Laboratory for a Laboratory Graduate appointment; and the U.S. Department of Energy for funding for research.

Finally, I thank my family, friends, and many people I know.
To the memory of
Professor Carl Sagan
Contents

Abstract iii

Acknowledgments v

1 Introduction 1

1.1 Study of impurity ion incorporation structures at the calcite cleavage surface 1

1.1.1 Impurity as an atomic-scale probe of surface structural properties 1

1.1.2 Trace element incorporation at the water-calcite interface 3

1.2 Overview of thesis 4

2 Experimental Techniques 7

2.1 Fundamentals of X-ray techniques 7

2.1.1 The X-ray standing wave technique 7

2.1.2 Surface extended X-ray absorption fine structure spectroscopy 13

2.1.3 The combination of XSW and SEXAFS as a tool for surface studies 16
2.2 Experimental setup ........................................... 17
2.3 Preparation of impurity ion adsorbate surfaces ........... 19

3 Calcite crystal structure; Structure of the cleavage surface; Structure of a bulk impurity 23
3.1 Calcite crystal structure ........................................ 23
3.2 Surface impurity structure considered as the structure of a bulk impurity located at a surface site: A hypothesis ............... 25
3.3 Structure of the calcite cleavage surface ...................... 26
3.4 Structure of a bulk impurity: Manganese in calcite .......... 28

4 Surface incorporation structure of calcite-type cations: Zinc on calcite 33
4.1 Introduction ...................................................... 33
4.2 Experimental ................................................... 34
4.3 Results ........................................................... 35
4.3.1 XSW analysis ............................................... 35
4.3.2 EXAFS analysis ............................................ 37
4.4 Discussion ....................................................... 41
4.4.1 Displaced substitution of Zn at the Ca site ............... 41
4.4.2 In-plane relaxations of neighboring carbonates: Conservation of the Zn-O distance ......................... 42
4.4.3 Vertical relaxation of Zn ion .............................. 43
4.5 Surface incorporation structure of cobalt .................... 46

viii
4.6 Surface incorporation structure of nickel .............................. 48
4.7 Surface incorporation structure of copper ............................ 50
  4.7.1 Vibrational amplitude of adsorbate ion .......................... 50
  4.7.2 Jahn-Teller ion as a probe of adsorbate vertical location ... 51

5 Surface incorporation structure of aragonite-type cations: Lead
  on calcite ........................................................................... 57
  5.1 Introduction ..................................................................... 57
  5.2 Experimental ............................................................... 58
    5.2.1 Sample preparation .................................................. 58
    5.2.2 Instrumental settings ............................................... 59
  5.3 Results .......................................................................... 60
    5.3.1 XSW analysis .......................................................... 60
    5.3.2 SEXAFS analysis ...................................................... 61
  5.4 Discussion ...................................................................... 65
    5.4.1 Substitution of Pb at the bulk-extrapolated surface Ca site . 65
    5.4.2 In-situ position of Pb on calcite surface ...................... 66
    5.4.3 In-plane expansion of neighboring carbonates: Conservation
          of the Pb-O distance .................................................... 67
  5.5 Surface impurity structure interpreted as the structure of a bulk
  impurity located at a surface site: A model ........................... 68
    5.5.1 Cation in-plane coordination: Conservation of cation-oxygen
          coordination distance .................................................. 68
6 Surface incorporation structure of pyramidal anions: Selenite and arsenite on calcite 74

6.1 Introduction: The role of molecular configuration in surface incorporation ........................................... 74
6.2 Pyramidal ion incorporation at surface carbonate site .............. 76
6.3 Experimental ......................................................... 77
   6.3.1 Surface preparation ............................................. 77
   6.3.2 Instrumental settings ........................................... 77
6.4 Results ............................................................. 78
   6.4.1 Selenite on calcite ............................................. 78
   6.4.2 Arsenite on calcite ............................................. 78
6.5 Discussion .......................................................... 81
   6.5.1 Substitution of trigonal pyramidal ion at the carbonate site. 81
   6.5.2 Possible orientation of a pyramidal ion at the surface carbonate site ............................................ 82

7 Surface incorporation structure of tetrahedral anions: Chromate on calcite 88

7.1 Introduction ......................................................... 88
7.2 Experimental ....................................................... 89
   7.2.1 Surface preparation ............................................. 89
   7.2.2 Instrumental settings ........................................... 89
7.3 Results .................................................. 90
7.4 Discussion .................................................. 92

8 Summary .................................................. 95

References .................................................. 97

Appendix. SWAN: A computer program for X-ray standing wave data analysis .................................................. 104
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cation radii and the first-neighbor cation-oxygen distances for carbonates of the calcite structure.</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>Local in-plane structure for Zn incorporated at the calcite (10\overline{1}4) surface according to SEXAFS measurement, compared with the local Zn environment in the bulk CaCO(_3) lattice as an impurity, in the ZnCO(_3) crystal, and the local Ca environment in the CaCO(_3) crystal.</td>
<td>43</td>
</tr>
<tr>
<td>3</td>
<td>Position of the Zn adsorbate ion (h_H) above the (H) lattice plane from the XSW measurements and according to the structure model.</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>XSW coherent fractions and positions of Co and Ca for the Co-on-CaCO(_3) sample.</td>
<td>46</td>
</tr>
<tr>
<td>5</td>
<td>Cation radii and the first-neighbor cation-oxygen distances for carbonates of the aragonite structure.</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>The coherent positions of Pb from the XSW measurements compared with that of the ideal Ca.</td>
<td>66</td>
</tr>
<tr>
<td>7</td>
<td>In-plane structure for Pb incorporated at the calcite (10\overline{1}4) surface according to SEXAFS measurement, compared with the local Pb environment in the PbCO(_3) crystal and the local Ca environments in the calcite and the aragonite structures of CaCO(_3).</td>
<td>68</td>
</tr>
</tbody>
</table>
8 Comparison of the geometry of the carbonate, selenite and arsenite ions. ................................. 77

9 Comparison of the height of As and Se atoms above the (10\overline{1}4) and (0006) lattice planes according to experiments and model. .......................... 85

10 List of Cr coherent fractions and coherent positions obtained for various CrO$_4$-on-CaCO$_3$ sample surfaces ................................. 91
# List of Figures

1. A schematic drawing showing the Bragg-reflection XSW at a crystal surface. .................................................. 9

2. The simulated curves for reflectivity and fluorescence yields for an atom located at various coherent positions relative to the diffracting lattice planes, for the calcite (10\(\overline{1}4\)) reflection. ................................. 11

3. A schematic showing the interference between an outgoing photo-electron wave from an X-ray absorbing atom and a backscattered wave from a neighboring atom. ............................................. 15

4. A diagram showing the arrangement of the main components for XSW measurements at the X-ray beamline X15A, at the National Synchrotron Light Source. .................................................. 19

5. The relative geometry of the calcite (10\(\overline{1}4\)) surface and the (a) the (10\(\overline{1}4\)), the (0006), and (b) the (02\(\overline{2}1\)) lattice planes. ....................... 20

6. A schematic drawing showing the adsorption of aqueous ions at the water-calcite interface. ............................................. 21

7. The hexagonal unit cell of calcite. ............................................. 24

8. The Ca cation octahedron in calcite, defined by the coordination with six O atoms from neighboring carbonate groups. ............ 25
<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Top view of the calcite (10(\overline{1}4)) lattice.</td>
</tr>
<tr>
<td>10</td>
<td>Side view of the calcite (10(\overline{1}4)) lattice.</td>
</tr>
<tr>
<td>11</td>
<td>Reflectivity (R) and Mn and Ca (K\alpha) fluorescence yields vs. incident angle of X-rays for the calcite (10(\overline{1}4)) Bragg reflection.</td>
</tr>
<tr>
<td>12</td>
<td>The amplitudes of Fourier transform of the (k^2)-weighted EXAFS functions for the Mn:CaCO(_3) data, and for the MnCO(_3) standard compound, before phase correction.</td>
</tr>
<tr>
<td>13</td>
<td>The filtered Mn-O first-shell EXAFS data, as (\chi k^2), after background subtraction and conversion to (k)-space, for Mn:CaCO(_3), and the best theoretical fit.</td>
</tr>
<tr>
<td>14</td>
<td>Reflectivity (R) and Zn (K\alpha) fluorescence yield (Y) vs. incident angle of X-rays for the calcite (10(\overline{1}4)), (0006) and (02(\overline{2}4)) Bragg reflections.</td>
</tr>
<tr>
<td>15</td>
<td>EXAFS spectra, as (\chi k^2), after background subtraction and conversion to (k)-space, for the in-plane Zn/CaCO(_3) sample data, the ZnCO(_3) standard compound, and the Fourier-filtered Zn-O first-shell component of the Zn/CaCO(_3) data, and the best fit to the filtered first-shell data.</td>
</tr>
<tr>
<td>16</td>
<td>The amplitudes of Fourier transform of the (k^2)-weighted EXAFS functions for the in-plane Zn/CaCO(_3) data and the ZnCO(_3) standard compound, before phase correction.</td>
</tr>
<tr>
<td>17</td>
<td>A model describing the lattice sites of the Zn ions incorporated at the calcite (10(\overline{1}4)) surface.</td>
</tr>
</tbody>
</table>
18 Experimental data and best theoretical fits for reflectivity $R$, and Co $K\alpha$ and Ca $K$ fluorescence yields vs. incident angle of X-rays for the calcite $(10\overline{4})$, $(01\overline{8})$ and $(2\overline{2}04)$ Bragg reflections.  

19 Experimental data and best theoretical fits for reflectivity $R$ and Ni $K\alpha$ fluorescence yield $Y$ vs. incident angle of X-rays for the calcite $(10\overline{4})$ Bragg reflection.  

20 Experimental data and best theoretical fits for reflectivity $R$ and Cu $K\alpha$ fluorescence yield $Y$ vs. incident angle of X-rays for the calcite $(10\overline{4})$, and $(20\overline{2}8)$ Bragg reflections.  

21 A side view of the calcite $(10\overline{4})$ surface showing the coherent positions of the Cu ion measured with respect to the $(10\overline{4})$ and the $(20\overline{2}8)$ lattice planes.  

22 A calcite surface schematic showing incorporated Cu ions located at two different sites.  

23 The amplitudes of Fourier transform of the $k^2$-weighted EXAFS function for the in-plane Cu-on-CaCO$_3$ data.  

24 A schematic of the reflection-geometry X-ray liquid cell used for in situ XSW measurements of Pb incorporation at the calcite $(10\overline{4})$ surface.  

25 Reflectivity and Pb $L\alpha$ fluorescence yield vs. incident angle of X-rays for the $(10\overline{4})$, $(0006)$ and $(02\overline{2}4)$ Bragg reflections.  

26 Reflectivity and Pb $L\alpha$ fluorescence yield for the in situ and the ex situ measurements vs. incident angle of X-rays for the $(10\overline{4})$ Bragg reflection.  

xvi
The amplitudes of Fourier transform of the $k^2$-weighted EXAFS functions for the in-plane Pb/CaCO$_3$ sample data and the PbCO$_3$ standard compound data, before phase correction.  

The Pb-O first-neighbor shell component of the in-plane EXAFS spectra for the Pb/CaCO$_3$ data after background subtraction, conversion to $k$-space and Fourier-filtering, as $\chi k^2$, and the best fit to the filtered first-shell data.  

A proposed structure model for a cation impurity on calcite, derived from the structures of a bulk Ca$^{2+}$ and a bulk cation impurity.  

The XSW measured [10$ar{T}$4] displacement $\Delta h$ vs. normalized first-neighbor cation-oxygen distance $r_a/r_{Ca}$ for various divalent cation impurities incorporated at the calcite (10$ar{T}$4) surface.  

X-ray reflectivity $R$ and Se $K\alpha$ fluorescence yield $Y$ as a function of the relative angle of X-ray incidence for the calcite (10$ar{T}$4), (0006) and, (11$ar{2}$0) Bragg reflections.  

Reflectivity $R$ and As $K\alpha$ fluorescence yield $Y$ vs. relative angle of X-ray incidence for arsenite incorporated at the calcite (10$ar{T}$4) surface, for the (10$ar{T}$4) and (0006) Bragg reflections.  

A model showing the XSW-determined Se lattice site and a proposed structure of the selenite ion at the calcite (10$ar{T}$4) surface.  

A model showing the XSW-determined As lattice site and a proposed structure of the arsenite ion incorporated at the calcite (10$ar{T}$4) surface.  

Reflectivity $R$ and Cr $K\alpha$ fluorescence yield $Y$ vs. incident angle of X-rays for the calcite (10$ar{T}$4) Bragg reflection.
A schematic calcite lattice showing the measured position of the Cr atom in the chromate adion. ........................................ 93

Flowchart diagram showing the algorithm for rocking curve calculation and fitting in SWAN. ........................................ 110

Flowchart diagram showing the algorithm for fitting the fluorescence yield in SWAN. ........................................ 111

A sample .ctl file for SWAN for the hexagonal (R) calcite structure. 112
Chapter 1

Introduction

1.1 Study of impurity ion incorporation structures at the calcite cleavage surface

1.1.1 Impurity as an atomic-scale probe of surface structural properties

A distinct difference between an ionic surface and a metal or a covalent surface is that the cohesive energy of an ionic surface is governed by the long range coulombic force among individual ions in the crystal. One difficulty in the theoretical evaluation of the structural properties of an ionic surface is that the Madelung potential for a bulk lattice may not be valid for use in calculating surface properties [1]. Analytical solutions of surface Madelung potential are only available for the simplest structures, such as NaCl(001) [2]. In recent years, with advances in computational techniques, there has been increasing reliance on simulation to calculate the ionic surface properties.

Structurally, however, an autocompensated ionic surface is generally stable, and retains the bulk lattice order (although not necessarily the bulk-equivalent positions) [3]. The high degree of structural order in an ionic surface offers a
unique experimental opportunity for investigating its structural behavior. One may potentially introduce an atomic-scale perturbation of known characteristics into the surface, and observe the structural response of the surface. The most straightforward way of achieving this is to incorporate an impurity ion into the surface lattice by substitution for a host ion. The idea of using an impurity as an atomic-scale structural probe has found successful applications in studying structural phase transition in perovskite oxide materials when paramagnetic ions were used as bulk probes [4]. Obviously, this may be applied to study surface structural properties as well. The surface system so designed is a two-dimensional analog of the extrinsic substitutional point-defect system in bulk crystal. The atomic-scale deformation of the surface to the impurity perturbation—local near neighbor distances and relaxation in lattice position—can be experimentally monitored by atomic-resolution techniques. These deformations directly reveal much about the structural properties of the surface. This experimental method also provides a way to complement theoretical studies and test simulation results.

Rigorous investigations of ionic surfaces lag substantially behind investigations of metal and semiconductor surfaces [3]. Among ionic surfaces, the better understood are simple binary systems; the examples of these are metal oxides and alkali halides, e.g., MgO(001) and NaCl(001) [5]. Although tertiary surfaces have been studied, systematic work has so far been limited to systems that are made up exclusively of monoatomic ions, mostly complex oxides [6]. Theoretical simulations reveal that molecular ions possess unique intramolecular potential functions. These potentials, mainly covalent, are much different than the interionic Madelung potential. Their existence makes available an entirely new set of molecular motions in a molecular ion when it is exposed to the perturbation of a defect, including the crystal surface. These new motions can potentially lead to a dramatic change in
the surface structural properties of the crystal. It is well known that a molecular crystal, e.g., CaCO$_3$, has a structural behavior very distinct from its stoichiometric counterparts in the complex oxides, e.g., CaTiO$_3$ [7]. Indeed, the calcite structure—made up of the calcium cation and the simple carbonate molecular anion, and with a small unit cell—is among the simplest of molecular ionic crystals. This structural simplicity offers an ideal opportunity for exploring the fundamental aspects of the structural properties of a molecular crystal surface.

1.1.2 Trace element incorporation at the water-calcite interface

Calcite is one of the most abundant minerals. The water-calcite interface occurring in natural environments is a gateway for material transport and transformation. The interaction of an aqueous ion with the calcite surface may determine its subsequent location, phase, or even its chemical state. This process is directly related to, among other practical issues, the environmental science of the temporal evolution of toxic trace elements in natural and industrially polluted waters.

The interaction of an aqueous ion at the water-solid interface may be divided into a few categories, according to the nature of its chemical bonding with the surface [8]. Surface complexation is the attachment of hydrated ion complexes at the surface; some of these complexes are only weakly bound to the surface, and are often removed if the solution is removed. Precipitation is the formation of a new solid phase, crystalline or amorphous, at the surface; in this process the crystal structure played no substantial role. Surface reaction refers to the change in chemical state of an aqueous element by reacting at the surface, such as oxidation. Chemisorption is the adsorption of an aqueous ion at the surface; it includes incorporation by surface ion exchange.
This last process is the most predominant at the water-calcite interface. Consequences of this process include solid-solution growth or surface passivation. For decades, it has relied on chemical evidence to infer that chemisorption of an aqueous ion at water-calcite interface takes place by substitution of the ion at the surface lattice. Although it has been quite generally accepted that a monoatomic ion substitutes for a host ion upon being chemisorbed at the calcite surface, this conclusion was derived from monitoring solution concentration changes in the exchanging ions before and after incorporation. Strictly speaking, the meaning of “ion substitution” in this conclusion is valid only in the stoichiometric sense, but not in a structural sense; solution chemistry data do not determine the location of the adsorbed ion at the surface.

A precise knowledge of the local lattice structure of a surface impurity ion is a critical factor needed for accurately assessing the properties of the impurity-doped surface. It helps resolve whether the doped surface preserves a sufficient order for further epitaxial growth, potentially into a macroscopic mixed solid solution phase (the buckled lattices observed in some mixed ionic crystals [9] demonstrate the geometric flexibility of ionic crystals in incorporating impurities), or, on the contrary, the impurity doping may passivate or chemically inactivate the surface. These fundamental issues have significance for predicting properties, such as, the temporal evolution of trace elements in water.

1.2 Overview of thesis

This thesis presents an extensive series of high-resolution X-ray measurements of the atomic-scale structures of divalent monoatomic and molecular impurity ions incorporated at the calcite (10\(\overline{4}\)) surface. These ion incorporation studies are aimed for both fundamental and practical purposes: (1) To probe the surface
through direct experimental observations of its atomic-scale structural changes; and (2) to provide quantitative data in the application of ion adsorption at the water-calcite interface. A variety of monoatomic and molecular ions are included in this study; they were selected based on their structural relationship to the host ions and the implications of their results to practical applications.

The contents of this thesis are organized as the following. Chapter 2 introduces the experimental techniques: X-ray standing wave (XSW) and surface extended X-ray absorption fine structure spectroscopy (SEXAFS). Chapter 3 lays down a foundation for studying impurity structures at the calcite (10\(\bar{1}4\)) surface, by considering separately the structure of a clean calcite (10\(\bar{1}4\)) surface, and the structure of an impurity cation in bulk calcite.

Chapters 4 to 7 describe the experimentally observed surface incorporation structures of various divalent ions. These ions are systematically divided into monoatomic cations and molecular anions. The results for monoatomic cation surface structures include XSW-determined three-dimensional lattice position and SEXAFS in-plane near-neighbor coordination environment. Those for molecular anion surface structures include only the XSW three-dimensional lattice position. Chapter 4 describes the incorporation structures of monoatomic cations whose carbonates are of the calcite (isomorphous) structure. Here the results of Zn\(^{2+}\) incorporation structure will be treated in depth; these results will be supported by results for other related cations, including Co\(^{2+}\), Ni\(^{2+}\) and Cu\(^{2+}\). With Cu\(^{2+}\), in particular, an experimental measurement of adsorbate vibrational amplitude is made. Also with Cu\(^{2+}\), the concept of using a Jahn-Teller ion as a probe of the near-surface location of an adsorbate cation is proposed.

In Chapter 5 we present the study of the surface impurity structure of a monoatomic cation whose carbonate is of the aragonite structure, Pb\(^{2+}\). We also
present here a comparison of the *in situ* and the *ex situ* measurements of adsorbate lattice site in the direction normal to the surface.

A model that interprets the cation incorporation structure data is then presented. This model is based on the assumption that the surface cation impurity structure is the superposition of the structures of a bulk impurity and a surface cation site.

Chapters 6 and 7 describe surface incorporation of molecular anions. We focus on the commonly occurring inorganic anions that have the \( BO_3 \) and the \( BO_4 \) forms, which are structurally most related to the host carbonate ions, i.e., with the basic three-fold rotational symmetry axis. In Chapter 6, we consider the incorporation of the trigonal pyramidal anions selenite (\( SeO_3^- \)) and arsenite (\( AsO_3^- \)). In Chapter 7, we consider the incorporation of the tetrahedral anion chromate (\( CrO_4^{2-} \)).

Chapter 8 summaries the results and conclusions in these findings.
Chapter 2

Experimental Techniques

2.1 Fundamentals of X-ray techniques

2.1.1 The X-ray standing wave technique

The standard, Bragg-reflection X-ray standing wave technique [10, 11] is based on the dynamical theory of X-ray diffraction from an ideal crystal [12]. Referring to Fig. 1, consider the traveling plane waves of the incident X-ray beam, and the Bragg-diffracted X-ray beam at a crystal surface:

\[
\begin{align*}
\mathcal{E}_0 &= E_0 \exp(-2\pi i K_0 \cdot r) \exp(i\omega t) \\
\mathcal{E}_H &= E_H \exp(-2\pi i K_H \cdot r) \exp(i\omega t).
\end{align*}
\]

The Bragg diffraction condition is described by the following reciprocal space vector equation:

\[ H = K_H - K_0, \]

where \( H \) is the \((hkl)\) reciprocal lattice vector, and \( K_0 \) and \( K_H \) are the wave-vectors. The resultant scalar equation reduces to Bragg’s law, \( \lambda = 2d_H \sin \theta \). The interference between \( E_0 \) and \( E_H \) at the crystal surface can be realized by the total
\[ E = [E_0 \exp(-2\pi i K_0 \cdot r) + E_H \exp(-2\pi i K_H \cdot r)] \exp(i\omega t), \] 

and the total \( E \)-field intensity \( I = E \cdot E^* \). The total \( E \)-field intensity \( I \) can be divided by the incident \( E \)-field intensity \( |E_0|^2 \) to give the normalized XSW intensity:

\[ \frac{I(\theta)}{I_0} = 1 + \left( \frac{E_H}{E_0} \right)^2 + 2 \left( \frac{E_H}{E_0} \right) \cos[\phi(\theta) - 2\pi H \cdot r] \] 

In this equation the quantity \( (E_0/E_H)^2 \) is the reflectivity \( R(\theta) \), \( \phi(\theta) \) is the phase of the interference field relative to the \( H \) diffracting planes.

The XSW intensity at the crystal surface would excite the photo effect of an adsorbate atom located at position \( r \), within the XSW, causing the atom to emit characteristic fluorescence X-rays with a yield proportional to the standing wave intensity \( I(\theta) \). If we ignore thermal vibration, we can assume a \( \delta \)-function distribution of adsorbate atoms within a crystal unit cell:

\[ \rho(r) = \sum_i^N \delta(r - r_i). \] 

In the dipole approximation of the photo effect, Eqs. 5 and 6 can be combined to give the normalized yield function \( Y(\theta) \) for this distribution of adsorbate atoms:

\[ Y(\theta) = 1 + R(\theta) + 2\sqrt{R(\theta)} \frac{1}{N} \sum_i^N \cos[\phi(\theta) - 2\pi H \cdot r_i] \] 

Eq. 7 can be rewritten as

\[ Y(\theta) = 1 + R(\theta) + 2\sqrt{R(\theta)} f_H \cos[\phi(\theta) - 2\pi P_H], \] 

by defining the coherent fraction \( f_H \) and coherent position \( P_H \) with the following relation:

\[ \mathcal{F}_H = \frac{1}{N} \sum_i^N \exp(-2\pi i H \cdot r_i) = f_H \exp(-2\pi i P_H). \]
Figure 1: A schematic drawing showing the Bragg-reflection XSW at a crystal surface.
This relation defines $f_H$ and $P_H$ as the amplitude and phase, respectively, of the $H$th Fourier component $F_H$ of the spatial distribution of the adsorbate atoms. Although $f_H$ and $P_H$ are model independent quantities, we typically use models to interpret XSW results.

The dependence of $Y(\theta)$ on $\theta$ is the result of the dependences of the reflectivity $R(\theta)$ and the phase $\phi(\theta)$ on $\theta$. These two latter functions are derived from the dynamical theory of X-ray diffraction. The details of their derivations are given in a review article [13]. The form of $R(\theta)$ for the $(10\,\overline{4})$ reflection of calcite are shown as the bottom curve in Fig. 2.

The XSW phase $\phi(\theta)$ decreases by $\pi$ radian as $\theta$ moves from slightly below the Bragg angle $\theta_B$ to slightly above it. Accordingly, from Eq. 5, the standing wave antinode also moves inward by half of a period, in the $-\mathbf{H}$ direction, as the incident beam moves over this same angular range. The positions of the standing wave relative to the crystal lattice for $\theta$ below and above $\theta_B$ is shown in Fig. 1.

Eq. 8 is the central working relation of the XSW technique. In an actual experiment, one acquires $R(\theta)$ and $Y(\theta)$ with detectors while scanning the sample crystal through the Bragg reflection. Then, the values of $f_H$ and $P_H$ are obtained by fitting Eq. 8 to the experimentally measured $Y(\theta)$. All the XSW structural information about the adsorbate atom is contained in $f_H$ and $P_H$, as explained below. In addition, the “off-Bragg” fluorescence yield gives the adsorbate coverage when compared to a calibrated standard.

The coherent fraction $f_H$ is a measure of the spatial distribution of the fluorescent atom about its mean position, and is usually considered to be made up of three components:

$$f_H = C a_H D_H.$$  \hfill (10)
Figure 2: The simulated curves for reflectivity and fluorescence yields for an atom located at various coherent positions relative to the diffracting lattice planes, for the calcite (10\(\overline{1}4\)) reflection.
All four parameters in this equation can range from zero to unity. The first term $C$, the ordered fraction, is the fraction of atoms that are coherently located (i.e., those not randomly distributed). The second term, $a_H$, the geometric factor, is related to the geometric arrangement (or sites) of the non-randomly distributed atoms. If $a_H = 1$, there is one atomic site along the $H$ direction in the unit $d$-spacing, whose fractioned $d$-spacing position $\Delta d/d$ is given directly by the coherent position $P_H$ (to be discussed below). If $a_H < 1$, there is more than one preferred atomic positions.

The last term in $f_H$ is the Debye-Waller factor, which accounts for thermal vibration, i.e., the time-averaged spatial distribution of the vibrating atoms about their average positions. When expressed explicitly in terms of the mean square amplitude $\langle \sigma^2 \rangle$ of this vibration,

$$D_H = \exp \left( -2\pi^2 \langle \sigma_H^2 \rangle / d_H^2 \right).$$

(11)

Note that the amplitude $\langle \sigma^2 \rangle$ is measured along the $H$ direction.

The coherent position $P_H$ is the average position of the atoms measured along the $H$ direction in units of $d_H$. In Fig. 2, the dependence of the form of $Y(\theta)$ on $P_H$, according to Eq. 8, was demonstrated in the simulation for an atom located at various positions above the $(10 \overline{1}4)$ lattice plane of calcite, with the coherent fraction $f_H$ fixed at the value of 0.8. For Fig. 2 and all other calcite XSW analysis throughout this thesis, we choose the origin for convenience to be located at the carbon site. The sensitivity in the functional form of $Y(\theta)$ to $P_H$ at a reasonably high $f_H$ is the basis of the high spatial resolution of the XSW technique.

The three-dimensional triangulation of an atomic site by XSW combines the XSW measurements made with respect to three non-colinear diffraction vectors $H$, and gives the three-dimensional lattice position of an adsorbate atom relative
to the substrate lattice. If there is one lattice site, it can be found by the XSW triangulation method [14]. Often a surface (or bulk) atomic site possesses certain geometric symmetry relative to the crystal lattice. In such a case a symmetry argument can be made, and with this symmetry less than three measurements are needed for triangulation [13].

As a unique tool for determining the lattice site of an atom at a single-crystal surface at high-resolution, the Bragg-reflection XSW technique has found extensive applications since 1980 [11]. It has been used to study the atomic-scale adsorption structures of various ad-atoms on Si, Ge and III-V semiconductor surfaces [13, and references therein], including some recent work [15, 16, 17]; and to study the adsorption structures of atoms and organic films at metal surfaces, including Cu [18, 19], Ni [20] and Au [21]. The application of the XSW technique to the investigation of ionic crystals and surfaces has been limited. The only system relatively thoroughly studied with XSW is the bulk impurity metal ion system in the complex oxide LiNbO$_3$ [22, 23]. Recently the study of trace elements at the surface and in bulk calcite was the first XSW done on a mineral crystal [24]. The limitation in the number of systems suitable for XSW study has been due to the requirement of perfect crystals; but as more intense synchrotron X-ray sources become available, reduced probing volume will allow more crystalline materials to be considered suitable for XSW studies.

### 2.1.2 Surface extended X-ray absorption fine structure spectroscopy

The principles and experimental techniques of EXAFS are reviewed in Refs. [25, 26]. In the dipole approximation, the absorption probability $W(E)$ of an X-ray photon of energy $E$ by a $K$-shell atomic electron is determined by the initial state
\langle s \rangle$ and the final state $|f\rangle$ of the electron, according to the relation:

$$W(E) \propto |\langle s|\mathbf{E} \cdot \mathbf{P}|f\rangle|^2 \phi(E_f).$$

In this equation, $\mathbf{E}$ is the electric field vector of the X-ray and $\mathbf{P}$ the momentum operator, and $\phi(E_f)$ is the density of state at the final state $|f\rangle$.

The “extended” energy regime of the final state of the electron refers to where $E_f$ is sufficiently above the Fermi level; therefore in this regime the density of state $\phi(E_f)$ is effectively constant. In such case, $W(E)$ depends solely on the matrix $\langle s|\mathbf{E} \cdot \mathbf{P}|f\rangle$.

The interference between an outgoing photoelectron wave from the absorbing atom and a backscattered wave from a neighboring atom, shown in Fig. 3, causes a modulation in the absorption probability $W(E)$. The oscillatory part of the absorption function can be expressed as the sum of the interferences from backscattering waves due to all neighboring atoms:

$$\chi(k) = \frac{\mu(k) - \mu_0}{\mu_0} = -\sum_i A_i(k) \sin[2k R_i + \phi_i(k)]$$

(13)

where $\mu_0$ is the absorption coefficient for an free atom, the sum is over the neighboring atoms $i$ at a radial distance $R_i$ from the absorbing atom. The photoelectron wavenumber $k$ is related to the photon energy $E$ with

$$E - E_0 = \frac{\hbar^2 k^2}{2m},$$

(14)

where $E_0$ is the threshold energy of the electron. The amplitude of the oscillation $A_i(k)$ in Eq. 13 can be written as

$$A_i(k) = \frac{N_i}{k R_i^2} F_i(k) \exp(-2k^2 \langle \sigma^2 \rangle) \exp(-2R_i/\lambda_i)$$

(15)

In this equation, $F_i(k)$ is the backscattering amplitude function of the $i$th neighboring atom, $R_i$ and $N_i$ are, respectively, the radial distance and coordination
number of the $i$th shell atoms, $\langle \sigma_i^2 \rangle$ is the mean square vibrational amplitude of the $i$th shell atoms in the radial direction, and $\lambda_i$ is the inelastic mean free path of the photoelectron. The first exponential function is the Debye-Waller factor; it takes into account the vibration of the scattering atoms relative to the absorbing atom. The second exponential function takes into account the inelastic dissipation of $F_i(k)$. Eq. 13, with $A_i(k)$ explicitly given in Eq. 15, is called the EXAFS equation.

In SEXAFS, backscattering from atoms whose positional vectors are in the direction of the polarization of the incident X-rays are preferentially probed. The effective coordination number $N_i^*$ is proportional to the square of the directional cosine of the angle $\alpha_{ij}$ between the $j$-th atom’s positional vector and the photon
polarization vector, at the absorbing atom site,

\[ N_i^* = 3 \sum_i N_i \cos^2 \alpha_{ij}. \]  \hspace{1cm} (16)

For isotropic systems such as crystals of cubic symmetry or polycrystalline materials, \( N^* = N \). For calcite, since each coordination shell of the cation site has an octahedral symmetry that is nearly cubic (see Section 3.1), the cation site of calcite can be considered isotropic.

The polarization dependence of the effective coordination number \( N^* \) is an essential feature of the SEXAFS technique. It allows one to selectively probe a particular bond in a crystal, by aligning the polarization vector of the incident X-rays along the bond direction [27].

If considering only the backscattering from the first neighbor atomic shell, \( i = 1 \), Eq. 13 and Eq. 15 can be combined and reduced to

\[ \chi(k) = \frac{N}{kR^2} F(k) \sin[2kR + \phi(k)] \exp(-2k^2 \langle \sigma^2 \rangle) \exp(-2R/\lambda) \]  \hspace{1cm} (17)

where the parameters, \( N, R, \) and \( \langle \sigma^2 \rangle \), \( F(k) \) all refer to the first neighbor quantities. (We will drop the bracket for \( \sigma^2 \) in subsequent chapters.)

The first-shell component is usually the most dominant and often most reliable part of the EXAFS raw data. It can be filtered out in real space from the remaining components, and analyzed with Eq. 17 in comparison with the corresponding first-shell data of a suitable standard compound, whose \( N, R, \) and possibly \( \langle \sigma^2 \rangle \), are known from its structure.

### 2.1.3 The combination of XSW and SEXAFS as a tool for surface studies

The combination of the XSW triangulation and the SEXAFS techniques allows one to simultaneously obtain two complementary pieces of structural information, both
with a precision approaching ±0.01 Å. From the XSW triangulation, we obtain the three-dimensional lattice site of the adsorbate atom relative to the substrate crystal. From SEXAFS, we obtain the coordination structure and distances of local host lattice atoms relative to the adsorbate atom. The combined information gives an unambiguous structure of the surface adsorbate site. These combined techniques are particularly valuable for the study of impurity structure at an ionic surface and within an ionic crystal. This is because the strain field of an impurity defect in an ionic crystal is often the size of many unit cells, so one cannot infer the impurity’s lattice site from its local bond distance, or vice versa, as one occasionally does when dealing with covalently bonded structures. Previously, the back-reflection XSW technique has been used with the SEXAFS technique to study surface relaxation [28]. The work described in Chapters 4 and 5 of this thesis represents the first extensive applications of the combined techniques of the Bragg-reflection XSW triangulation and SEXAFS.

### 2.2 Experimental setup

Most of the XSW and SEXAFS studies included in this thesis were performed at the X-ray beamline X15A at the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory. A portion of one XSW study was also carried out at beamline 12ID-D at the Advanced Photon Source (APS), at Argonne National Laboratory. One SEXAFS study was done at beamline 12BM-B at APS.

In this section the general experimental setup at beamline X15A at NSLS is described. A schematic drawing of the main components and arrangement at beamline X15A is shown in Fig. 4. The white X-ray beam from the synchrotron is monochromated inside the experimental hutch by a double-crystal monochromator. Usually either Si or Ge crystal mirrors are used. The monochromator serves both
beam monochromation and collimation. For the latter purpose, a monochromator crystal with a suitable surface miscut is installed as the first crystal, so that the X-ray beam reflected from this crystal has a reduced angular divergence.

A pair of ion chambers (not shown in Fig. 4) are located respectively before and after the incident beam slit. The current in the first ion chamber measures the output intensity of the monochromator; the current in the second ion chamber is used to monitor the incident beam intensity.

The sample stage is a four-circle diffractometer. Desired sample environments, such as helium gas circulation and liquid cell for in situ measurements, can be mounted on the sample stage. The X-rays reflectivity $R(\theta)$ in Eq. 8 is recorded by a Si photodiode detector mounted on the 2θ-circle of the diffractometer. The fluorescence X-ray spectrum from the sample is recorded by a Si(Li) solid-state detector placed near the sample surface. A slit controls the take-off angle of the fluorescence signal from the sample.

Data acquisition with a PC with LINUX operating system was computer controlled by the commercial software SPEC (Certified Scientific Software). For XSW experiments, an “in-house” macro package developed by T.-I. Lee, Northwestern University, was used for collecting fluorescence spectra at each angular step of the rocking curve. Both EXAFS and XSW were done by energy scans with the monochromated X-rays. In XSW, energy scans of the incident beam are equivalent to angular scans of the sample, since $\Delta E \propto -\Delta \theta / \sin^2 \theta_B$ from Bragg’s law.

For XSW triangulation with calcite lattices, the normal (10\(\overline{4}\)) lattice planes and two off-normal, non-collinear lattice planes are used. Fig. 5, as an example, shows the relative geometry of the (10\(\overline{4}\)), the (0006), and the (02\(\overline{2}\)4) lattice planes to the surface.
Figure 4: A diagram showing the arrangement of the main components for XSW measurements at the X-ray beamline X15A, at the National Synchrotron Light Source.

### 2.3 Preparation of impurity ion adsorbate surfaces

The samples of impurity ions on the calcite (10\(\overline{4}\)) surface examined in this work were prepared by reaction with an aqueous phase. Large single crystals of naturally-grown calcite originated from Russia and Brazil were cut into suitable sizes, typically 8 mm \(\times\) 8 mm, with the face parallel to the (10\(\overline{4}\)) plane. A freshly cleaved (10\(\overline{4}\)) surface is immersed in the adsorption solution where ion incorporation occurs. The drawing in Fig. 6 describes the adsorption process.

The solution is a de-ionized, CaCO\(_3\)-saturated water solution maintained at room temperature and mild alkaline acidity (typically pH 8–9). The aqueous ion to be incorporated at the calcite surface is added to the solution by dissolving a trace amount of an inorganic salt of that ion. The concentration of the ion in the solution is usually between 10 and 500 \(\mu\)M. In the case of metal cations, the solution also
Figure 5: The relative geometry of the calcite (10\(\overline{1}4\)) surface and the (a) the (10\(\overline{1}4\)), (0006) and, (b) the (02\(\overline{2}4\)) lattice planes. Note that with the choice of the origin at the C atom lattice site, the Ca coherent positions are \(P_{10\overline{1}4} = 0\) or 1, \(P_{0006} = 0.5\), and \(P_{02\overline{2}4} = 0\).
Figure 6: A schematic drawing showing the adsorption of aqueous ions at the water-calcite interface.
contained an excess amount of ethylenediaminetetraacetatic acid (EDTA), which was used to prevent formation of separate solid adsorbate phases. The reaction time ranged from minutes to hours, for different cases. After adsorption, the samples were extracted by removing the solution above the surface with a jet of nitrogen gas. The sample surfaces were maintained in a helium atmosphere during X-ray measurements.
Chapter 3

Calcite crystal structure;
Structure of the cleavage surface;
Structure of a bulk impurity

3.1 Calcite crystal structure

Calcite has the rhombohedral (hexagonal) structure [29]. Its primitive rhombohedral unit cell contains two CaCO$_3$ molecules; its conventional hexagonal non-primitive cell contains six CaCO$_3$ molecules. The hexagonal cell parameters are: $a = b = 4.989$ Å, $c = 17.061$ Å [30]. The hexagonal unit cell is shown in Fig. 7. In calcite, each Ca$^{2+}$ ion is octahedrally coordinated to six neighboring CO$_3^{2-}$ molecular groups. The coordinating atoms are the O atoms. The CaO$_6$ octahedron is nearly cubic in symmetry; the only minor distortion is its slight elongation in the [0001] direction, such that the ratio of the longer to shorter edges of the octahedron is 1.04. The CaO$_6$ octahedron is shown in Fig. 8; its orientation relative to the lattice can be identified by recognizing that the normal of the CO$_3^{2-}$ plane is in the [0001] direction. The calcite structure can be considered as a distorted form of the NaCl structure. It can be generated from the NaCl structure by replacing
Figure 7: The hexagonal unit cell of calcite.

$Na^+ \text{ with } Ca^{2+}$, replacing $Cl^-$ with $CO_3^{2-}$, and compressing the resultant structure along the $CaCO_3\ [0001]$ axis. This compression along the $[0001]$ axis can be imagined as equivalent to an expansion in the lateral direction of the $CO_3^{2-}$ axis, which occurs in order to spatially accommodate the $O$ atoms in the $CO_3^{2-}$ group.
3.2 Surface impurity structure considered as the structure of a bulk impurity located at a surface site: A hypothesis

Given the background of the currently poor existing knowledge in the structure of ion incorporation at calcite surfaces, in approaching the problem of an isolated surface impurity ion, it is helpful to adopt an intuitive hypothesis as a guide for interpreting experimental results. As a starting point we put forward the hypothesis that the surface impurity structure can be considered as the superposition of two structures: (1) The structure of an isolated substitutional impurity in the bulk calcite lattice; and (2) the structure of a cation site at the clean calcite (10\(\overline{4}\)) surface. The validity of this hypothesis is to be tested, and its contents refined, by experimental results.

To proceed according to this approach, it is logical to first consider the two structures—a substitutional impurity in the bulk and the calcite (10\(\overline{4}\)) surface sites—separately. This will lay down the foundation for later interpreting the
integrated structure of an impurity at the surface. Therefore, we present in this chapter the structure of a clean calcite (10\bar{4}4) surface, and the structure of a substitutional cation in bulk calcite. For the former we mainly rely on results in the recent literature; for the latter we describe results from the XSW and EXAFS study of the bulk impurity system of Mn$^{2+}$:CaCO$_3$.

### 3.3 Structure of the calcite cleavage surface

The calcite (10\bar{4}4) cleavage surface is equivalent to the type I lattice in the Tasker classification [31]; it is an electrostatically compensated surface made up of alternating Ca$^{2+}$ cations and CO$_3^{2-}$ anions in stoichiometric proportion. The molecular arrangement in the (10\bar{4}4) surface plane viewed from the top and the side are shown in Figs. 9 and 10, respectively. The primitive two-dimensional unit cell in the (10\bar{4}4) lattice plane contains two CaCO$_3$ molecules; the rectangular cell dimensions are $a = 4.9$ Å and $b = 8.1$ Å, as indicated with the dashed-line rectangle in Fig. 9. The planar triangular CO$_3$ groups are oriented such that their three-fold axis is pointing at 45° away from the (10\bar{4}4) plane normal, as shown in Fig. 10. The three O atoms in the CO$_3$ group are located, respectively, at 0.8 Å below, in, and at 0.8 Å above the (10\bar{4}4) plane. Each of the two CaO$_6$ octahedrons (marked with solid lines in Fig. 9) is oriented with one of its axes pointing at 20° away from the (10\bar{4}4) plane normal.

A number of recent atomic-resolution experimental and simulation studies have been performed to characterize the structure of a clean calcite (10\bar{4}4) surface, in both the in-plane and the surface normal directions. The truncated (10\bar{4}4) surface is found to be stable in air, in CaCO$_3$-saturated alkaline aqueous environment, and in ultrahigh vacuum [32, 33]. For the in-plane surface structure, an X-ray crystal truncation rod (CTR) study [33] in water under alkaline conditions shows that
the surface is made up of atomically-flat terraces of characteristic sizes of 100 Å across; these terraces are separated by monolayer-high steps (3.04 Å). The surface molecules in the terrace region are well-ordered, showing a mean roughness of 0.35 ± 0.1 Å in the normal direction. Molecular static simulation indicates negligible reconstruction in the surface layer [34]. The lateral structure of the surface has been studied with atomic-resolution AFM. The surface unit cell dimensions were measured according to images originated from the top oxygen atoms of the surface CO$_3$ group. These dimensions have nearly identical values as in the bulk (10\(\overline{1}4\)) plane, with parameters \(a = 8.1\) Å, and \(b = 5.0\) Å according to Ref. [35], and \(a = 8.1 \pm 0.5\) Å, and \(b = 4.9 \pm 0.3\) Å according to Ref. [36].

In the surface normal direction, existing X-ray reflectivity results show that the near surface layers of the (10\(\overline{1}4\)) planes roughly maintain their bulk-extrapolated position [33, 37]. This is basically consistent with the general observation that
inter-plane relaxation normal to the surface is very limited in a type I ionic surface [3].

Within the top molecular layer, however, structural changes may occur to minimize surface energy. In a binary surface, such as NaCl(001), rumpling may occur to minimize surface energy [1]. In the calcite (10\(\overline{4}\)4) surface, however, the options for energy minimization by structural change also include re-orientation of the carbonate molecules. The bulk-terminated (10\(\overline{4}\)4) surface, with the O atom extending above the plane, is probably unstable. Since the cohesive energy of an ionic surface is mainly coulombic, energy can be minimized by minimizing nearest neighbor distance among ions. As a result, the O atom above the surface may be brought toward the surface to reduce the Ca-O distance, either by bending or re-orienting the carbonate molecule. A recent X-ray reflectivity experiment [38] finds results consistent with the re-orientation of the carbonate groups.

3.4 Structure of a bulk impurity: Manganese in calcite

The structure of a substitutional cation impurity in bulk calcite can be fully described by the cation lattice position and the structure of its neighboring \(\text{CO}_3^{2-}\) groups. All this information can be obtained with a combined XSW and EXAFS study. The XSW coherent position for the Mn\(^{2+}\), along with a symmetry argument, give the mean lattice site of Mn\(^{2+}\). The spatial distribution of Mn\(^{2+}\) about its mean position can be estimated through an analysis of the XSW coherent fractions. From EXAFS, the radial distance and number of the coordinating O atoms provide information about the relaxation of the surrounding \(\text{CO}_3^{2-}\) groups at the Mn\(^{2+}\) site.
Figure 11: Reflectivity $R$, and Mn and Ca $K\alpha$ fluorescence yields vs. incident angle of X-rays for the calcite (1014) Bragg reflection. The solid curves are best theoretical fits of Eq. 18 to the data.
The sample was a natural calcite crystal that contained 332 ppm of Mn$^{2+}$ in the bulk. The XSW measurements for Mn$^{2+}$ and Ca$^{2+}$ in calcite were made with respect to the (10T4) Bragg reflection with incident X-rays of 9.00 keV; the results are shown in Fig. 11. A low-angle fluorescence slit was used to limit fluorescence signal attenuation. The Mn coherent position is determined to be $P_{\text{Mn}} = 0.00 \pm 0.01$, and coherent fraction $f_{\text{Mn}} = 0.79 \pm 0.01$, and Ca coherent position $P_{\text{Ca}} = 0.00 \pm 0.01$, and coherent fraction $f_{\text{Ca}} = 0.79 \pm 0.01$, according to a best fit to the data with the equation

$$Y(\theta) = [1 + R(\theta) + 2\sqrt{R(\theta)f_H \cos(\phi(\theta) - 2\pi P_H)}]Z(\theta). \quad (18)$$

This equation is simply Eq. 8 (page 8) multiplied with the effective thickness $Z(\theta)$, in order to take into account the attenuation in the primary beam and in the fluorescence signal [24, 39], since we are now dealing with an impurity in the crystal bulk. Note that from calcite crystal structure, we know $P_{\text{Ca}} = 0$.

We define the relative coherent position and fraction,

$$P_r = P_{\text{Mn}} - P_{\text{Ca}} \quad (19)$$
$$f_r = \frac{f_{\text{Mn}}}{f_{\text{Ca}}} \quad (20)$$

Substituting the experimentally determined coherent positions and fractions into these Eqs., we obtain $P_r = 0.00 \pm 0.02$ and $f_r = 1.00 \pm 0.02$. The structural interpretations of these quantities are: From $P_r = 0.00$, we know that Mn$^{2+}$ is located at the Ca$^{2+}$ site; this confirms an earlier XSW result [24]. From $f_r = 1.00$, we know that the spatial distribution of Mn$^{2+}$ about its mean position in the [10T4] direction is the same as that of Ca$^{2+}$, i.e., this distribution is limited to thermal vibration, and Mn$^{2+}$ is therefore located on-center at the Ca$^{2+}$ site.

Since the calcite structure has a three-fold symmetry about the [0001] axis, we know that the Mn$^{2+}$ position relative to the (1T04) and the (0T14) lattice planes
is the same as relative the (1014) lattice. But since these three lattice directions are mutually non-collinear in space, we conclude that Mn$^{2+}$ is located on-center at the Ca$^{2+}$ site in the three-dimensional lattice.

The EXAFS scan on a powder Mn$^{2+}$-in-calcite sample was performed over the Mn K absorption edge, in the energy range 6,490–7,090 eV. Fig. 12 shows the amplitude of the Fourier transform of the $k^2$-weighted EXAFS function after background subtraction; it is compared to that of a MnCO$_3$ standard compound. MnCO$_3$ has the calcite structure. The correspondence of the peaks between the sample and the standard qualitatively indicates that the ordering of the neighboring CO$_3^{2-}$ is preserved. The integrated area of the first peak, corresponding to the Mn-O first coordination shell, are approximately equal for both spectra; this means that Mn$^{2+}$ in calcite has the same coordination number as it does in MnCO$_3$, i.e., it is octahedrally coordinated. Fig. 13 shows the filtered Mn-O first-shell EXAFS function, as $\chi k^2$, in $k$-space. The theoretical fit of Eq. 17 to the filtered data was performed with the first-neighbor coordination number $N$ fixed at 6 (for octahedral coordination). From the best fit, we find that the first-neighbor Mn-O distance is $R = 2.18 \pm 0.01$ Å. Comparing to the Mn-O distance in MnCO$_3$, $R = 2.19$ Å [30], and the Ca-O distance in CaCO$_3$ of $R = 2.36$ Å, we see that the surrounding CO$_3^{2-}$ groups in calcite relax toward the smaller Mn$^{2+}$ until the first-neighbor Mn-O distance reaches its value in MnCO$_3$. We refer to this as conservation of nearest-neighbor bond distance in the bulk lattice.

The conservation of nearest-neighbor cation-oxygen bond distance was also observed in the impurity systems of Co$^{2+}$ and Zn$^{2+}$ in calcite, respectively, according to EXAFS studies [40]. For Sr$^{2+}$ in calcite, however, the nearest neighbor Sr-O distance was determined to be $2.58 \pm 0.03$ Å [41], whereas in SrCO$_3$, the Sr-O distance is 2.63 Å.
Figure 12: The amplitudes of Fourier transform of the $k^2$-weighted EXAFS functions for the Mn:CaCO$_3$ data, and for the MnCO$_3$ standard compound, before phase correction.

Figure 13: The filtered Mn-O first-shell EXAFS data, as $\chi k^2$, after background subtraction and conversion to $k$-space, for Mn:CaCO$_3$ (solid line), and the best theoretical fit (dashed-line).
Chapter 4

Surface incorporation structure of calcite-type cations: Zinc on calcite

4.1 Introduction

Zinc (II) is among the class of divalent cations whose anhydrous carbonates are of the calcite structure. These carbonates are listed in Table 1; we shall refer to these cations as calcite-type cations. The Ca$^{2+}$ ion is the largest of the calcite-type cations. Because of the isomorphicity of their carbonates, the incorporation of a calcite-type cation at the calcite surface offers the simplest case of cation surface incorporation. It has been shown that Zn$^{2+}$ impurity in bulk calcite is octahedrally coordinated [40]. For Zn$^{2+}$ at the calcite surface, its coordination environment is likely to be the same as in ZnCO$_3$ or in bulk calcite. The only difference between Zn$^{2+}$ and Ca$^{2+}$ is their ionic sizes. In such a way, Zn$^{2+}$ is considered an ideal probe, since the structure it induces at the calcite surface is solely the effect of difference in ionic size.
Table 1: Cation radii and the first-neighbor cation-oxygen distances for carbonates of the calcite structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cation radius (Å)</th>
<th>A-O distance (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCO₃</td>
<td>0.65</td>
<td>2.1018</td>
<td>[30]</td>
</tr>
<tr>
<td>CoCO₃</td>
<td>0.72</td>
<td>2.110</td>
<td>[42]</td>
</tr>
<tr>
<td>NiCO₃</td>
<td>0.72</td>
<td>2.076</td>
<td>[42]</td>
</tr>
<tr>
<td>ZnCO₃</td>
<td>0.74</td>
<td>2.1107</td>
<td>[30]</td>
</tr>
<tr>
<td>MnCO₃</td>
<td>0.80</td>
<td>2.1900</td>
<td>[30]</td>
</tr>
<tr>
<td>CdCO₃</td>
<td>0.97</td>
<td>2.288</td>
<td>[30]</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.99</td>
<td>2.3598</td>
<td>[30]</td>
</tr>
</tbody>
</table>

4.2 Experimental

Zn²⁺ ions from a dilute ([Zn²⁺] = 0.63 mM) aqueous solution were adsorbed at a freshly-cleaved natural calcite (1014) surface. The process was described in Section 2.3. The reaction time ranged from 4 to 20 minutes for various samples.

Both XSW and SEXAFS experiments were carried out at NSLS, at beamline X15A, in August, 1996. The XSW triangulation experiments were performed using the (1014) normal lattice planes, and the (0006) and (0224) off-normal lattice planes. The incident X-ray was monochromated to 11.00 keV. The monochromator crystals were Si(111) for the (1014) and (0006) measurements, and Si(022) for the (0224) measurement.

For the SEXAFS experiment, the X-rays were monochromated with a pair of symmetric Si(111) crystals, and scanned over the Zn K-edge over an energy range of 9,600–10,100 eV. The beam was incident on the sample surface at a glancing angle of approximately 10°, so that the σ-polarized E-field preferentially sampled bonding that was within the (1014) lattice plane. Data were collected in the fluorescence mode by monitoring the Zn Kα peak in the fluorescence spectrum.
A thin Ho$_2$O$_3$ foil between the sample and the fluorescence detector was used to preferentially attenuate Compton and elastically scattered X-rays. The X-ray fluorescence emission from the sample surface was controlled by a low-angle slit placed between the sample and the detector to enhances the surface sensitivity of the fluorescence signal.

4.3 Results

4.3.1 XSW analysis

The XSW data were analyzed with the program SWAN, described in Appendix A. The experimentally measured reflectivity $R(\theta)$ and Zn $K\alpha$ fluorescence yield $Y(\theta)$ for the (10\(\overline{1}4\)), (0006) and (02\(\overline{2}4\)) reflections for a typical sample are presented in Fig. 14, along with the best-fit curves based on Eq. 8 to these data. The corresponding coherent positions $P_H$ and coherent fractions $f_H$ obtained from the best-fits are given in the figure.

This sample had a total Zn adsorbate coverage of $\Theta_T = 0.10 \pm 0.02$ ML (1 ML = 5.04 $\times$ 10$^{14}$ atoms/cm$^2$), as measured against a Ga-implanted silicon standard crystal that had been calibrated by Rutherford backscattering spectroscopy. Using the coherent fraction for the (10\(\overline{1}4\)) reflection, $f_{10\overline{1}4} = 0.77$, the coherent coverage $\Theta_c$ can be estimated with the relation

$$\Theta_c = f_H \times \Theta_T$$

(21)

to be $\Theta_c = 0.09 \pm 0.02$ ML. The 0.02 ML uncertainty was shown by a separate XSW scan on a control calcite substrate to be due to background signals not originating from the sample surface or substrate. Independently, chemical analysis of the calcite substrate showed that it contained < 3 ppm of Zn as bulk impurities.
Figure 14: Reflectivity $R$ and Zn $K\alpha$ fluorescence yield $Y$ vs. incident angle of X-rays for the calcite (a) (1014), (b) (0006) and (c) (0224) Bragg reflections. The solid lines are the best fits of Eq. 8 to the data; the best-fit parameters and their uncertainties are inserted in the figure.
For the Zn-adsorbed samples, although the Zn fluorescence signal in principle could have originated from anywhere within the off-Bragg extinction depth of 14.6 μm of the Zn Kα X-ray, careful experiments for the (10 14) reflection with fluorescence slit set at various take-off angles (from 1 to a few degrees) from the sample surface gave identical results in coherent position. This indicates that the Zn signal was from the surface. Furthermore, the best fits for Y(θ) were only obtained with the assumption that the Zn signal was from the surface.

The XSW measurements were done on seven adsorption surfaces prepared with different adsorption reaction time periods, from 4 to 20 minutes. The $P_H$ values for all reacted surfaces remained unchanged within experimental uncertainty; the average $P_{10\overline{1}4}$ over all samples is 0.87, with a standard deviation of 0.008. The corresponding average $f_{10\overline{1}4}$ over these samples is 0.61, with a standard deviation of 0.13. The average $\Theta_T$ over all samples is 0.13 ML, with a standard deviation of 0.04 ML. These data suggest that the adsorption site is constant, while $f_{10\overline{1}4}$ fluctuates slightly due to variations in substrate surface quality and difference in sample preparation details.

4.3.2 EXAFS analysis

SEXAFS data analysis was performed using the MacXAFS software package [43] according to standard procedures [44]. After background subtraction and conversion to the angular momentum ($k$) space, the $k^2$-weighted experimental EXAFS $\chi(k)$ function, shown in Fig. 15(a), displays a dominant first-shell feature that is of the same frequency as the first-shell component in the ZnCO$_3$ standard compound, shown in Fig. 15(b). The $\chi(k)k^2$ EXAFS function was Fourier-transformed into the real ($R$) space over the range $2.81 \leq k \leq 10.48\text{Å}^{-1}$, with the modified Hann-ning windows of $0.4\text{Å}^{-1}$. The amplitudes of Fourier transforms for the Zn/CaCO$_3$
sample and for the ZnCO$_3$ standard compound are again compared, in Fig. 16, before phase correction. In this figure, the peaks represent the atomic shells at radial distance $R$ from the Zn central atom. The correspondence of peak positions indicates that the Zn atom has an atomic environment at the calcite surface layer that is similar to that in the ZnCO$_3$ structure. This is to be taken as evidence that the Zn ion is incorporated at the Ca$^{2+}$ site of the calcite lattice.

Quantitative analysis is performed for the first shell. The first-shell contribution of the Fourier transformed data from both the sample and the ZnCO$_3$ standard were filtered in the range $1.09 \leq R \leq 2.16$ Å with Hanning windows of 0.202 Å. The filtered data from the sample is shown as a solid line in Fig. 15(c). This data was fit in phase and amplitude with respect to that for the ZnCO$_3$ standard, according to Eq. 17 (page 16).

The best-fit parameters are obtained by minimizing the normalized $\chi^2$ value. This value is defined to be the difference in phase and amplitude of the filtered data of the experimental sample data and computer-generated data. For the transform range $2.81 \leq k \leq 10.48$ Å$^{-1}$ used in this analysis, the maximum number of fit parameters allowed to vary at one time is more than 5, according to Ref. [45]. In addition to an energy shift variable ($\Delta E$), three parameters were allowed to vary while determining the best fit to the data; the Zn-O radial distance, $R$, the coordination number, $N$, and the mean-square relative displacements due to static disorder and thermal vibration, $\sigma^2$. The best-fit values for these parameters are: $\Delta E = 0.65$ eV, $R = 2.11 \pm 0.01$ Å, $N = 3.81 \pm 0.67$ and $\Delta \sigma^2 = 0.0013 \pm 0.001$ Å$^2$. The coordination number value quoted here has been normalized to account for a maximum allowed in-plane Zn-O coordination number of 4. The $\Delta \sigma^2$ value represents a difference relative to the ZnCO$_3$ standard. Additionally, the uncertainties quoted in the best-fit values for $R$ and $\Delta \sigma^2$ represent an increase
Figure 15: EXAFS spectra, as $\chi k^2$, after background subtraction and conversion to $k$-space, for (a) the in-plane Zn/CaCO$_3$ sample data, (b) the ZnCO$_3$ standard compound, and (c) the Fourier-filtered Zn-O first-shell component of the Zn/CaCO$_3$ data (solid line), and the best fit (dash line) to the filtered first-shell data.
Figure 16: The amplitudes of Fourier transform of the $k^2$-weighted EXAFS functions for (a) the in-plane Zn/CaCO$_3$ data and (b) the ZnCO$_3$ standard compound, before phase correction.
in the $\chi^2$ value from approximately 0.5 to 2 as each fitting variable was stepped across its best-fit value while allowing the remaining fit variables to float. The uncertainty for $N$ is estimated according to Ref. [44]. The $\Delta E$ value never varied by more than 0.15 eV from the best-fit value of 0.65 eV. The best fit to the Fourier filtered data is shown as a dash line in Fig. 15(c).

4.4 Discussion

In this section we present a structural interpretation of the XSW and SEXAFS results. First, by comparing the Zn coherent positions to those for Ca and considering the number of nearest-neighbor coordinated O atoms, we establish that Zn$^{2+}$ substitutes for Ca$^{2+}$ on the surface lattice plane. We then describe the local in-plane relaxation of the surrounding O atoms by considering the first nearest-neighbor Zn-O distance. Finally, from the Zn coherent positions measured with respect to the three non-coplanar lattice planes, we determine the exact lattice sites of the Zn$^{2+}$ adsorbate ions. A quantitative structural model of the Zn$^{2+}$ ions incorporated in the calcite (1014) surface that is consistent with the experimental observations is then presented.

4.4.1 Displaced substitution of Zn at the Ca site

The $P_H$ value for each of the two non-equivalent ideal Ca sites with respect to the (1014), (0006), and (0224) lattice planes are 1, 0.5, and 1, respectively. The corresponding measured $P_H$ values for Zn, of 0.87, 0.45, and 0.85, indicate that Zn$^{2+}$ is located within the CaO$_6$ octahedron, slightly displaced from its center where the Ca$^{2+}$ would be located. This leads to the conclusion that Zn$^{2+}$ substitutes for Ca$^{2+}$. This is, to our knowledge, the first direct structural evidence that Zn$^{2+}$
substitutes for Ca$^{2+}$ upon adsorption on calcite surface from solution; previous assertions of this generally accepted notion have been based on indirect inference from solution ion concentration changes from before to after adsorption, e.g. [46].

To resolve whether the Zn$^{2+}$ ion is located above the surface or incorporated in the surface layer, we examine the SEXAFS Zn-O nearest-neighbor coordination number. The coordination number $N$ for a surface cation site is expected to be approximately 4, and the measured Zn-O coordination number of 3.81 ± 0.67 indicates that Zn$^{2+}$ is indeed incorporated in the surface layer. If the Zn$^{2+}$ adsorbate were located above the surface, it would be identified by a set of EXAFS $R$ and $N$ values different from that measured. In which case, if the Zn$^{2+}$ ion is not ligandized, the value of $N$ would approach to zero; if the Zn$^{2+}$ ion is ligandized, the value of $R$ would be that of the characteristic amorphous Zn-O bond length (i.e., 1.8 to 1.9 Å), which is noticeably smaller than that measured (2.11 Å). Furthermore, the correspondence of the atomic shells beyond the nearest neighbor clearly seen in Fig. 16 is also a direct evidence that the Zn$^{2+}$ ion was incorporated in the surface layer.

4.4.2 In-plane relaxations of neighboring carbonates: Conservation of the Zn-O distance

Since the size of the Zn$^{2+}$ ion is only about three quarters that of Ca$^{2+}$, an inward relaxation of its nearest-neighbor CO$^{2-}_3$ groups at the incorporation site of the surface lattice may occur. This was indeed observed in the Zn-O nearest neighbor distance, of 2.11 ± 0.01Å. Since the Ca-O nearest-neighbor distance in the ideal calcite lattice is 2.36Å, an inward relaxation of 0.25Å occurred. Note that this measured Zn-O nearest-neighbor distance is within uncertainty equal to the Zn-O distance in ZnCO$_3$, of 2.111Å Ref. [30]. That is, the nearest-neighbor O atoms in
Table 2: Local in-plane structure for Zn incorporated at the calcite (10\(\bar{1}4\)) surface according to SEXAFS measurement, compared with the local Zn environment in the bulk CaCO\(_3\) lattice as an impurity, in the ZnCO\(_3\) crystal, and the local Ca environment in the CaCO\(_3\) crystal.

<table>
<thead>
<tr>
<th></th>
<th>A-O distance (Å)</th>
<th>(N)</th>
<th>(\Delta\sigma^2) (Å(^2))</th>
<th>(\chi^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn/CaCO(_3) (0.09 ML)</td>
<td>2.10 ± 0.01</td>
<td>3.81 ± 1</td>
<td>0.006</td>
<td>0.00016</td>
</tr>
<tr>
<td>Zn:CaCO(_3) (250 ppm) [40]</td>
<td>2.12 ± 0.02</td>
<td>6.80 ± 1</td>
<td>0.003</td>
<td>-</td>
</tr>
<tr>
<td>ZnCO(_3) crystal</td>
<td>2.1107</td>
<td>6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaCO(_3) crystal</td>
<td>2.3598</td>
<td>6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

the adjacent CO\(_3^{2-}\) groups have relaxed fully so that Zn and O are ‘in contact’. This suggests that, at the (10\(\bar{1}4\)) surface, the attractive electrostatic interaction between Zn\(^{2+}\) and its nearest-neighbor O atoms is the driving force of this local relaxation.

4.4.3 Vertical relaxation of Zn ion

The relaxation of the Zn\(^{2+}\) ion in the out-of-plane direction reflects the effect of surface truncation. The dominance of the nearest-neighbor electrostatic interaction in the in-plane structure considered above suggests that the out-of-plane relaxation may be along the Zn-O direction as well—between the surface Zn and the O atom in the second layer. We may construct a hypothetical surface lattice model for the two sites of the surface Zn\(^{2+}\) ions, assuming they relax in the out-of-plane nearest-neighbor Zn-O direction by such a distance that their positions projected in the (10\(\bar{1}4\)) lattice normal agree with that XSW-measured. We then verify the validity of this model by checking its quantitative consistency in the Zn\(^{2+}\) positions with respect to the off-normal (0006) and (02\(\bar{2}4\)) planes with that from the XSW measurements. The model is shown in Fig. 17. The quantitative positions \(h_H\) of the Zn\(^{2+}\) ions above the lattice plane \(H\) at the two generally non-equivalent
Table 3: Position of the Zn adsorbate ion $h_H$ above each lattice plane $H$ from the XSW measurements and according to the structure model described in the text. Units are Å.

<table>
<thead>
<tr>
<th>$H$</th>
<th>$d_H$</th>
<th>$h_H$ Experimental</th>
<th>$h_H$ Site 1</th>
<th>$h_H$ Site 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1014)</td>
<td>3.04</td>
<td>2.64 ± 0.03</td>
<td>2.64 ± 0.03</td>
<td>2.64 ± 0.03</td>
</tr>
<tr>
<td>(0006)</td>
<td>2.84</td>
<td>1.28 ± 0.14</td>
<td>1.20 ± 0.04</td>
<td>1.20 ± 0.04</td>
</tr>
<tr>
<td>(0221)</td>
<td>1.93</td>
<td>1.64 ± 0.06</td>
<td>1.75 ± 0.05</td>
<td>1.56 ± 0.05</td>
</tr>
</tbody>
</table>

cation sites in a surface unit cell derived from this model are listed in Table 3, and compared to $h_H$ derived from the XSW measurements with the relation

$$h_H = d_H \times P_H.$$  \hspace{1cm} (22)

The agreement between the values from the model and from the XSW experiments indicate that the model is valid within uncertainties. Furthermore, if we assume the oxygen atoms coordinated to the Zn$^{2+}$ ion from the second-layer CO$_3^{2-}$ are bulk-like in position, the Zn-O nearest-neighbor distance in the out-of-plane direction is deduced to be 1.95 Å from the model. This distance is comparable to the Zn-O bond distance found in binary compounds, e.g., ZnO. The shorter Zn-O bond distance in the out-of-plane direction compared to that in plane is not unexpected, and is best explained by the bonding asymmetry at the surface.

It is noteworthy that the extent of the in-plane relaxation of the nearest-neighbor O atoms towards Zn$^{2+}$ at the calcite (1014) surface is equivalent within uncertainty to that occurring at an isolated Zn$^{2+}$ impurity site in bulk calcite, where the Zn-O distance is 2.12 ± 0.02 Å Ref. [40]. The significance of this comparison between the surface and the bulk impurity structure is that it implies that the calcite (1014) surface, in addition to being structurally bulk-like, may also possess bulk-like parameters in its interaction potentials, at least at the cation sites.
Symbols:

- Zn$^{2+}$
- Ca$^{2+}$
- CO$_3^{2-}$

Figure 17: A model describing the lattice sites of the Zn ions incorporated at the calcite (10T4) surface. The Zn lattice sites in the model are constructed assuming that the ions are in the surface monolayer, and their out-of-plane relaxation is along the direction of the nearest-neighbor Zn-O bond between the first and second molecular layers. (a) Side view of the adsorption surface containing the (10T4) and the (0006) planes. (b) Side view containing the (10T4) and the (0224) planes.
Table 4: XSW coherent fractions and positions of Co and Ca for the Co-on-CaCO₃ sample.

<table>
<thead>
<tr>
<th></th>
<th>Co²⁺</th>
<th>Ca²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f</td>
<td>P</td>
</tr>
<tr>
<td>(1014)</td>
<td>0.65 ± 0.02</td>
<td>0.89 ± 0.01</td>
</tr>
<tr>
<td>(01T8)</td>
<td>0.45 ± 0.02</td>
<td>0.88 ± 0.02</td>
</tr>
<tr>
<td>(2204)</td>
<td>0.36 ± 0.03</td>
<td>0.87 ± 0.02</td>
</tr>
</tbody>
</table>

4.5 Surface incorporation structure of cobalt

The incorporation structure of Zn²⁺ impurity on the calcite (10T4) surface is expected to be representative of other calcite-type cations (listed in Table 1), and the proposed model in Section 4.4.3 should generally be valid for these ions. In this and the following two sections, we describe results of some XSW and SEXAFS experiments in the incorporation of three other calcite-type cations: Co²⁺, Ni²⁺, and Cu²⁺, to support the results obtained for Zn²⁺.

Co²⁺ incorporation at the calcite (10T4) surface was prepared using the liquid chemistry technique described in Section 2.3; the adsorption solution had a Co²⁺ concentration of about 500 μM. X-ray measurements were conducted at NSLS, at beamline X15A in June, 1997. The Co²⁺ surface sample selected for complete XSW measurements had a total Co coverage of ~ 0.05 ML, according to coverage calibration against a Ga-implanted surface standard.

The XSW triangulation of Co²⁺ was performed with the (10T4), (01T8), and (2204) Bragg reflections of calcite, with incident X-rays of 9.00 keV. Data for Co and Ca, and best theoretical fits to these data are shown in Fig. 18. These data were collected with the fluorescence detector guarded by a low take-off angle slit. The $f_H$ and $P_H$ values for Co and Ca obtained from the best fits to the data are tabulated in Table 4.
Figure 18: Experimental data and best theoretical fits for reflectivity $R$, and Co $K\alpha$ and Ca $K\alpha$ fluorescence yields vs. incident angle of X-rays for the calcite (a) $(10\bar{1}4)$, (b) $(01\bar{1}8)$, and (c) $(2\bar{2}04)$ Bragg reflections.
4.6 Surface incorporation structure of nickel

The incorporation of Ni$^{2+}$ at the calcite (1014) surface was prepared with the sample surface preparation technique described in Section 2.3. The solution was calcite saturated water that contained about 500 µM Ni$^{2+}$; the reaction time was about 5 minutes. The X-ray measurements were made at beamline X15A at NSLS in June, 1997. XSW measurements for the (1014) reflection was made with incident X-rays of 9.80 keV.

The XSW measurement on the Ni/CaCO$_3$ surface for the (1014) reflection is shown in Fig. 19. The measured Ni$^{2+}$ coherent position is $P = 0.88$, a value comparable to that for Zn$^{2+}$. Considering the comparable sizes between these two ions, and the comparable Ni-O and Zn-O nearest-neighbor bond lengths in their respective carbonates, a Ni$^{2+}$ coherent position comparable to that for Zn$^{2+}$ is reasonable.

One noticeable feature for the Ni/CaCO$_3$ impurity surface is that the highest coherent fractions for normal measurements were always limited to about 0.50, and coherent fractions for off-normal measurements (not shown) were below 0.3. This indicates that the ordered fraction for Ni$^{2+}$ at the incorporated surface was low compared to that for Zn$^{2+}$ and Co$^{2+}$, suggesting a certain degree of adsorbate disorder. Comparing the normal to off-normal coherent fractions, it appears that the disorder is more pronounced in the in-plane direction than in the surface normal direction. In the present case it seems that a low ordered fraction, and not the Debye-Waller factor, causes the low coherent fraction (in Eq. 10, page 10).
Figure 19: Experimental data and best theoretical fits for reflectivity $R$ and Ni $K\alpha$ fluorescence yield $Y$ vs. incident angle of X-rays for the calcite $\{10\bar{1}4\}$ Bragg reflection.
4.7 Surface incorporation structure of copper

4.7.1 Vibrational amplitude of adsorbate ion

The incorporation structure of Cu\(^{2+}\) at the calcite (10\(\bar{4}\)) surface was investigated with XSW and SEXAFS at beamline X15A at NSLS in October, 1998. The Cu/CaCO\(_3\) surface was prepared with the technique described in Section 2.3; the reaction solution contained about 500 \(\mu\)M of Cu\(^{2+}\) ion. Multiple-order XSW measurements were made with the (10\(\bar{4}\)) and (20\(\bar{2}\)) reflections. The Cu/CaCO\(_3\) sample had a total Cu coverage of 0.16 ML, calibrated with a Ga-implanted surface standard.

The multiple-order XSW results are shown in Fig. 20. According to the calcite structure, the transformation relating \(P_{10\bar{4}}\) and \(P_{20\bar{2}}\) is

\[
P_{20\bar{2}} = 2P_{10\bar{4}} - 1.
\]  

(23)

The experimentally measured Cu\(^{2+}\) coherent positions, \(P_{10\bar{4}} = 0.86 \pm 0.01\), and \(P_{20\bar{2}} = 0.71 \pm 0.01\), satisfy this relation, as shown in the model in Fig. 21. This is evidence that there is a single incorporation site for Cu\(^{2+}\) in the [10\(\bar{4}\)] direction.

From the coherent fractions in the multiple-order reflection XSW measurements, we are able to directly evaluate the vibrational amplitude of the Cu\(^{2+}\) adsorbate ion in the [10\(\bar{4}\)] direction, using the relations given in Eq. 10, \(f_H = C_a H D_H\), and Eq. 11 Ref. [47]. For a given surface, the value of the ordered fraction \(C\) in Eq. 10 is expected to be constant in a given crystallographic orientation. In addition, since there is a single Cu\(^{2+}\) site in the [10\(\bar{4}\)] direction, \(a_{10\bar{4}} = a_{20\bar{2}} = 1\) in Eq. 10. Then, by writing \(f_{10\bar{4}}\) and \(f_{20\bar{2}}\) in the form of Eq. 10, and combining both equations, we obtain the relation

\[
\langle \sigma_{[10\bar{4}]}^2 \rangle\!\!^T = \frac{d_{10\bar{4}}}{2\sqrt{6\pi}} \sqrt{\ln\left(\frac{f_{10\bar{4}}}{f_{20\bar{2}}}\right)},
\]  

(24)
where \( \langle \sigma_{[10ar{1}4]}^2 \rangle^{1/2} \) is the root-mean-square vibrational amplitude in the [10\(\bar{1}4\)] direction, i.e., the surface normal direction. Inserting into Eq. \ref{eq:24} the measured coherent fractions, \( f_{10\bar{1}4} = 0.60 \pm 0.02 \), and \( f_{20\bar{2}8} = 0.57 \pm 0.02 \), we obtain \( \langle \sigma_{[10\bar{1}4]}^2 \rangle^{1/2} = 0.045 \pm 0.05 \) Å for Cu\(^{2+}\) incorporated at the \((10\bar{1}4)\) surface. For comparison, this value is smaller than but within the order of magnitude of the vibrational amplitude of Zn\(^{2+}\) in the in-plane Zn-O bond direction, obtained in SEXAFS, where \( \langle \sigma^2 \rangle^{1/2} = 0.077 \) Å (from Table 2). It is reasonable that the normal vibration amplitude is smaller than the in-plane vibration amplitude, since at the surface cation site the vertical bond may be stronger after the removal of the O atom above the surface plane; but the uncertainty in \( \langle \sigma_{[10\bar{1}4]}^2 \rangle^{1/2} \) is too large to ascertain this comparison.

### 4.7.2 Jahn-Teller ion as a probe of adsorbate vertical location

When positioned at a lattice site of symmetric electrostatic field, such as the octahedral site of calcite, the degenerate ground state of the Cu\(^{2+}\) ion will interact with the symmetric field to lead to Jahn-Teller distortion \cite{48, 49}. In calcite, in particular, the Jahn-Teller effect is expected to cause an octahedral-to-tetragonal structural transition of the cation site \cite{50}.

Unlike other divalent transition metal cations (Table 1), a stable anhydrous copper carbonate compound of the calcite structure (i.e., with the cation located at the center of the O octahedron) is not known to exist. Instead, the stable carbonate of Cu\(^{2+}\) is hydrated, with the chemical formula Cu\(_2\)(OH)\(_2\)CO\(_3\). The first-neighbor coordination of Cu\(^{2+}\) is a \((2 + 4)\) tetragonal coordination. In each unit cell, the average distance of the four equilateral tetragonal Cu-O bonds is 1.985 Å; the average distance of the two axial Cu-O bonds is 2.465 Å \cite{51}.
Figure 20: Experimental data and best theoretical fits for reflectivity $R$ and Cu Kα fluorescence yield $Y$ vs. incident angle of X-rays for the calcite (1014), and (2028) Bragg reflections.
Figure 21: A side view of the calcite (10\overline{1}4) surface showing the coherent positions of the Cu ion measured with respect to the (10\overline{1}4) and the (20\overline{2}8) lattice planes.

Figure 22: A calcite surface schematic showing incorporated Cu ions located at two sites relative to the surface layer. At the top-most monolayer (ion 1), the Cu ion is located in a truncated (and maybe distorted) octahedron and is displaced from the center. At a deeper subsurface layer (ion 2), the Cu ion is located at the center of a perfect octahedron. At the latter site, an octahedral-to-tetragonal transition is expected to occur.
The investigation in the incorporation of the Cu\(^{2+}\) ion at the (10\(\overline{1}4\)) surface is in part motivated in view that the Jahn-Teller deformation may potentially be used to discriminate the near-surface vertical location of the adsorbate ion—a structural information that neither XSW or EXAFS explicitly provides. As explained in Fig. 22, in the top-most monolayer of the (10\(\overline{1}4\)) surface, the octahedral symmetry of the cation site that would lead to Jahn-Teller structural deformation is partially removed. The structure of a Cu\(^{2+}\) ion incorporated at the top-most monolayer (ion 1 in Fig. 22) is expected to behave like other calcite-type cations. In a deeper subsurface layer, however, the cation octahedron remains in cubic symmetry. A Cu\(^{2+}\) ion incorporated in this layer (ion 2 in Fig. 22) could cause an octahedral-to-tetragonal transition in its coordination structure. Therefore, by probing the first-neighbor Cu-O coordination structure of the Cu\(^{2+}\) ion with EXAFS, one can determine whether the Cu\(^{2+}\) ion is located at the top-most monolayer, or in a sublayer below the surface.

The concept of using a Jahn-Teller ion as a probe of the vertical location of a surface incorporated ion, as far as we know, has not appeared in scientific literature. It is a specific application of using impurities as atomic-scale structural probes—the underlying principle stated at the beginning of this thesis (Section 1.1.1).

In-plane SEXAFS measurements for the Cu/CaCO\(_3\) sample were performed on the same sample on which XSW measurements were made. The EXAFS raw data was taken in fluorescence mode by scanning over the Cu K\(\alpha\) absorption edge across the X-ray energy range of 8,940–9,350 eV, in 1-eV scan steps. The Fourier transform of the background-subtracted EXAFS data is shown in Fig. 23. This spectrum should be compared to that for Zn/CaCO\(_3\) (Fig. 16, page 40). The close resemblance between them suggests that the Cu\(^{2+}\) coordination structure is similar to that of a calcite-type cation. If the concept discussed above holds, this indicates
Figure 23: The amplitudes of Fourier transform of the $k^2$-weighted EXAFS function for the in-plane Cu-on-CaCO$_3$ data.
that the Cu$^{2+}$ ion is located at the top-most monolayer of the (10$ar{4}$4) surface. To date, there is no existing data in the literature on the structure of a Cu$^{2+}$ impurity in bulk calcite for structural comparison.
Chapter 5

Surface incorporation structure of aragonite-type cations: Lead on calcite

5.1 Introduction

Four divalent cations whose radii are equal or larger than that of Ca$^{2+}$ form anhydrous carbonates of the aragonite structure. We shall refer to these cations as aragonite-type cations. The cation in the aragonite carbonate is coordinated to 9 first-neighbor O atoms from adjacent CO$_2^2$ groups. Table 5 lists the aragonite carbonates, their cationic radii, and the mean first-neighbor A-O distances.

The relatively large ionic sizes raise the question of whether the aragonite-type cations would incorporate at the calcite surface as the calcite-type cations do. X-ray diffraction studies showed that at finite concentration Pb$^{2+}$ formed a distinct powdered PbCO$_3$ phase on the calcite (10$ar{1}$4) surface [52]. This is in contrast to the overgrowth of the calcite-type Cd$^{2+}$ ion on the calcite (10$ar{1}$4) surface, in which case a CdCaCO$_3$ solid-solution of the calcite structure formed [53].

The comparison of these two overgrowth experiments suggests that Pb$^{2+}$ may
Table 5: Cation radii and the first-neighbor cation-oxygen distances for carbonates of the aragonite structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cation radius</th>
<th>A-O distance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$</td>
<td>0.99</td>
<td>2.528</td>
<td>[54]</td>
</tr>
<tr>
<td>SrCO$_3$</td>
<td>1.13</td>
<td>2.636</td>
<td>[54]</td>
</tr>
<tr>
<td>PbCO$_3$</td>
<td>1.21</td>
<td>2.695</td>
<td>[54]</td>
</tr>
<tr>
<td>BaCO$_3$</td>
<td>1.35</td>
<td>2.807</td>
<td>[54]</td>
</tr>
</tbody>
</table>

have difficulty to structurally fit in the calcite lattice at a finite concentration. However, EXAFS [41] and XSW [55] evidences of the existence of impurity Sr$^{2+}$ located at the Ca$^{2+}$ site in the bulk calcite crystal clearly suggest that, at trace concentration, an aragonite cation can incorporate into the calcite lattice.

Of particular current importance in environmental science is the issue of the transport of trace aqueous Pb$^{2+}$ ions at the water-mineral interface [56]. An earlier normal Bragg-reflection XSW experiment showed that Pb$^{2+}$ was located in the (1014) lattice plane [24]. In this chapter, we describe a full XSW triangulation in the incorporation site of Pb$^{2+}$ at the calcite (1014) surface, an in-situ normal reflection XSW measurement that proves that the Pb$^{2+}$ site was not altered by the removal of solution above the sample surface, and an in-plane SEXAFS measurement that provides information about the local coordination environment of the Pb$^{2+}$ adsorbate ion.

5.2 Experimental

5.2.1 Sample preparation

The Pb$^{2+}$-on-calcite surface was prepared by immersing a crystal with a freshly-cleaved (1014) face in an adsorption solution, as described in Section 2.3.
solution was de-ionized water at room temperature and pH between 8.55 and 8.99. It contained 100 μM aqueous Pb and 100 μM EDTA compound. The reaction times ranged from 5.3 to 92.5 hours, for various samples.

5.2.2 Instrumental settings

The XSW experiments were carried out at beamline X15A at NSLS, in September, 1995. The XSW triangulation measurements were performed in situ with the (1014), (0006) and (0224) reflections of calcite, with an incident X-ray of 13.8 keV. A series of in situ measurements with the normal reflection only were performed, with a range of solution thicknesses above the sample surface. Each in situ measurement was followed by an ex situ measurement to check the consistency of results.

An X-ray liquid cell of the reflection geometry, shown in Fig. 24, was used for the in situ measurements. The cell was filled with the adsorption solution. The thickness of the solution above the sample surface was kept to under 10 μm, so that the Pb fluorescence signals from aqueous Pb species was small compared to the Pb signal from the calcite surface. The solution thickness was controlled by applying a suitable suction, which pulled the 12 μm-thick polypropylene window of the cell against the sample surface.

For the ex situ samples, total Pb coverage on the calcite surface was measured according to X-ray fluorescence yield under an off-Bragg condition. The calibration standard used was a Pb-implanted Si substrate.

The SEXAFS measurement was performed at beamline 12BM-B at the APS in November, 1997. This set-up was similar to that at beamline X15A. The X-ray beam was incident on the sample surface below the critical angle, i.e., under the total external reflection condition, in order to minimize elastically scattered signals.
Figure 24: A schematic of the reflection-geometry X-ray liquid cell used for in situ XSW measurements of Pb incorporation at the calcite (10\(\overline{4}\)) surface.

from the substrate.

The incident X-rays were scanned over the energy range from 12,980 to 13,480 eV, at 2-eV steps. Data was collected in fluorescence mode with a nine-element solid-state detector, with single channel analyzers set over the Pb L\(\alpha\) fluorescence peak. A reference spectrum of PbCO\(_3\) powder standard compound was acquired in transmission mode.

5.3 Results

5.3.1 XSW analysis

The ex situ XSW triangulation results for Pb\(^{2+}\) on calcite are shown in Fig. 25. In Fig. 25, the solid lines are the best \(\chi^2\)-fits of Eq. 8 to the data. The values of coherent fraction \(f_H\) and coherent position \(P_H\) extracted from the best fit for each of the three measurements are written in the figure.

The total Pb coverage is \(\Theta_T = 0.08 \pm 0.02\) ML. This value is typical of the coverage measured for other samples. Using the coherent fraction from the (10\(\overline{4}\))
measurement, \( f_{10\text{a}_4} = 0.59 \), and Eq. 21, \( \Theta_c = f_{10\text{a}_4} \times \Theta_T \), the coherent coverage of Pb\(^{2+}\) is \( \Theta_c = 0.05 \pm 0.02 \) ML.

The result of an \textit{in situ} XSW measurement made with the normal reflection is shown in Fig. 26, in comparison with an \textit{ex situ} measurement on the same sample after removing the solution from the sample surface. An identical coherent position was obtained for both measurements. The coherent fractions before and after the solution removal are \( f_{10\text{a}_4} = 0.48 \pm 0.01 \) and \( f_{10\text{a}_4} = 0.55 \pm 0.01 \), respectively; the lower \( f_{10\text{a}_4} \) value for the \textit{in situ} measurement is apparently due to a fraction of uncoherent Pb signals from Pb-bearing species in the solution.

### 5.3.2 SEXAFS analysis

The in-plane SEXAFS data for Pb/CaCO\(_3\) was analyzed using the MacXAFS software [43] according to standard procedures [44]. After background removal and conversion to \( k \)-space, the EXAFS function, in \( \chi(k)k^2 \), was Fourier transformed into \( R \)-space. The amplitude of Fourier transform for the Pb/CaCO\(_3\) data and for the PbCO\(_3\) reference are compared in Fig. 27, before phase correction.

The Pb-O first-neighbor shell component of the Pb/CaCO\(_3\) data was filtered from the Fourier transform with a window \( 1.34 \leq R \leq 2.83 \) Å. This first-shell data was shown as the solid-line in Fig. 28. It was fit in phase and amplitude with Eq. 17 (page 16) with respect to that for the PbCO\(_3\) standard, which had been transformed with identical window widths as the sample data.

The best fit was obtained at an edge shift of \( \Delta E_0 = -6.3 \) eV, with the following the best-fit values: \( R = 2.69 \pm 0.03 \) Å \( N = 4.87 \), and \( \sigma^2 = 0.008 \pm 0.003 \) Å\(^2\). The uncertainty in \( N \) is estimated to be \( \pm 1 \), according to Ref. [44].
Figure 25: Reflectivity and Pb $L\alpha$ fluorescence yield vs. incident angle of X-rays for the (a) (10T4), (b) (0006) and (c) (0224) Bragg reflections. The structures of these diffraction planes are shown in the inserts, where the Ca, C, and O atoms are represented by shaded, solid, and open circles, respectively.
Figure 26: Reflectivity and Pb $L\alpha$ fluorescence yield for the \textit{in situ} and the \textit{ex situ} measurements vs. incident angle of X-rays for the (10\bar{1}4) Bragg reflection. The coherent positions are shown in the figure; the coherent fractions are given in Section 5.3.1.
Figure 27: The amplitudes of Fourier transform of the $k^2$-weighted EXAFS functions for (a) the in-plane Pb/CaCO$_3$ sample data, and (b) the PbCO$_3$ standard compound data, before phase correction.
Figure 28: The Pb-O first-neighbor shell component of the in-plane EXAFS spectra for the Pb/CaCO₃ data (solid line) after background subtraction, conversion to $k$-space and Fourier-filtering, as $\chi(k^2)$, and the best fit (dash line) to the filtered first-shell data.

5.4 Discussion

5.4.1 Substitution of Pb at the bulk-extrapolated surface Ca site

The coherent position $P_H$ for Pb$^{2+}$ for each of the three lattice planes $H$ with which the XSW measurements were made are listed in Table 6; they are compared to the corresponding coherent positions for ideal Ca$^{2+}$. From this comparison, we see that the surface Pb$^{2+}$ is located at the bulk-extrapolated Ca$^{2+}$ lattice site within uncertainties. Thus, unexpectedly, the vertical relaxation in adsorbate ions that were consistently observed in the surface incorporation of the calcite-type cations is totally absent in Pb$^{2+}$ incorporation.

The exact match between the surface Pb$^{2+}$ site and the ideal Ca$^{2+}$ site is possibly the result of a fortuitous cancellation of two equal and opposite displacements, caused by two surface forces acting in opposite directions on the Pb$^{2+}$ ion. These displacements may be: an upward extension due to the larger size of Pb$^{2+}$, and a
downward relaxation due to vertical bond asymmetry. Recall that in the discussion of the Zn$^{2+}$ surface site in Chapter 4, we calculated from the model in Fig. 17 that the vertical Zn-O first-neighbor distance—assuming that the atoms in second layer are in bulk positions—is smaller than the in-plane Zn-O first-neighbor distance by about 0.16 Å. This extra amount of downward relaxation is perhaps the net effect of vertical bond asymmetry at the surface cation site. Similar effect should affect the Pb$^{2+}$ surface position as well. Since the out-of-plane Pb-O direction is nearly in the direction of the surface normal, in which the upward extension due to ionic size supposedly lies. Therefore, a structural relaxation of the surface Pb$^{2+}$ will not be observable if these two relaxations are of the same magnitude.

The impurity Pb/CaCO$_3$ surface similarly prepared was studied with specular X-ray CTR [37]. It was concluded from this study that the best fit was obtained if the assumption that the Pb$^{2+}$ ions were located in the top-most monolayer of the calcite (10T4) lattice was made. This piece of information complements the XSW data on Pb$^{2+}$ lattice site to provide a complete solution to the ion surface registration problem [14].

### 5.4.2 In-situ position of Pb on calcite surface

The identical coherent positions for the *in situ* and the *ex situ* measurements in Fig. 26 prove that the removal of the solution did not affect the lattice site of

<table>
<thead>
<tr>
<th>$\hat{H}$</th>
<th>$d_H$ (Å)</th>
<th>$P_H$ (Pb)</th>
<th>$P_H$ (Ca)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10T4)</td>
<td>3.04</td>
<td>0.00 ± 0.01</td>
<td>0</td>
</tr>
<tr>
<td>(0006)</td>
<td>2.84</td>
<td>0.52 ± 0.02</td>
<td>0.5</td>
</tr>
<tr>
<td>(02T4)</td>
<td>1.93</td>
<td>−0.01 ± 0.01</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6: The coherent positions of Pb from the XSW measurements compared with that of the ideal Ca.
the incorporated Pb\(^{2+}\). It appears that, once incorporated, the impurity cation is likely to be sufficiently tightly bonded by five first-neighbor A-O bonds to maintain its lattice position.

In many water-calcite interface systems, very often the impurity concentration in the solution is too high to permit \textit{in situ} X-ray spectroscopy measurements. This \textit{in situ} measurement, and its comparison with the \textit{ex situ} measurement, suggests that at least in some cases, \textit{ex situ} results can be used to imply \textit{in situ} surface structures.

### 5.4.3 In-plane expansion of neighboring carbonates: Conservation of the Pb-O distance

The local bonding environment of an aragonite cation at a calcite surface lattice has not been previously determined. For the Pb\(^{2+}\) incorporated at the calcite (10\(\overline{1}4\)) surface investigated here, at the coverage \(\Theta_c = 0.05\) ML, the in-plane first-neighbor Pb-O distance (2.69 ± 0.03 Å) is within uncertainty equal to the Pb-O bond distance in PbCO\(_3\) (2.695 Å); a conservation in first-neighbor A-O distance is therefore observed (Table 7). The in-plane first-neighbor coordination number is 4.87±1 when normalized to the total of 4 in-plane Pb-O bonds. This suggests that the local bonding environment of Pb\(^{2+}\) at the calcite (10\(\overline{1}4\)) surface is octahedral coordination—the same as that of a calcite-type surface impurity ions. That is, for the impurity Pb\(^{2+}\) on calcite, the local Pb-O distance is determined by that in PbCO\(_3\) (aragonite), whereas its local coordination symmetry is determined by the host surface lattice (calcite).
Table 7: In-plane structure for Pb incorporated at the calcite (10\overline{1}4) surface according to SEXAFS measurement, compared with the local Pb environment in the PbCO$_3$ crystal and the local Ca environments in the calcite and the aragonite structures of CaCO$_3$.

<table>
<thead>
<tr>
<th></th>
<th>A-O distance (Å)</th>
<th>N</th>
<th>$\Delta \sigma^2$ (Å$^2$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb/CaCO$_3$ (~ 0.05 ML)</td>
<td>2.69 ± 0.03</td>
<td>4.87 ± 1</td>
<td>0.008</td>
<td>0.00002</td>
</tr>
<tr>
<td>PbCO$_3$</td>
<td>2.695</td>
<td>9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaCO$_3$ calcite</td>
<td>2.359</td>
<td>6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaCO$_3$ aragonite</td>
<td>2.528</td>
<td>9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

5.5 Surface impurity structure interpreted as the structure of a bulk impurity located at a surface site: A model

In this section, the results of impurity cation surface incorporation structures from this and the previous chapter are summarized. Observations of common characteristics are generalized.

5.5.1 Cation in-plane coordination: Conservation of cation-oxygen coordination distance

The details of cation impurity coordination to nearest-neighbor CO$_3^{2-}$ groups in the host calcite surface are not dependent on whether the ion is of the calcite-type or the aragonite-type. The coordination characteristics can be summarized as the following:

**Coordination structure** The in-plane first-neighbor coordination structure of the impurity cation is that of the cation site of the host calcite, i.e., an octahedral coordination, regardless whether the adsorbate ion is of the calcite- or the aragonite-type.
Coordination distance The in-plane first-neighbor coordination distance of the impurity cation with the O atoms of the adjacent CO$_3^{2-}$ groups is the same as the cation-oxygen first-neighbor distance in the native carbonate of the impurity ion, regardless whether that carbonate is of the calcite or the aragonite structure.

One may be tempted to attribute this conservation of cation-oxygen coordination distance to the effect of the surface, where the missing of one of the six cation-oxygen bonds may help free the CO$_3^{2-}$ groups to relax fully toward the impurity. But the effect of the surface should not be overestimated, and it should be remembered that bulk impurity cations in calcite, to great extent, also observe first-neighbor distance conservation (See Section 3.4). If we compare bulk and surface cation-oxygen distance conservation, we are led to believe that this conservation is most likely the effect of the CO$_3^{2-}$ molecule. If so, the CO$_3^{2-}$ molecule plays the role of localizing the extent of the strain field of the impurity defect, by absorbing a fraction of the strain through internal structural re-conformation. Indeed, for comparison, it has been observed that cation substitutions in tertiary complex oxides do not lead to full relaxation of neighboring monoatomic anions [57, references therein].

5.5.2 Lattice site: Adsorbate ion vertical relaxation

The independence of an impurity’s local coordination structure from that in its native carbonate suggests that the surface incorporation of both calcite- and aragonite-type cations can be discussed together. We may construct a structural model based on the hypothesis made in Section 3.2, to provide a unified interpretation in the observed surface incorporation sites for all cations studied. We consider the impurity displacements in the [1014] direction only. The model is shown in Fig. 29.
We explain it in the following:

We start with the coordination structure of a bulk Ca\(^{2+}\) ion in calcite. In Fig. 29(a), the octahedral coordination of the Ca\(^{2+}\) ion is described as a sphere with the Ca\(^{2+}\) ion centered at the origin, \(O\). The intersecting points of a set of cubic axes with the surface of the sphere give the six first-neighbor Ca-O ionic bonds (four of which, \(OR, OP, OS\) and \(OQ\), are indicated in the figure; the remaining two lie perpendicular to the paper). The radius of the sphere is \(r_{Ca} = 2.36\) Å, the Ca-O distance in calcite.

Next we describe the structure of an impurity cation in bulk calcite, e.g., Mn\(^{2+}\), as shown in Fig. 29(b). The only change here is the reduction (or increase) of the radius of the sphere, from \(r_{Ca}\) to \(r_a\), where \(r_a\) is the impurity first-neighbor A-O distance. Assuming bulk A-O distance conservation, \(r_a\) can be taken to be the A-O distance in the native carbonate of the impurity cation.

We now translate this impurity sphere to a Ca\(^{2+}\) site at the (1\(0\)\(\bar{4}\)) surface of the crystal, and allow it to be displaced and deformed to account for the surface forces that act on it. In this process, we assume a rigid second and subsequent layers. First, surface in-plane first-neighbor A-O distance conservation requires that the horizontal radius be still \(r_a\). However, in the vertical direction, the removal of the upper cation-oxygen bond [the equivalent of \(OR'\) in (b)] by surface truncation creates a vertical bonding asymmetry. Consequently, the lower vertical cation-oxygen bond [the equivalent of \(OS'\) in (b)] now has a reduced length, of \(r_c\), where \(r_c < r_a\). As a result, the sphere has become an ellipsoid. Furthermore, the geometric asymmetry in the surface normal direction will cause the impurity to relax (or expand) vertically. We shall assume this relaxation to be along the vertical cation-oxygen direction. We express this relaxation by translating the center of the ellipsoid downward (or upward) along the vertical cation-oxygen bond, until
Figure 29: A proposed structure model for a cation impurity on calcite (c), derived from the structures of (a) a bulk Ca$^{2+}$, and (b) a bulk cation impurity.
the bottom surface of the ellipsoid touches the O atom site in the second layer, S. This final structure is an ellipsoid located at a new center \( O' \), not necessarily in the \( (10\overline{1}4) \) plane, with equilateral radius \( r_a \) and axial radius \( r_c \), where \( r_c = |O'S| \). This model is shown in Fig. 29(c).

The vertical nearest-neighbor cation-oxygen bond length \( r_c \) is in general not known. However, it can be derived from an XSW measurement, with the following relation to the impurity displacement \( \Delta h \) in the \([10\overline{1}4]\) direction

\[
\Delta h = -(r_{Ca} - \frac{r_a}{\rho}) \cos \gamma
\] (25)

where \( \gamma \approx 20^\circ \) is the angle between the ellipsoidal axis \( O'S \) and the \( (10\overline{1}4) \) surface normal, and \( \rho = r_a/r_c \) is the ratio of the equilateral to axial radius of the ellipsoid.

Taking the Zn/CaCO\(_3\) surface impurity system discussed in Chapter 4 as an example, we have, from SEXAFS, \( r_a = 2.11 \) Å; from XSW, \( \Delta h = 0.4 \) Å; and \( r_c = 1.94 \) Å by deduction, assuming the second layer is rigid.

In Fig. 30, the vertical displacement \( \Delta h \) for various adsorbate ions from the bulk-extrapolated \( (10\overline{1}4) \) surface plane is plotted against the normalized equilateral radii of impurity ellipsoids, \( r_a/r_{Ca} \). In this plot, the values of \( \Delta h \) are from the XSW measurements; the values of \( r_a \) are obtained either by SEXAFS measurements or assuming cation-oxygen distance conservation. These data include all cations investigated in this and the previous chapter. The dependence of \( \Delta h \) on \( r_a \) should be taken as an evidence that the adsorbate ions are located at the surface, since in the bulk, we expect \( \Delta h = 0 \) by lattice symmetry, i.e., Fig. 29(b). Furthermore, from this plot, it appears to be possible that the relation between \( \Delta h \) and \( r_a/r_{Ca} \) is linear; additional data are needed to determine this relationship, especially near \( r_a/r_{Ca} \approx 1 \) (e.g., Cd\(^{2+}\)).

If, however, the dependence of \( \Delta h \) on \( r_a/r_{Ca} \) is indeed linear, the ratio \( \rho = r_a/r_c \)
Figure 30: The XSW measured [1014] displacement $\Delta h$ vs. normalized first-neighbor cation-oxygen distance $r_a/r_{Ca}$ for various divalent cation impurities incorporated at the calcite (1014) surface.

is a constant for all cations. Then, one can perform a linear fit of Eq. 25 to the data points in Fig. 30. From this fit the displacement $\Delta h$ can be obtained for any impurity cation whose A-O distance (i.e., the radius $r_a$) is known. Taking two cations from Tables 1 and 5 as examples: For Mg$^{2+}$, $r_a=2.102$ Å, with which we obtain $\Delta h = -0.35$ Å; for Ba$^{2+}$, $r_a=2.807$ Å, with which we obtain $\Delta h = 0.09$ Å.
Chapter 6

Surface incorporation structure of pyramidal anions: Selenite and arsenite on calcite

6.1 Introduction: The role of molecular configuration in surface incorporation

Molecular ions differ from monoatomic ions by having geometric shapes. Like monoatomic ions, incorporation of molecular ions at an ionic surface is often a result of ion exchange at the aqueous-solid interface, and is a phenomenon commonly encountered in a wide range of natural and engineering systems, most typically in such fields as environmental science, chemical engineering and geochemistry [56]. The structure of a molecular ion doped surface also often reveals crucial information about the dominating forces that bind a molecular ion to the surface lattice, which is fundamental to understanding surface ion exchange.

However, in considering surface incorporation, there are major differences between molecular and monoatomic ions. For a monoatomic ion, its geometry can be simply described by its ionic radius, and its charge distribution by a point
charge. In contrast, for a molecular ion, an adequate description in its configuration requires specifying its geometric shape and the electrostatic distribution among its constituent atoms. Consequently, the criteria that are frequently used for estimating the probability of surface incorporation by monoatomic ions—i.e., the relative ionic radii and valence of the exchanging ions [58]—are not sufficient for predicting molecular ion adsorption. Few experiments have been performed towards understanding the basic factors and interactions that determine the surface incorporation of a molecular ion. The atomic-scale structure of molecular ions incorporated at an ionic crystal surface remains today a poorly understood area in surface studies [3]. This lack of basic knowledge limits one’s ability for quantitative assessment in real issues which involve molecular ion adsorption and transport at liquid-solid interfaces.

The configurational compatibility between an adsorbate ion and a surface site as the key requirement for surface ion exchange to take place should remain valid for molecular ions. But this requirement is now more specific. How stringent this compatibility requirement is has general implications in applied issues. If only molecular ions of precisely identical configuration could mutually exchange, few ions would satisfy this requirement, and the probability of exchange would be extremely restricted. Consequently, the roles of molecular ion incorporation in practical issues would be very limited. If, on the other hand, molecular ions of roughly comparable structures can exchange regardless of their detailed configurations, the structural selectivity of a surface in incorporation would be reduced. One important question in the surface incorporation of molecular ions is: To what extent a configurational difference between two molecular ions is allowed while their surface exchange may still take place?
6.2 Pyramidal ion incorporation at surface carbonate site

A systematic approach toward answering this question is to examine, for a given ionic surface, the incorporation of a series of molecular ions whose structural symmetry is related to that of the surface ion. Of the many structural classes of molecular ions, one of the simplest and most common are the trioxyanions with the stoichiometric form of $BO_3$. This class of anions, along with the $BO_4$ anions to be considered in the next chapter, represents the anionic portions of the salts of many most common inorganic acids. The $BO_3$ anions have the basic trigonal geometry, but are further divided into two groups. Those with a $B$ atom that has lone-pair valence electrons assume the pyramidal trigonal shape; these ions include $PO_3^{3-}$, $AsO_3^{3-}$, $SO_3^{2-}$, $SeO_2^{2-}$ and $BrO_3^-$. Those with a $B$ atom without the lone-pair valence electrons have a planar trigonal shape, such as $CO_3^{2-}$ and $NO_3^{2-}$.

Because of their closely related symmetries, a study of the incorporation of the pyramidal $BO_3$ ions at the planar $CO_3$ sites at the calcite surface is an ideal starting point for investigating whether ions of different shapes may mutually exchange at the calcite surface. If this exchange does take place, furthermore, one would wish to know if there is a common surface structure shared by the entire class of pyramidal $BO_3$ ions. In this chapter, we describe the XSW study in the structures of $SeO_3^{2-}$ and $AsO_3^{2-}$ ions incorporated at the calcite (10$ar{1}$4) surface [59, 60], and discuss the common structural features observed in both cases. In Table 8, the geometries of the $CO_3^{2-}$, $SeO_3^{2-}$ and $AsO_3^{2-}$ ions are compared.

Aqueous Se and As, even at trace concentration, are a potential cause of human toxicity [63, 64]. As the dominant carriers of these elements in the aqueous phase, the interaction of $SeO_3^{2-}$ and $AsO_3^{2-}$ (and of $SeO_4^{2-}$ and $AsO_4^{3-}$) with solid
Table 8: Comparison of the geometry of the carbonate, selenite and arsenite ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Structure</th>
<th>Symmetry</th>
<th>B-O distance</th>
<th>Dihedral angle</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_3$</td>
<td>planar triangular</td>
<td>$D_3^h$</td>
<td>1.22 Å</td>
<td>120°</td>
<td>[30]</td>
</tr>
<tr>
<td>SeO$_3$</td>
<td>trigonal pyramidal</td>
<td>$C_3$</td>
<td>1.69 Å</td>
<td>101°</td>
<td>[61]</td>
</tr>
<tr>
<td>AsO$_3$</td>
<td>trigonal pyramidal</td>
<td>$C_3'$</td>
<td>1.84 Å</td>
<td>110°</td>
<td>[62]</td>
</tr>
</tbody>
</table>

surfaces plays a critical role in determining Se and As distribution, their aqueous concentration and their degree of toxicity.

Adsorption of Se ions by mineral surfaces has been studied experimentally on oxides and hydroxides [65, 66, 67]. Recently there have also been an increased number of investigations on the oxidation of AsO$_3^{3-}$ to AsO$_4^{3-}$ by oxide surfaces [68]. However, we are unaware of any published report on the incorporation of SeO$_3^{2-}$ and AsO$_3^{3-}$ at ionic surfaces by ion exchange, including the specific case of their incorporation at the calcite (10T4) surface.

6.3 Experimental

6.3.1 Surface preparation

Sample preparations for SeO$_3^{2-}$ and AsO$_3^{3-}$ on calcite surface were similar to that described in Section 2.3. The SeO$_3^{2-}$ solution contained 100 µM Na$_2$SeO$_3$ at pH 8.9. The AsO$_3^{3-}$ solution contained 51 µM Na$_2$HAsO$_3$ at pH 9.8.

6.3.2 Instrumental settings

The SeO$_3^{2-}$ experiments were performed at beamline X15A at NSLS in April, 1995. The AsO$_3^{3-}$ experiments were first performed at beamline 12ID-D at APS in October, 1997, and were completed at beamline X15A at NSLS in June, 1998.
For the SeO$_3^{2-}$ experiments, the incident X-rays were monochromated to an energy of 14.80 or 16.00 keV. For the AsO$_3^{2-}$ experiments, the incident X-rays were monochromated to 12.9 keV.

### 6.4 Results

#### 6.4.1 Selenite on calcite

For the SeO$_3^{2-}$ sample, the XSW measurements were performed using the calcite (10̅14) normal reflection, and the (0006) and (11̅20) off-normal reflections. The experimental results and best theoretical fits for reflectivity $R(\theta)$ and Se Kα fluorescence yield $Y(\theta)$ for these measurements are shown in Fig. 31. The coherent fractions $f_H$ and coherent positions $P_H$ extracted from the best fits are indicated in the figure.

For a typical sample, the total Se surface coverage is $\Theta_T = 0.02 \pm 0.01$ ML. This coverage is comparable to the 0.05 ML coverage reported in Ref. [58]. The Se coverage did not show noticeable dependence on adsorption reaction time within the range of 3 to 11 hours. Neither the coverage nor the incorporation structure underwent an observable evolution or degradation during the XSW data acquisition, which lasted for more than 100 hours. This indicates that the SeO$_3^{2-}$ incorporated calcite (10̅14) surface was stable under helium atmosphere at room temperature.

#### 6.4.2 Arsenite on calcite

For the AsO$_3^{2-}$ sample, the XSW measurements were done using the (10̅14) and the (0006) reflections. The XSW results are shown in Fig. 32. The $f_H$ and $P_H$ values from the best theoretical fits of the data are also indicated in the figure.
Figure 31: X-ray reflectivity $R$ and Se $K\alpha$ fluorescence yield $Y$ as a function of the relative angle of X-ray incidence for the calcite (a) (1014), (b) (0006) and, (c) (1120) Bragg reflections. The solid lines are the best theoretical fits to the data. The best-fit parameters and their uncertainties are given in the figure. Also shown in dashed lines for comparison are the simulated fluorescence yield functions for the ideal C position at the measured Se coherent fraction.
Figure 32: Reflectivity $R$ and As $K\alpha$ fluorescence yields $Y$ vs. relative angle of X-ray incidence for arsenite incorporated at the calcite $(10\bar{1}4)$ surface, for the (a) $(10\bar{1}4)$ and (b) $(0006)$ Bragg reflections. The solid lines are the best theoretical fits to the data. Also shown in dashed lines for comparison are the simulated fluorescence yields for the ideal C position at As coherent fractions.
6.5 Discussion

6.5.1 Substitution of trigonal pyramidal ion at the carbonate site

In calcite, each $\text{CO}_3^{2-}$ anion resides within a rhombohedral space defined by six adjacent $\text{Ca}^{2+}$ cations. The C atom is located at the center of the rhombohedron. The lateral C-Ca distance of the rhombohedron is $a = b = 3.21 \, \text{Å}$. The axial C-Ca distance of the rhombohedron is $c = 4.26 \, \text{Å}$.

The C atom in the $\text{CO}_3^{2-}$ molecule, located on both the (10\overline{4}) and the (0006) lattice planes, projects a height of zero length along these lattice normals. The projected heights of the Se and the As atoms in the [10\overline{4}] and the [0006] directions from the measured XSW coherent positions can be calculated according to Eq. 22, $h_H = P_H \times d_H$. These values are tabulated in Table 9. For both Se and As, these $h_H$ quantities have non-zero values. They indicate a spatial displacement of the Se and the As surface positions from the ideal C position. The size of this displacement, however, is small compared to the C-Ca distances that define the rhombohedral volume of the $\text{CO}_3^{2-}$ site, such that the entire $\text{SeO}_3^{2-}$ or $\text{AsO}_3^{3-}$ ion is still located within the Ca-cornered rhombohedron. We therefore conclude from the XSW results that the $\text{SeO}_3^{2-}$ and the $\text{AsO}_3^{3-}$ ions occupy the $\text{CO}_3^{2-}$ lattice site upon incorporation at the CaCO$_3$ (10\overline{4})$ surface.

A schematic drawing that describes the location of the Se atom as $\text{SeO}_3^{2-}$ becomes incorporated at the CaCO$_3$ (10\overline{4})$ surface lattice is shown in Fig. 33. In Fig. 33(a), the projected heights of Se above the (10\overline{4}) and the (0006) planes are indicated with dashed-lines. The intersecting point of these dashed-lines is the Se position viewed in the plane containing the [10\overline{4}] and the [0006] lattice vectors. A similar schematic for As position as $\text{AsO}_3^{3-}$ incorporated at the CaCO$_3$ (10\overline{4})$
surface is shown in Fig. 34.

Fig. 33(b) shows the height of Se above the (1120) plane. Since the calcite (10\overline{1}4) surface unit cell has a two-fold symmetry about the [1\overline{2}10] direction, the average position of the Se atom projected in the direction normal to this plane must be zero. The position relative to the (1120) plane shown in Fig. 33(b) agrees with this symmetry argument.

### 6.5.2 Possible orientation of a pyramidal ion at the surface carbonate site

Given the Se and As atomic lattice site determined by XSW triangulation, Figs. 33 and 34 further depict a geometric orientation for the whole SeO$_3^{2-}$ and AsO$_3^{2-}$ molecules at the CO$_2^{2-}$ site. This structure is proposed from the following considerations. First, the dominant force that binds the SeO$_3^{2-}$ and AsO$_3^{2-}$ molecules to the CO$_2^{2-}$ site is the electrostatic force between the partially negatively charged O atoms and the positively charged Ca$^{2+}$ ions. Second, there is a common three-fold rotational symmetry about the normal axis that is shared between the SeO$_3^{2-}$ ion (or the AsO$_3^{2-}$ ion) and the CO$_2^{2-}$ ion, and a reduced symmetry along this axis. Finally, we assume that the nearest neighbor Ca-O distance to be more or less conserved; this is an implication from the observed local bond distance conservation in cation incorporation [69]. A structure that agrees with this set of conditions is one that the SeO$_3^{2-}$ ion (or the AsO$_3^{2-}$ ion) is oriented with its triangular oxygen base positioned in overlap with the bulk-extrapolated CO$_2^{2-}$ triangle position. Using the AsO$_3^{3-}$ case as an example, the As-O distance is 1.84 Å and the O-As-O angle of 110° [62]. Assuming the oxygen base of the AsO$_3^{3-}$ ion is coincide with the ideal CO$_2^{2-}$, the projected height of the As atom in the [10\overline{1}4] and the [0006] directions are $(h_{10\overline{1}4}, h_{0006}) = (0.43, 0.60)$ Å if the As apex pointing
Figure 33: Side view of a model showing the XSW-determined Se lattice site and a proposed structure of the selenite ion at the calcite (10\bar{1}4) surface. The surface is shown projected in the (a) [1\bar{2}10] direction, and (b) the [0001] direction. The XSW-measured positions for Se are indicated with dashed lines; their intersecting point locates the Se atom.
Figure 34: Cross sectional view of a model showing the XSW-determined As lattice site and a proposed structure of the arsenite ion incorporated at the calcite (10\(\overline{4}\)) surface. Calcite lattice points not in the cross sectional plane are abbreviated as small solid dots. The dashed lines indicate the XSW-measured positions; their intersecting point locates the As atom. The dotted-line indicates the c-axis of the lattice. It is suggested that partially positively-charged As atom in the AsO\(_3^2-\) ion may electrostatically interact with the first nearest neighbor Ca\(^{2+}\), located in the second layer along the c-axis, to cause the upward-pointing orientation of AsO\(_3^2-\) to be the energetically preferred orientation.
Table 9: Comparison of the height of As and Se atoms above the (10\(\overline{4}\)) and (0006) lattice planes according to experiments and model. Units are Å.

<table>
<thead>
<tr>
<th>(H)</th>
<th>(h_H) (As)</th>
<th>(h_H) (Se)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10(\overline{4}))</td>
<td>(0.46 \pm 0.06)</td>
<td>0.43 0.54 (\pm 0.06)</td>
</tr>
<tr>
<td>(0006)</td>
<td>0.76 (\pm 0.17)</td>
<td>0.60 0.63 (\pm 0.11)</td>
</tr>
</tbody>
</table>

in \(+[0001]\) direction. This As position agrees with the XSW results, which are \((h_{10\overline{4}}, h_{0006}) = (0.46 \pm 0.06, 0.76 \pm 0.17)\) Å. Therefore, this inferred AsO\(_3^{3-}\) orientation is consistent with the As experimental results for an upward-pointing AsO\(_3^{3-}\), as shown in Fig. 34.

A similar analysis would demonstrate that the upward-pointing geometry for the SeO\(_3^{2-}\) ion also agrees with the XSW-determined Se position. For SeO\(_3\)/CaCO\(_3\), we measured experimentally the height \((h_{10\overline{4}}, h_{0006}) = (0.54 \pm 0.06, 0.63 \pm 0.11)\) Å. The corresponding values according to the upward-pointing incorporation geometry is \((h_{10\overline{4}}, h_{0006}) = (0.52 \pm 0.01, 0.73 \pm 0.02)\) Å. Table 9 compares the \(h_H\) values from the XSW experiments and for the model.

Both the SeO\(_3^{2-}\) and the AsO\(_3^{3-}\) structures are satisfactorily interpreted with the same model. It is logical to believe that their similar geometric and charge configurations are the principle reasons for their shared incorporation structure. Other pyramidal BO\(_3\) ions of similar geometric and charge configurations may incorporate at the calcite (10\(\overline{4}\)) surface in a similar manner as well. In a more general sense, the results with SeO\(_3^{2-}\) and AsO\(_3^{3-}\) demonstrate a correlation between molecular configuration and incorporation structure. This opens up the possibility that one may predict incorporation structure from molecular configuration.

From the energy point of view, the selective upward-pointing orientation of
the pyramidal ion must be justified in defect energy consideration. That is, an upward-pointing orientation should be energetically favored when compared to, say, a downward-pointing orientation. The difference in binding energy between these two orientations is essentially electrostatic, and can be compared, since in this case the asymmetry is limited to in the [0001] direction. A comparison in the structural symmetry about the apical atom for the upward and downward positions reveals that this energy difference is predominantly sensitive to the interactions between the apical atom and the ions located along the [0001] axis (indicated with a short dashed line in Fig. 34). The inverse-square terms of the partial Madelung energy summation for ions along the [0001] axis is

\[
\sum_{n=1}^{\infty} \frac{1}{(2n-1)d + \Delta d} - \frac{1}{2nd + \Delta d},
\]

where \(d = 4.26 \text{ Å} \) is the first-neighbor C-Ca distance along the [0001] axis, \(n\) is the near neighbor number, and \(\Delta d\) is the height of the pyramid, \(\Delta d\) is positive if the pyramid is upward-pointing, and negative if downward pointing. This summation for the upward and downward orientation for the AsO\(_3\) case gives the quantities of 0.034 and 0.063 Å\(^{-2}\), respectively. That is, the upward-pointing orientation of AsO\(_3\) is the energetically favored of the two orientations.

The Se and As coherent positions from the XSW results only indicate that the SeO\(_3^{2-}\) and AsO\(_3^{3-}\) ions occupy the CO\(_3^{2-}\) lattice site in a calcite unit cell, but do not provide direct information about its position relative to the surface. However, a consideration in the bonding structure of CO\(_3^{2-}\) (and of SeO\(_3^{2-}\) and AsO\(_3^{3-}\)) with its coordinating Ca\(^{2+}\) may help identify the most likely location of SeO\(_3^{2-}\) and AsO\(_3^{3-}\) in the surface normal direction. Of the six O-Ca ionic bonds that each CO\(_3^{2-}\) establishes with neighboring Ca\(^{2+}\), four lie on the (10\(\overline{4}\)) lattice plane, one each above and below (see Fig 10, page 27). Assuming SeO\(_3^{2-}\) and AsO\(_3^{3-}\) are identically coordinated with Ca\(^{2+}\) as CO\(_3^{2-}\) is, for the geometry with
the pyramidal ion located above the surface, it would have to be held to the surface layer by only one of the six O-Ca bonds; this is quite unlikely considering the high adsorbate ordering indicated by the high XSW coherent fractions. If, on the other hand, SeO$_3^{2-}$ and AsO$_3^{3-}$ were located below the surface, they should be equally likely to be in an upward as in a downward orientation, giving an average $\Delta h$ of zero. With these arguments, it is most likely that the SeO$_3^{2-}$ and the AsO$_3^{3-}$ ions are incorporated within the surface monolayer.
Chapter 7

Surface incorporation structure of tetrahedral anions: Chromate on calcite

7.1 Introduction

The tetrahedral ion possesses the three-fold rotational symmetry about the triad axis as the trigonal planar ion does, but the apical to base distance is longer than that in the trigonal ion. Because of its increased height, it is larger in size. This often leads to naive predictions that the tetrahedral ion is too large to fit in the surface CO$_3^{2-}$ site for incorporation to take place, assuming the incorporation is substitutional. A closer look at the geometry of the BO$_4$ ion reveals that its equilateral cross sectional area is in fact comparable to that of the CO$_3^{2-}$ ion. Given this, if the BO$_4$ ion is to retain the CO$_3^{2-}$ axial orientation once adsorbed, one sees no geometric hindrance to place a BO$_4$ ion at the surface CO$_3^{2-}$ site. Therefore, the logical next step in investigating molecular ion incorporation at calcite (10$ar{1}$4) surface is to examine the BO$_4$ anions.

The study of the BO$_4$ incorporation on calcite, however, is driven equally by
the potential of vast applications. The \( \text{BO}_4 \) ions are among the most common of inorganic ions [7]. Given their abundance, even if the probability of incorporation of a particular \( \text{BO}_4 \) ion on calcite is limited, the significance of its general implication is undiminished, since the large number of molecules to which this process is relevant compensates its limitation in one.

Of these ions, the chromium (VI) tetra-oxide (\( \text{CrO}_4^{2-} \)), or chromate, anion is a typical example. In this chapter, we report an X-ray standing wave investigation in the incorporation of the \( \text{CrO}_4^{2-} \) anion at the \( \text{CaCO}_3 \) \( (10\overline{4}) \) surface. In addition to shedding light on the fundamental aspects of molecular ion incorporation, this study is itself directly relevant to the environmental science of \( \text{CrO}_4^{2-} \) partitioning at the water-calcite interface.

### 7.2 Experimental

#### 7.2.1 Surface preparation

The adsorption of \( \text{CrO}_4^{2-} \) on the calcite surface took place by immersing the sample surface in a de-ionized water solution that contained ca. 200 \( \mu \text{M} \) of \( \text{Na}_2\text{CrO}_4 \). The reaction proceeded at room temperature at about \( \text{pH} \ 8 \). The exposure time of the sample surface to the solution was typically 10 min.

#### 7.2.2 Instrumental settings

The XSW experiments were performed at NSLS, at beamline X15A. The XSW measurements were made for the normal \( (10\overline{4}) \) reflections with incident X-rays of 8.00 keV.
7.3 Results

One critical factor in quantitative spectroscopy with dilute systems is the minimization of background noise and other unwanted signals that would interfere with the desired signal. This is particularly crucial in the acquisition of the X-ray fluorescence spectra for the submonolayer-coverage adsorbed species studied here. For work described in this thesis, the difficult task of signal optimization was usually accomplished by skillful arrangements of experimental devices and settings. These arrangements often determine whether a measurement is feasible. For the current CrO$_4^{2-}$ on calcite experiment, however, experimental arrangement alone was not sufficient in reducing the background Cr $K\alpha$ X-ray signal to a negligible degree compared to the desired signal from the CrO$_4^{2-}$ molecules adsorbed at the sample surface. This is because a small fraction of Cr in the metal alloy of the detector nozzle emitted background signal by scattered X-rays.

This background Cr signal, however, can be distinguished from the Cr signal from the sample surface, because its intensity was insensitive to the X-ray incident angle around the Bragg reflection. Therefore, by performing a control scan with a blank calcite substrate sample, its intensity can be quite accurately estimated. This amount of intensity can then be subtracted from the total Cr signal in the scan for a CrO$_4^{2-}$-adsorbed sample. This background subtraction procedure was adopted in this experiment. Table 10 lists the XSW results for the normal (10$ar{1}$4) reflection for four samples. The data and best theoretical fit for the sample that had the highest coherent fraction is shown in Fig. 35.
Table 10: List of Cr coherent fractions and coherent positions obtained for various CrO$_4$-on-CaCO$_3$ sample surfaces

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Coherent position ($P$)</th>
<th>Coherent fraction ($f$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.95 ± 0.01</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td>2</td>
<td>0.99 ± 0.03</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>3</td>
<td>1.03 ± 0.01</td>
<td>0.44 ± 0.02</td>
</tr>
<tr>
<td>4</td>
<td>0.99 ± 0.02</td>
<td>0.23 ± 0.02</td>
</tr>
</tbody>
</table>

Figure 35: Reflectivity $R$ and Cr $K\alpha$ fluorescence yield $Y$ vs. incident angle of X-rays for the calcite (10$ar{1}$4) Bragg reflection. The solid curve is the best theoretical fit to the data.
7.4 Discussion

Fig. 36 shows the cross-sectional view of a calcite lattice that contains the [10\textoverline{4}] and the [0001] lattice vectors, as well as the (10\textoverline{4}) surface. For clarity of visualization, only atoms in this cross-section are shown in the figure, and those lattice points not on this cross-section are abbreviated as small solid dots. In Fig. 36, the dash line indicates the average XSW-determined position of the Cr atom relative to the (10\textoverline{4}) lattice.

The background subtraction method used for the (10\textoverline{4}) measurements is not suitable for off-normal XSW measurements, since the weak fluorescence intensity do not warrant an accurate data reduction. For this reason off-normal reflection measurements were not used to triangulate the lattice site of the Cr atom. Lacking the off-normal reflection XSW measurements, one can only be certain from the (10\textoverline{4}) measurement of the ordering of the adsorbed CrO$_4^{2-}$ in the surface normal direction. This does not exclude the possibility that an ordered layer of CrO$_4^{2-}$ precipitated above the (10\textoverline{4}) surface. However, a precipitated layer normally would exhibit a high degree of spatial disorder, or a low ordered fraction. This is not quite agreeable with the reasonably high coherent fractions observed.

Instead, it seems more reasonable to suggest that the CrO$_4^{2-}$ ion is incorporated in the (10\textoverline{4}) surface lattice. The most likely site is obviously the CO$_3^{2-}$ site, assuming the incorporation takes place by anion substitution. In the model in Fig. 36, a suggested position of the CrO$_4^{2-}$ ion is drawn at the calcite (10\textoverline{4}) surface lattice. In this suggested position, the triad axis of the CrO$_4^{2-}$ ion retains the orientation of the CO$_3^{2-}$ ion. The tetrahedron is oriented in such a way that one of the corner O atom is directly facing a Ca$^{2+}$ in the second layer.
Ave. $h_{10\overline{1}4} = -0.12 \pm 0.09 \, \text{Å}$

Symbols:
- Ca
- CO$_3$
- CrO$_4$

Figure 36: A schematic calcite lattice showing the measured position of the Cr atom in the chromate adion (intersecting point of the dash lines), as well as the proposed model for the adsorption structure of the CrO$_4$ ion, as explained in the text.
This orientation of the CrO$_4^{2-}$ ion in Fig. 36 was proposed based on considerations in its axial and lateral structures. Its lateral orientation is determined by the common three-fold symmetry about the triad axis as the CO$_3^{2-}$ ion; this is based on the argument already made for the orientations of the surface incorporated pyramidal ions in Chapter 6. The axial orientation is based on the speculation that a strong electrostatic force between the partially negatively charged O atom at the corner of the CrO$_4^{2-}$ ion and the positively charged Ca$^{2+}$ in the second layer will align the molecule so that the O atom is pointing toward the Ca$^{2+}$ ion.

In addition to CrO$_4^{2-}$, XSW experiments conducted on calcite (10$\overline{1}4$) surfaces that had been reacted in SeO$_4^{2-}$ and AsO$_4^{3-}$ solutions of $\sim$500 $\mu$M concentration had shown insignificant amount (< 0.02 ML) of adsorption of these anions. In the simulation of substitution of CO$_3^{2-}$ by the HPO$_4^{2-}$ ion on calcite, it was shown that HPO$_4^{2-}$ was energetically favored for incorporation at other surfaces than the (10$\overline{1}4$) surface [70]. This may be why the adsorption of the tetrahedral ion at the (10$\overline{1}4$) surface was very low in coverage.

The incorporation of the BO$_4$ ion in bulk calcite has also been detected by EXAFS studies of SeO$_4^{2-}$ impurities in bulk calcite. It was concluded from these experiments that SeO$_4^{2-}$ substituted CO$_3^{2-}$ in bulk calcite [71, 72].
Chapter 8

Summary

This thesis presents a survey of the atomic-scale structures of impurity ions incorporated at the calcite (1014) surface from dilute water solution. The cations included in this study are monoatomic cations that are related to the Ca\(^{2+}\) ion in calcite in that their carbonates are of either the calcite or the aragonite structures of CaCO\(_3\); these ions are Zn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) and Pb\(^{2+}\). The anions included in this study are molecular anions whose structural symmetries are related to the planar triangular structure of the CO\(_3^{2-}\) ion in calcite; these ions are the trigonal pyramidal SeO\(_3^{2-}\) and AsO\(_3^{3-}\) ions, and the tetrahedral CrO\(_4^{2-}\) ion.

Two common characteristics are observed in the local surface structures of the incorporated impurity cations. First, the in-plane first-neighbor distance between the impurity ion and its coordinating O atoms is the same as the first-neighbor cation-to-oxygen distance in the native carbonate of the cation. Second, the first-neighbor coordinating structure of the impurity is that of Ca\(^{2+}\) in calcite, i.e., the octahedral coordination.

The lattice sites of the surface incorporated cations show relaxation in the direction of the bulk. A model was constructed, in which this relaxation is taken to be due to the conservation of the cation-oxygen nearest-neighbor distance, and
due to the vertical bond asymmetry at the surface cation site.

For the surface incorporation of impurity pyramidal and tetrahedral anions, substitution of the surface $\text{CO}_3^{2-}$ ion occurs. It is further speculated that the orientation of the molecular impurity is determined by its charge distribution in relation to the incorporation site.

These atomic-resolution data provide the first structural evidence of ion substitution at the water-calcite interface. They provide a view of the structural properties of the calcite surface. Future work should extend these studies to in situ conditions, under a wide range of thermodynamic conditions.

The experimental techniques used in this investigation—XSW triangulation and SEXAFS—are a combination of complementary, sub-Angstrom resolution surface probes. This combination of techniques is particularly important in studying extrinsic impurity defect structures—both at the surface and in the bulk—of ionic crystals, since the coulombic field of the defect is of long range.
Bibliography


Appendix. SWAN: A computer program for X-ray standing wave data analysis

A Fortran program for analyzing Bragg-reflection XSW data was developed. The software, named SWAN (acronym for Standing Wave ANalysis), was to substantial extent developed on the basis of an earlier, simpler program, DARE, written by M. Bedzyk and J. Zegenhagen (1986).

SWAN performs executions for any crystal structure with a definable unit cell. The atomic scattering factors are calculated analytically using the method described in International Tables of X-ray Crystallography, Vol. 4, Section 2.2 [73]. The calculation of the anomalous corrections to atomic scattering factors is done by calling a Cromer-McMaster routine. In writing the subroutine for structure factor calculations, a similar routine by S. Brennan and P. Cowan [74] was referred to.

In scientific literature, Debye-Waller factors have been determined only for a limited number of crystals. Currently, SWAN calculates Debye-Waller factors from Debye temperatures using the formulation described in Ref. [75].

The main functions of SWAN are: (1) To calculate the monochromator and sample crystal reflectivity curves from dynamical diffraction theory, and to fit
the convolution of these two curves to experimental rocking curve data; (2) To fit
the theoretically calculated fluorescence yield function to experimental fluorescence
data, according to Eq. 8 (page 8). The flowchart diagrams describing the computing
algorithm for the rocking curve and fluorescence function calculations and fittings
are shown in Figs. 37 and 38, respectively. In addition to these main functions,
SWAN also calculates a set of useful physical parameters for a selected crystal
under dynamical diffraction condition, including the structure factors, electrical
susceptibility, ideal Darwin width, and extinction depths.

SWAN has been implemented as a user software on Power Macintosh. Currently
at version 1.8, the program is routinely used for analyzing Bragg-reflection XSW
data, and is frequently upgraded.

**Guide to .ctl file:**

The crystal structure data input file for SWAN is given the extension name ‘.ctl’; it
contains crystal lattice constants, Debye temperature, linear coefficients of thermal
expansion, and atomic coordinates in the unit cell. As an example, the .ctl file
for the hexagonal (R) calcite is given in Fig. 39. The following is a line-by-line
description of the .ctl file; unless specified, data are read format-free:

*Line 1:* Title of file (*Comment line*)

*Line 2:* $a, b, c, \alpha, \beta, \gamma$. (Crystal lattice constants in Å and degree, at 293 K.)

*Line 3:* Crystal Debye temperature (K).

*Line 4:* Linear coefficients of thermal expansion along principle axes, in $10^{-6}$/deg.

*Line 5:* $N \ N1 \ (N2 \ N3...NN)$. ($N$: Number of basis in the unit cell, $N1$: Num-
ber of atom types occupying the first basis,..., $NN$: Number of atom types
occupying the Nth basis.)

Line 6: Comment line.

Line (6+1): (Format specific: 2x, a4, 2x, i2, 2x, f5.3). Elemental symbol, (ionization state if ionized), atomic number, occupation fraction. (Write this line N1 times.)

Line (6+2): M (Number of atom sites for the current basis).

Line (6+2+1) to Line (6+2+M): x(1), y(1), z(1); x(2), y(2), z(2);...; x(M), y(M), z(M). (Atomic coordinates for the current basis.)

Continue with basis N2, N3,..., by repeating Line 6 through Line (6+2+M).

Guide to setting fitting parameters (rp):

The following is a description of the command-line inputs for setting fitting parameters in SWAN:

Number of iterations: Enter the number of iteration cycles to be performed before program terminates fitting. Usually 40 iterations is sufficient to reach the best fit. Default is zero.

Angular range (yfin): The angular range in units of rocking curve width to be used in convolution. Default is 2.5.

Convolution points (irf): The number of evenly spaced points over the range \(-2.5 \leq \eta \leq 2.5\) for which the emittance curve from the asymmetric monochromator is calculated. Range is 1–128; usually set at 40.
Number of points for dispersion spread (ndsp): Related to yfin and irf: ndsp = X(\text{irf} - 1)/(2yfin + X), where X = 2SS(1 - \tan \theta_h/\tan \theta_m)/(SD\omega_m). SS and SD are the source size and source distance.

Sample crystal asymmetry factor: Enter the asymmetry factor b for the sample crystal. Default is -1.

Beam polarization: Polarization of incident beam. Default is 1, for \sigma polarization.

Guide to rocking curve fit (r0) commands:

The following is a description of the command-line inputs for rocking curve fitting in SWAN:

Enter .da3 file name: Select in the pop-up dialog box the experimental rocking curve datafile.

Monochromator .ctl file name: Enter the .ctl file name for the monochromator crystal; this file must be located in the same directory as the executable program.

Monochromator reflection planes: Enter h, k, l, the Miller indices of the monochromator reflection.

Monochromator asymmetry factor: Enter the effective monochromator asymmetry factor b.

Incident X-ray energy: Enter the incident X-ray energy in keV.

Sample .ctl file name: Enter the .ctl file name for the sample crystal; the file must be located in the same directory as the executable program.
Sample reflection planes: Enter $h$, $k$, $l$, the Miller indices of the sample reflection.

Angular scan range: Set initial angular scan range, in $\mu$rad.

Sweep range fixed (y/n): Reply whether the angular range is to be fixed during fitting.

SWAN performs fitting, outputs best-fit parameter values: Angular range, Bragg angle, angular position at the lower limit of the angular range, and reflectivity.

Write .rcf file (y/n): Reply whether a .rcf output file from the rocking curve fit should be written; the .rcf file is a parameter file to be used in subsequent fluorescence yield fitting.

Guide to fluorescence yield fit (f1) commands:

The following is a description of command-line inputs for fluorescence yield fitting in SWAN:

Coherent fraction, step size: Enter coherent fraction, iteration step size.

Coherent position, step size: Enter coherent position, iteration step size.

Fit offset (y/n): Reply whether an off-set in the fluorescence yield is assumed.

Yield attenuation correction: (0): No attenuation correction, if fluorescence emission is from sample surface. (1): Attenuation for a uniform depth distribution in the crystal [$Y(\theta)$ is multiplied with the effective thickness $Z(\theta)$]. If (1), program will ask for fluorescence X-ray energy and take-off angle.

Enter .rcf file name: Select the proper .rcf file in pop-up dialog box.
Enter fluorescence data name: Select the experimental fluorescence yield datafile in pop-up dialog box.

SWAN performs fitting of the fluorescence yield, outputs best-fit parameter values: The off-Bragg fluorescence yield (the first parameter), coherent faction, and coherent position.
Figure 37: Flowchart diagram showing the algorithm for rocking curve calculation and fitting in SWAN.
Subroutine FOLD:
Calculates monochromator reflectivity.

Start F1

Keyboard: Enter initial F, P, iteration step-sizes.

Keyboard: Enter attenuation correction:
(0) Surface, (1) Infinite depth, (-1) Finite depth.

Keyboard: Enter Fluorescence X-ray Energy (EF), take-off angle.

Keyboard: Enter Depth.

Subroutine RFIFI:
Reads reflectivity information.

Subroutine DA3IN:
Reads fluorescence data file.

Subroutine FUMILI:
Fits fluorescence data.
Calculates \( \mu(\varepsilon_F) \).

Subroutine RDLAT:
Reads sample .ctl file.

Subroutine STRUFACT:
Calculates sample structure factor \( F(\varepsilon_F) \).

Output fitting parameters F, P.

Output graphics.

Output fit data file.

Subroutine DA3OUT:
Writes [fit].DA3 file.

Subroutine QKDRAW:

Return

Figure 38: Flowchart diagram showing the algorithm for fitting the fluorescence yield in SWAN.
CaCO₃ H
4.989 4.989 17.062 90.00 90.00 120.00
495.
-5.6  -5.6  25.0
3 1 1 1
Atoms in basis # 1 u=0.2593
ca 20 1.000
6
0.000 0.000 0.2500
0.000 0.000 -0.2500
0.6667 0.3333 0.5833
0.6667 0.3333 0.0833
0.3333 0.6667 0.9167
0.3333 0.6667 0.4167
Atoms in basis # 2
c 06 1.000
6
0.0000 0.0000 0.0000
0.0000 0.0000 0.5000
0.6667 0.3333 0.3333
0.6667 0.3333 0.8333
0.3333 0.6667 0.6667
0.3333 0.6667 0.1667
Atoms in basis # 3
o 08 1.000
18
0.2593 0.0000 0.0000
0.0000 0.2593 0.0000
-0.2593 -0.2593 0.0000
-0.2593 0.0000 0.5000
0.0000 -0.2593 0.5000
0.2593 0.2593 0.5000
0.9260 0.3333 0.3333
0.6667 0.5926 0.3333
0.4074 0.0740 0.3333
0.4074 0.3333 0.8333
0.4074 0.3333 0.3333
0.6667 0.0740 0.8333
0.9260 0.5926 0.8333
0.5926 0.6667 0.6667
0.3333 0.9260 0.6667
0.0740 0.4074 0.6667
0.0740 0.6667 0.1667
0.3333 0.4074 0.1667
0.5926 0.9260 0.1667

Figure 39: A sample .ctl file for SWAN for the hexagonal (R) calcite structure.