Nano-indentation of Cubic and Tetragonal Single Crystals

by

Qin Zhang

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Professor John C. Lambropoulos

Department of Mechanical Engineering
The College
School of Engineering and Applied Sciences

University of Rochester
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Curriculum Vitae

The author was born in Nanchang, Jiangxi providence, China on January 26, 1977. She attended high school at Jianggang High School and graduated in 1994. She enrolled at Hunan University in 1994 and finished her B.S. degree program in Engineering Mechanics in 1998. After graduation, she was hired by 602 Helicopter Research Institute and worked there as a design engineer for one year. She continued her graduate study at Hunan University and graduated with a Master’s degree in Engineering Mechanics in 2002.

In Fall 2002, she was accepted into the doctoral program at the University of Rochester under the supervision of Professor John C. Lambropoulos. She received her second Master’s degree in Mechanical Engineering from the University of Rochester in 2004.

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Abstract

Due to the nature of their material properties, Calcium Fluoride (CaF$_2$), Magnesium Fluoride (MgF$_2$), and Potassium Dihydrogen Phosphate (KDP) are widely used for industrial purposes. A better understanding of the mechanical properties of these materials is of technological and scientific importance. The indentation nano-mechanical response of CaF$_2$ (cubic), MgF$_2$ (tetragonal), and KDP (tetragonal) optical crystals were studied and compared by using nano-indentation tests and finite element simulation with a mesoplastic formulation. Appropriate values of material parameters were determined by correlating the load-displacement curves from numerical simulations with the corresponding experimental data. The effects of elastic anisotropy and crystallographic symmetry on the load-deflection curves, surface profiles, contact radius, hardness, stress distributions, and cleavage underneath the spherical indenter at two stages, namely at maximum indentation load and after the load has been removed were also examined.
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1 Introduction

Due to the nature of their material properties, Calcium Fluoride (CaF₂), Magnesium Fluoride (MgF₂) and Potassium Dihydrogen Phosphate (KDP) are widely used for optical instrumental applications. Their chemical, physical and optical properties have been thoroughly examined [1]. Some of those properties are displayed in Tables 1.1-1.2.

CaF₂ is an insoluble ionic compound that occurs naturally as the mineral fluorite. It adopts a cubic structure wherein calcium is coordinated to eight fluoride anions and each F⁻ ion is surrounded by four Ca²⁺ ions. CaF₂ has many important properties for industrial purposes such as a wide transmission range, low refractive index, high permeability, and low birefringence. It is widely used in the laser, infrared (IR), and ultraviolet (UV) optics applications. Some of these include mirrors, lenses, windows, and prisms. MgF₂ occurs naturally as the mineral sellaite. It is a tetragonal solid with the rutile structure. MgF₂ provides both a wide transparent range and a high transmissibility and is often used as an optical window transmitting from the vacuum ultraviolet (VUV) into the IR. It is also a birefringent material that supplies polarizing optics for the UV region. KDP is a transparent dielectric material best known for its nonlinear optical and electro-optical properties. It has been incorporated into various laser systems for harmonic generation and optoelectrical switching. Above its ferroelectric Curie
temperature (123 K), the crystal structure of KDP is tetragonal.

The mechanical properties of CaF$_2$, MgF$_2$, and KDP have also been examined due to the obvious scientific and technological significance. Evans and Pratt investigated the structures of dislocations of CaF$_2$ and measured the temperature dependence of the dislocation density [2]. Boyarskaya et al. studied the dislocation structures produced by pyramid indentation on the (111) surface of CaF$_2$ [3]. It was found that the form of the profiles of dislocation rosettes on the (111) cleavage planes alters with the orientation of these planes relative to the indentations. Using transmission electron microscopy (TEM), Sherry and Sande examined the work hardening behavior of CaF$_2$ at 2000°C, 3000°C, and 4000°C under uniaxial compression [4]. Also, the effect of the temperature of deformation and the crystallographic orientation of the compression axis on the deformation behavior were analyzed. Munoz et al. studied the slip systems of CaF$_2$ with various orientations deformed by compression between 200°C and 6000°C [5]. It was found that {100} family planes are the easiest to activate and {110} are the most difficult. Speziale and Duffy measured the second-order elastic constants of CaF$_2$ under various pressures ranging up to 9 GPa at 200°C [6]. Their calculations showed the elastic constants increased linearly with the pressure. A recent review by Ladison et al. has summarized mechanical properties of CaF$_2$ from microindentation tests, elastic moduli measurement, and cleavage [7].

The optical performance of CaF$_2$ is highly correlated to its surface quality. For instance, Stenzel et al. investigated laser damage behavior of CaF$_2$ under various polishing steps [8]. As opposed to conventional hard polish, advanced methods, such as ductile machining or chemical polishing, lead to a distinct increase in its damage threshold. Using optical interferometry and atomic force microscopy (AFM), Retherford et al. examined the effect of surface quality on transmission performance for the (111) surface of CaF$_2$ [9]. Their results showed that improved surface quality and lower subsurface damage could lead to a greater increase in
transmittance. Kukleva et al. measured the dependence of the coefficient of specular light reflection on the surface roughness for the (100), (110), and (111) planes of CaF$_2$ [10]. Their calculations showed the specular reflection coefficient increased for smoother surfaces.

To thoroughly exploit its optical characteristics, a great deal of effort has been devoted to investigating the mechanical properties of CaF$_2$ during its surface finishing process to produce high quality finished parts. For example, the finished surface characteristics and polishing parameters of CaF$_2$ under different methods such as magnetorheological finishing (MRF), single-point diamond turning (SPDT), ultra-precision float polishing, and ultra-precision grinding have been examined and compared [11; 12; 13; 14]. It was found that microfracturing and crystallographic anisotropy are the main factors affecting surface preparation. Structural defects, such as dislocations, are usually generated during material removal. Crack propagation is then initiated at such defects. In addition, the mechanisms of microfracturing and material removal are both shown to be dependent on the crystalline orientation of the work surface. Kukleva et al. measured the microhardness, grinding hardness, and tensile strength for the (100), (110), and (111) planes of CaF$_2$ and the effects of the anisotropy of these physical and mechanical properties of CaF$_2$ on the shape accuracy of a polished surface were investigated [10]. Yan et al. examined the crystallographic effects of CaF$_2$ in micro/nano-machining [15]. The finished surface texture and microfracturing mechanism were found to differ significantly with crystalline orientation. Such research [10; 11; 12; 13; 14; 15] suggests that the crystallographic anisotropy affects the machined surface roughness and subsurface damage of CaF$_2$ by affecting the degrees of slip deformation and cleavage fracture.

Compared with CaF$_2$, there is a much smaller body of work concerning the mechanical behavior of MgF$_2$. Kandil et al. measured the six independent elastic constants of MgF$_2$ over the temperature range 4.2-300K [16]. Negative tempera-
ture dependences were observed for all six constants. Davies measured ultrasonically the elastic moduli of MgF$_2$ under various pressures ranging up to 7 kbars [17]. Barber examined single crystals of MgF$_2$ by means of chemical etching and optical and electron microscopy [18]. In as-grown crystals, dislocations were found decorated with impurity particles. Also, low temperature dislocation glide was observed to proceed by shear in the favor of $<100>$ directions on {110} planes. Mecholsky et al. analyzed the crack branching patterns in MgF$_2$ disks by using the fractal geometric approach [19]. Swab and Quinn characterized stable crack extension of MgF$_2$ around Knoop indentation surface cracks [20]. They suggested that the crack growth is initiated by indentation-induced residual stresses. Using high pressure X-ray diffraction, Haines et al. examined the structures and phase transitions in MgF$_2$ [21]. The transition from the tetragonal rutile-type to an orthorhombic phase was observed at 9.1 GPa and followed by the transformation to the cubic phase at near 14 GPa.

As a prominent material in optical applications, it is essential to understand the mechanical behavior of MgF$_2$ during surface preparation in order to improve its optical performance. MgF$_2$ is relatively hard and usually shaped with diamond tools. Reichling et al. investigated ablation thresholds and damage behavior of MgF$_2$ prepared by diamond turning [22]. They suggested that damage and ablation are determined by local surface imperfections.

The mechanical properties of KDP have previously been studied by using indentation experiments. Fang and Lambropoulos measured the Vickers and Knoop micro-hardness of KDP and the resulting cracking on (100) and (001) faces [23]. They reported the anisotropy of the hardness and the crack sizes among these faces. The fracture toughness was also extracted by assuming elastic and plastic isotropy. Kucheyev et al. studied the deformation behavior of KDP under spherical nano-indentation [24]. Multiple “pop-in” events were observed during loading portion in the load-displacement curves. They suggested that slip is the
major mode of plastic deformation in KDP and pop-in events are caused by the initiation of slip. Guin et al. examined the mechanical properties of KDP by the methods of uniaxial compression, selective etching, and indentation [25]. They observed plasticity of KDP by indentation at room temperature and identified two types of slip systems in KDP. The first system consists of slip planes \{110\}, \{101\}, \{112\}, and \{123\}, with a common Burgers vector, \( <111>/2 \). The other slip system was identified as \{010\} \( <100> \). Shaskolskaya et al. estimated the microhardness, microbrittleness, and microstrengh of KDP with the aid of Vickers microindentation [26]. Chen et al. studied the critical condition of brittle-ductile transition of KDP by carrying out Vickers indentation on the surface (001) with various loads and various orientation angles [27]. The experimental results by AFM showed strong anisotropy and suggested that at load small enough, KDP may only generate ductile deformation (plastic dent). These observations were then used to analyze the influence factors on the surface quality of crystal KDP in SPDT.

Indentation experiments are a useful tool for evaluating a variety of mechanical properties of solids. This is especially true for brittle solids. Current technology allows indentation experiments to be carried out with the load as low as a few \( \mu N \). Therefore, it is possible to obtain material characterization at sub-micrometer scale by nano-indentation. On the other hand, surface preparation, for example by grinding or polishing, involves a sequence of micro-indentation and micro-scratching effects [9]. Accordingly, the examination of indentation behavior of CaF\(_2\), MgF\(_2\), and KDP not only provides a better understanding of their mechanical properties, but also their performance during surface preparation.

Semi-empirical analyses of indentation mechanics have received extensive attention. Oliver and Pharr established the relationships between material properties (elastic modulus, hardness, etc.) and their corresponding load-displacement curves for isotropic materials [28]. Another common technique is to use numerical
methods such as FEM and molecular dynamics (MD) simulations to investigate the indentation related material properties and phenomena (fracture, dislocation nucleation, microstructure evolution, etc.) [29; 30]. To date, however, a systematic study of the mechanical properties of CaF$_2$, MgF$_2$, and KDP under indentation, and specifically nano-indentation has not been reported. The object of this work is to provide such an investigation using FEM methods and nanoindentation tests.

FEM simulation is often used to supplement experimental methods in the study of material properties under indentation. The undefined material parameters are usually obtained as input parameters in the FEM simulation by fitting the simulated load-displacement curves to the experimental data. As a result, the indentation mechanics and material performance can be effectively examined. With the appropriate material constitutive laws, FEM simulation can model material behavior in multiple length scales. There are two general approaches used to study plasticity: macroplasticity and microplasticity. Macroplasticity is based on classical continuum mechanics which relies on empirical assumptions for different material response. Microplasticity analysis, however, is linked with detailed material deformation mechanisms and micro-structural parameters. This allows for microplasticity techniques to distinguish various plastic deformation mechanisms on a microstructural level. Mesoplasticity is introduced as a combination of solid mechanics and material science. It provides a connection between the continuum-based macroplasticity and the physical theory of microplasticity.

Plastic deformation of crystalline materials generally takes the form of crystalline slip with dislocations gliding along the corresponding slip systems. To investigate the effects of its crystalline anisotropy and the underlying dislocation evolution, a mesoplastic formulation with the length scale of crystalline slip is a suitable approach. A systematic study on the mesoplasticity of single crystals originates from the historic works of Taylor and Elam [31]. It was here where plastic slip along various orientations was first observed and examined. A mathe-
matical description of the constitutive relations of mesoplasticity for single crystals is provided by Hill [32] and Hill and Rice [33]. These mesoplastic formulations can be coded into FEM programs and have been used to solve complex problems. For instance, Peirce et al. analyzed the nonuniform and localized deformation in ductile single crystals subject to tensile loading [34], Yoshino et al. investigated the dislocation generation and propagation during indentation of a single-crystal silicon [35], Liu et al. examined the mechanical behavior of single crystal copper under spherical indentation [36], and Wang et al. studied the dependence of nano-indentation pile-up patterns and of microtextures on the crystallographic orientation of copper single crystals [37].

In this paper, the mechanical properties of CaF$_2$, MgF$_2$, and KDP under spherical indentation were investigated in detail by using nano-indentation tests and finite element method with a mesoplastic formulation. The mesoplastic constitutive laws were implemented as a user-material subroutine in ABAQUS/Standard [38]. Indentation on the main crystallographic planes: (100), (110), and (111) of CaF$_2$; (001), (101), and (111) of MgF$_2$; (100) and (001) of KDP was analyzed. Appropriate values of material parameters were determined by correlating the load-displacement curves from numerical simulations with the corresponding experimental data. We have examined the effects of crystallographic anisotropy on the load-deflection curves, surface profiles, contact radius, spherical hardness, stress distributions, and cleavage at two stages, namely at maximum indentation load and after the load has been removed. Our model results are compared with available experimental observation of surface microroughness, subsurface damage, and material removal rate in grinding. This provides a better understanding of microfractures and crystalline anisotropy of these materials, and their effect on the surface quality during manufacturing.
### Table 1.1 Chemical/physical/optical properties of CaF$_2$ [1]

<table>
<thead>
<tr>
<th>Properties</th>
<th>CaF$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(Chemical)</strong></td>
<td></td>
</tr>
<tr>
<td>Crystal system/structure</td>
<td>Cubic/Fluorite</td>
</tr>
<tr>
<td>Lattice constant (Å$^0$)</td>
<td>5.46</td>
</tr>
<tr>
<td>Color</td>
<td>Colorless</td>
</tr>
<tr>
<td><strong>(Physical)</strong></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>2.329(25°C)</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1360</td>
</tr>
<tr>
<td>Thermal conductivity (cal/cm sec°C)</td>
<td>2.32E-2 (36°C)</td>
</tr>
<tr>
<td>Thermal expansion (°C)</td>
<td>24E-6(20～60°C)</td>
</tr>
<tr>
<td>Specific heat (cal/g°C)</td>
<td>0.204(0°C)</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>6.76 (1MHz)</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>75.8</td>
</tr>
<tr>
<td>Shear modulus (GPa)</td>
<td>33.77</td>
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<tr>
<td>Bulk modulus (GPa)</td>
<td>88.41</td>
</tr>
<tr>
<td>Rupture Modulus (MPa)</td>
<td>36.5</td>
</tr>
<tr>
<td>Hardness (Knoop Number)</td>
<td>160&lt;110&gt;, 178&lt;100&gt;</td>
</tr>
<tr>
<td>CRSS (critical shear stress, MPa)</td>
<td>15</td>
</tr>
<tr>
<td>Apparent elastic limit (MPa)</td>
<td>36.54</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.26</td>
</tr>
<tr>
<td>Cleavage plane</td>
<td>(111)</td>
</tr>
<tr>
<td>Elastic coefficient (GPa)</td>
<td>164/53/34</td>
</tr>
<tr>
<td>C11/C12/C44</td>
<td></td>
</tr>
<tr>
<td>Solubility index (number of grams for 100g of water)</td>
<td>0°C 1.31E-3, 20°C 1.51E-3</td>
</tr>
<tr>
<td><strong>(Optical)</strong></td>
<td></td>
</tr>
<tr>
<td>Reflection loss (for 2 surfaces)</td>
<td>5.6% (4µm)</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.39908 (5µm)</td>
</tr>
<tr>
<td>Transmission range (µm)</td>
<td>0.13～12.0</td>
</tr>
<tr>
<td>Reststrahlen Peak (µm)</td>
<td>35</td>
</tr>
<tr>
<td>Absorption coefficient (cm$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>dN/dT (°C)</td>
<td>-10.6E-6</td>
</tr>
</tbody>
</table>
### Table 1.2 Chemical/physical/optical properties of MgF₂ and KDP [1]

<table>
<thead>
<tr>
<th>Properties</th>
<th>MgF₂</th>
<th>KDP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(Chemical)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal system/structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Lattice constant ($\text{Å}^0$)</td>
<td>$a=4.64$, $c=3.06$</td>
<td>$a=7.453$, $c=6.975$</td>
</tr>
<tr>
<td><strong>(Physical)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density ($\text{g/cm}^3$)</td>
<td>3.18(25°C)</td>
<td>2.34(25°C)</td>
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<tr>
<td>Melting point (°C)</td>
<td>1255</td>
<td>252</td>
</tr>
<tr>
<td>Thermal conductivity (W/m/K)</td>
<td>0.3 at 300K</td>
<td>-</td>
</tr>
<tr>
<td>Thermal expansion (/K)</td>
<td>13.7E-6(para)</td>
<td>48E-6(perp)</td>
</tr>
<tr>
<td>Specific heat (J/kg/K)</td>
<td>920</td>
<td>-</td>
</tr>
<tr>
<td>Dielectric constant at 1MHz</td>
<td>4.87 (para)</td>
<td>5.45 (perp)</td>
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<tr>
<td>Young’s modulus (GPa)</td>
<td>138.5</td>
<td>33.0</td>
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<tr>
<td>Shear modulus (GPa)</td>
<td>54.66</td>
<td></td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>101.32</td>
<td>19.8</td>
</tr>
<tr>
<td>Rupture Modulus (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness (Knoop Number)</td>
<td>415</td>
<td></td>
</tr>
<tr>
<td>Apparent elastic limit (MPa)</td>
<td>49.6</td>
<td></td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.276</td>
<td>0.3</td>
</tr>
<tr>
<td>Cleavage axis</td>
<td>C- axis</td>
<td></td>
</tr>
<tr>
<td>Elastic coefficient (GPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{11}/C_{12}/C_{33}/C_{44}/C_{13}/C_{66}$</td>
<td>140/89/205/57/63/96</td>
<td>72/-6.3/56.4/12.5/15/6.2</td>
</tr>
<tr>
<td>Solubility index</td>
<td>0.0002g (100g water)</td>
<td></td>
</tr>
<tr>
<td>Solubility in acids</td>
<td>Soluble</td>
<td></td>
</tr>
<tr>
<td>Solubility in organic solvents</td>
<td>Unsoluble in alcohol</td>
<td></td>
</tr>
<tr>
<td><strong>(Optical)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reflection loss (2 surfaces)</td>
<td>5.2% (0.6µm)</td>
<td></td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.37608 (0.7µm)</td>
<td>1.494(para) 1.46(perp) at 1.064µm</td>
</tr>
<tr>
<td>Transmission range (µm)</td>
<td>0.13-7.0</td>
<td>0.2-1.5</td>
</tr>
<tr>
<td>Optical spectral range (mkm)</td>
<td>0.25-1.7</td>
<td></td>
</tr>
<tr>
<td>Reststrahlen Peak (µm)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Absorption coefficient (cm⁻¹)</td>
<td>0.04 (0.27µm)</td>
<td>0.03</td>
</tr>
<tr>
<td>Optical damage threshold (GW/cm²)</td>
<td>5 ($\lambda=1.064\mu$m, $\tau=10\text{ns}$)</td>
<td></td>
</tr>
<tr>
<td>Nonlinear coefficient (pm/V)</td>
<td></td>
<td>D36=0.44</td>
</tr>
<tr>
<td>Electro-optical coefficients (pm/V)</td>
<td></td>
<td>R41=8.8, R63=10.3</td>
</tr>
<tr>
<td>$dN/dT$ (/°C)</td>
<td>2.3 (parallel)</td>
<td>1.7E-6 (perp) at 0.4µm</td>
</tr>
<tr>
<td>$dN/d\mu=0$</td>
<td>1.4µm</td>
<td></td>
</tr>
</tbody>
</table>
2 Formulation of Crystal Plasticity

2.1 Meso-plasticity for single crystals

For crystalline materials, plastic deformation generally takes the form of crystalline slip with dislocations gliding along corresponding slip systems. Each slip system is described by two vectors, the unit normal to the slip plane \( m \) and the unit vector \( s \) in the slip plane along the slip direction.

A mathematical description of the constitutive relations of meso-plasticity for single crystals is provided by Hill, and Hill and Rice based on the pioneering work of Taylor and Elam [31; 32; 33]. A comprehensive account of reviews and contributions to this area can be found in Asaro, Peirce, and Needleman [39; 40; 41; 42]. For this reason, we present only a brief overview of the theory.

A mathematical description of the kinematics and constitutive relations usually begins with the computation of the velocity gradient \( L (= \partial v / \partial x) \) which can be expressed

\[
L = \dot{F} \cdot F^{-1}.
\] (2.1)

Here \( F \), the deformation gradient, has the well-known decomposition formula

\[
F = F^* \cdot F^p
\] (2.2)
where $F^p$ denotes plastic deformation corresponding to the material flow caused by plastic slip motion on its active slip systems and $F^*$ represents the lattice distortion and rotation caused by elastic straining and rigid body rotation. It is assumed that the lattice configuration and the elastic properties are unaffected by plastic slip. The plastic deformation for a single crystal can be expressed as

$$F^p = 1 + \sum_{\alpha=1}^{n} \gamma^\alpha s^\alpha m^\alpha$$

(2.3)

where superscript $\alpha$ denotes different slip systems, $\gamma^\alpha$ represents the amount of shear along the slip system $(m^\alpha, s^\alpha)$, and $n$ denotes the number of active slip systems. An alternate expression for the second rank tensor $L$ is provided by the sum

$$L = D + \Omega$$

(2.4)

where $D$ represents the symmetric deformation rate and $\Omega$ the skew-symmetric spin tensor. From equations (2.1) and (2.2), $D$ and $\Omega$ can be further decomposed into their elastic and plastic parts as follows:

$$D = D^* + D^p$$

(2.5)

and

$$\Omega = \Omega^* + \Omega^p.$$  

(2.6)

Using equations (2.3) and (2.4), the plastic parts of $D$ and $\Omega$ can be related to the plastic shear rates along corresponding slip systems (denoted $\dot{\gamma}^\alpha$ for $\alpha = 1, \ldots, n$) by

$$D^p = \sum_{\alpha=1}^{n} \mu^\alpha \cdot \dot{\gamma}^\alpha$$

(2.7)

and

$$\Omega^p = \sum_{\alpha=1}^{n} \omega^\alpha \cdot \dot{\gamma}^\alpha.$$  

(2.8)

The dependence of the second rank symmetric tensor $\mu^\alpha$ and skew-symmetric tensor $\omega^\alpha$ on the current slip system $\alpha$ of the single crystal is now given by

$$\mu^\alpha = \frac{(s^\alpha m^\alpha + m^\alpha s^\alpha)}{2}$$

(2.9)
and
\[ \omega^\alpha = (s^\alpha m^\alpha - m^\alpha s^\alpha)/2. \quad (2.10) \]

This, when combined with the above, provides a description of the kinematics formulation of meso-plasticity for single crystals up to the choice of the current slip system vectors \( m \) and \( s \).

An accessible form of the constitutive relations can be derived from the rate-form equation for the elastic distortion of crystal lattice
\[ \dot{\sigma}^* = C : D^*. \quad (2.11) \]

Here \( C \) is the fourth rank lattice elasticity tensor and \( \dot{\sigma}^* \) is the Jaumann rate of Kirchhoff stress which rotates with the crystal lattice. Specifically,
\[ \dot{\sigma}^* = \dot{\sigma} - \Omega^* \cdot \sigma + \sigma \cdot \Omega^* \quad (2.12) \]

where \( \dot{\sigma} \) is the ordinary time rate of the Kirchhoff stress. In contrast, the Jaumann rate of Kirchhoff stress that rotates with the material is given by
\[ \dot{\sigma} = \dot{\sigma} - \Omega \cdot \sigma + \sigma \cdot \Omega. \quad (2.13) \]

Combining equations (2.11)-(2.13) and expressing \( D^* \) and \( \Omega^* \) in terms of \( D \) and \( \Omega \) using equations (2.5) and (2.6), it can now be obtained that
\[ \dot{\sigma} = C : \left\{ D - \sum_{\alpha=1}^{n} \left\{ \mu^\alpha + C^{-1} : (\omega^\alpha \cdot \sigma - \sigma : \omega^\alpha) \right\} \dot{\gamma}^\alpha \right\}. \quad (2.14) \]

From this, the constitutive relations of single crystals are completely defined provided that the plastic shear rates \( \dot{\gamma}^\alpha \), for \( \alpha = 1, \ldots, n \), are known. The choice of the plastic shear rates can lead to either a rate-independent or rate-dependent formulation.
2.2 Finite element simulation

Three dimensional FEM indentation models for the corresponding crystallographic planes of CaF$_2$, MgF$_2$, and KDP were created using ABAQUS/Standard 6.3. For a conical indenter with a flank angle of 90 degrees and 10 $\mu$m tip radius which was later used for CaF$_2$ and MgF$_2$ indentation experiments, the material essentially contacts with its spherical tip up to the depth of 2 $\mu$m. This depth is much above the maximum indentation depth under the various external loads for both materials. Thus, for simplicity, a spherical indenter with radius of 10 $\mu$m was used in the simulation for these two materials. For KDP, a spherical indenter with radius of 1 $\mu$m was used in the simulation to match the indentation test done by Kucheyev et al.[24]. A major concern for the simulation accuracy and efficiency is modeling the semi-infinite body. Due to the crystalline symmetry, planes (100)/(110)/(111) of CaF$_2$ have four-, two-, and three-fold rotational symmetry, respectively. Because of the reflection symmetry within each rotational section, one-eighth (or 45 degrees) of the indented body, which was modeled as cylinder, was numerically analyzed for (100) plane indentation, and one-fourth (90 degrees) and one-sixth (60 degrees) of the indented body were used for the (110) and (111) planes indentation, respectively. On the other hand, planes (100)/(001)/(101)/(111) of MgF$_2$ and KDP have two-, four-, two-, and zero-fold rotational symmetry, respectively. Therefore, one-fourth (90 degrees), one-eighth (45 degrees), one-fourth, and half (180 degrees) of the indented body were used for the (100), (001), (101) and (111) planes indentation, respectively. As an illustration, the entire domain of (111) plane indentation of CaF$_2$ and the ABAQUS analysis coordinate system are displayed in Figure 2.1(a). For all three plane indentations, the radius of the indented body is 100 micron and the height is 50 micron. The indented body is bounded by five characteristic surfaces, labeled as surfaces I-V. Surface I is the indented surface. The surfaces II-IV can only displace in their own planes. The cylindrical surface V is traction free. The indentation simulations were made...
along the $y$-direction. For CaF$_2$ with a cubic structure, this is also the [100], [110], and [111] direction for the (100), (110), and (111) crystallographic plane indentation, respectively (Figure 2.2). Whereas for MgF$_2$ and KDP with a tetragonal structure whose crystallographic direction is not perpendicular to a plane having the same indices, this direction is the [100], [001], [c 0 a], and [c c a] direction for the (100), (001), (101), and (111) crystallographic plane indentation, respectively (Figure 2.3). Figure 2.1(b) shows the detailed mesh at the region of contact ($x-y$ plane). Approaching the region of contact, a refined mesh was generated in order to obtain the convergent contact solution.

Three dimensional isoparametric linear brick elements were used to discretize the half-space. During the simulation, 2720 elements, 3536 elements, 5440 elements, and 10880 elements were used in the CaF$_2$ (100)/MgF$_2$ (001)/KDP (001), CaF$_2$ (111), CaF$_2$ (110)/MgF$_2$ (101)/KDP (100), and MgF$_2$ (111) plane indentation, respectively. The size of the smallest elements is 0.125 micron. Four FEM models for the corresponding crystallographic planes with this mesh density were verified to be sufficiently precise to represent the semi-infinite body and to converge to the right solutions. This was done by comparing the numerical results of the elastic pressure distribution underneath the spherical indenter with Willis’ analytical solution [43]. The spherical indenter was described by an analytical rigid surface with infinite modulus as provided by ABAQUS. Therefore no discretization was necessary for the rigid indenter. The contact between the indenter and material was modeled as frictionless. In this calculation, the vertical displacement was applied to the reference node of the analytical rigid surface until the maximum indentation depth was attained. The indentation force can be obtained by calculating the reaction force at the reference node.
2.2.1 Numerical Model for CaF$_2$

CaF$_2$ has a cubic structure with three main orientations: (100), (110), and (111). This leads to its anisotropic material properties. Three elastic stiffness constants $C_{11}$, $C_{12}$, and $C_{44}$ are needed to define the material behavior. These are taken to be 168.16 GPa, 48.54 GPa and 33.81 GPa, respectively [6; 44]. Unlike isotropic materials, the Young’s modulus $E$ is dependent on direction. Its values along <100>, <110>, and <111> directions are 168.2 GPa, 142.2 GPa, and 133.5 GPa, respectively, and the anisotropic constant $A = 2C_{44}/(C_{11} - C_{12}) = 0.56$ (it is 1.0 for isotropic solids). This shows that for CaF$_2$, <100> direction is the stiffest, while <111> direction is the most compliant.

The elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ were used to analyze the (100) plane indentation. The study of the (110) and (111) planes necessitates an appropriate coordinate transformation

$$C'_{ijkl} = a_{im} \cdot a_{jn} \cdot a_{ko} \cdot a_{lp} \cdot C_{mnop}$$

(2.15)

where $C'_{ijkl}$ and $C_{mnop}$ correspond to the elastic stiffness matrix (fourth rank elastic tensor in equation (2.11)) and the $a_{ij}$ represent the direction cosines of axes ($a_{11} = o_{x1}' \cdot o_{x1}, a_{12} = o_{x1}' \cdot o_{x2}$, etc.). The tensor symmetry allows the transformation process to be reduced to twenty-one independent transformation equations, each composed of twenty-one terms.

At room temperature (23°C), CaF$_2$ has six crystallographic slip systems defined by the 100 family of slip planes along the <110> family of slip directions [5]. This was used to study the (100) plane indentation. The analysis of the (110) and (111) planes requires a coordinate transformation of the crystallographic slip directions and the unit normal to each slip plane using

$$m^{\alpha'}_i = a_{ij} \cdot m^{\alpha}_j$$

(2.16)

and

$$s^{\alpha'}_i = a_{ij} \cdot s^{\alpha}_j.$$  

(2.17)
Here the direction cosines $a_{ij}$ correspond to equation (2.15).

The shear rates of corresponding slip systems in the constitutive equations were represented by the rate-dependent power-law relation \[45\]

$$\dot{\gamma}^\alpha = \dot{\gamma}_0^\alpha \left| \tau^\alpha / g^\alpha \right|^{(1-\mu)/\mu} \left( \tau^\alpha / g^\alpha \right).$$

(2.18)

Here $\dot{\gamma}^\alpha$ denotes a reference shear strain rate and the exponent $\mu$ characterize the rate sensitivity (varying from zero to one). $\tau^\alpha$ and $g^\alpha$ represent the Schmid resolved shear stress and the current shear strength in the slip system $\alpha$. The Schmid resolved shear stress is given by the relation

$$\tau^\alpha = m^\alpha \cdot \sigma \cdot s^\alpha$$

(2.19)

where $\sigma$ is the Kirchhoff stress (equations (3.11)-(3.14)). The evolution of $g^\alpha$ is governed by the formula

$$g^\alpha = g_{\text{int}} + h_\alpha \dot{\gamma}^\alpha$$

(2.20)

where $g_{\text{int}}$ is the initial value of the shear strength and $h_\alpha$ is the self-hardening coefficient. The initial value of the shear strength and the self-hardening coefficient were assumed to be the same in all slip systems.

### 2.2.2 Numerical Model for MgF$_2$

As a tetragonal material, MgF$_2$ is anisotropic and six elastic stiffness constants $C_{11}, C_{12}, C_{13}, C_{33}, C_{44}$, and $C_{66}$ are needed to define its elastic behavior. These are taken to be 140.22 GPa, 89.50 GPa, 62.9 GPa, 204.65 GPa, 56.76 GPa, and 95.7 GPa, respectively\[16\]. The study of the (001), (101) and (111) planes of MgF$_2$ necessitates an appropriate coordinate transformation for these elastic constants in the ABAQUS analysis system (Figure 2.1(a)) by using equation (2.15).

At room temperature ($23^\circ$C), MgF$_2$ has six crystallographic slip systems defined by the \{110\} family of slip planes along the <001> family of slip directions
Notice that the directions in the crystallographic system might not be the same as those in the ABAQUS analysis coordinate system due to the tetragonal structure of MgF$_2$. For example, the crystallographic direction [101] is in fact the direction [$a\ 0\ c$] in the analysis coordinate system. The study of the (001), (101), and (111) planes of MgF$_2$ requires a coordinate transformation of the slip directions and the unit normal to each slip plane in the analysis system using equations (2.16) and (2.17).

The shear rates of corresponding slip systems in the constitutive equations of MgF$_2$ were taken to be the same as equations (2.18)-(2.20) with the assumptions that the initial value of the shear strength and the self-hardening coefficient were the same for all slip systems.

### 2.2.3 Numerical Model for KDP

Similar as MgF$_2$, KDP has a tetragonal crystal structure. The six elastic stiffness constants $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$, and $C_{66}$ for KDP are taken to be 71.65 GPa, -6.27 GPa, 14.94 GPa, 56.40 GPa, 12.48 GPa, and 6.21 GPa, respectively[25]. At room temperature (23°C), two types of slip systems were identified in KDP. The first system consists of slip planes {110}, {101}, {112}, and {123}, with a common Burgers vector, $<111>/2$. The other slip system was identified as {010} $<100>$ [25]. The study of the (100) and (001) planes of KDP necessitates an appropriate coordinate transformation for the elastic constants, the slip directions and the unit normal to each slip plane in the ABAQUS analysis system using equations (2.15)-(2.17).

The shear rates of slip systems in the constitutive equations and the assumptions about the initial shear strength and the self-hardening coefficient follow the analysis of CaF$_2$ and MgF$_2$ in the previous sections.
Figure 2.1 FEM model. (a) Entire FEM domain for (111) plane indentation of CaF$_2$ and ABAQUS analysis coordinate system. (b) Detail of the mesh at the region of contact.
Figure 2.2 Crystallographic planes of CaF$_2$ and ABAQUS analysis coordinate system.
Figure 2.3 Crystallographic planes of MgF$_2$ / KDP and ABAQUS analysis coordinate system.
3 Load-displacement for CaF$_2$

3.1 Nano-indentation Experiments

3.1.1 Material

Three oriented crystallographic faces of CaF$_2$ (100), (110), and (111) were chosen for the nano-indentation experiments. These faces were grown and cut to specific orientations (ISP Optics, Irvington, N.Y.). Following polishing to optical standards, the samples were examined in a Zygo NewView 5000 white light interferometer (Zygo Corp., Middlefield, C.T.). The RMS (measured surface roughness) averaged among 3 measures of (100)/(110)/(111) faces are 0.18 nm, 0.35 nm, and 0.26 nm, respectively. Such values of surface roughness are representative of high precision optical-quality polishing.

3.1.2 Experiment

Nano-indentation experiments were performed on three crystallographic planes (100)/(110)/(111) of CaF$_2$. These experiments were carried out using a nano-indentation Instruments II (Nano Instruments, Inc., Oak Ridge, Tennessee). This instrument has a displacement resolution of 0.04 nm and load resolution of 50
nN. The experiments were performed at room temperature (23°C). The indenter is conical with a 90 degrees included angle blending tangentially with a spherical tip of 10 \( \mu m \) radius. Load-deflection curves with maximum loads of 5 \( mN \), 10 \( mN \), and 15 \( mN \) obtained from experiments are shown in Figure 3.1. For the trial with a maximum load of 10 \( mN \), the case we simulated using finite elements, the indentation depths of (100)/ (110)/ (111) crystallographic planes are 96 \( nm \), 102 \( nm \), and 126 \( nm \), respectively.
3.2 Numerical Results for Uniaxial Compression

To facilitate the numerical simulation of the constitutive laws for the three crystallographic planes of CaF$_2$, the explicit relations derived in the previous chapter were coded into the user material subroutine UMAT provided by ABAQUS. Two simple cases, free uniaxial compression and constrained uniaxial compression, were used to test the user material subroutine. Both cases were simulated using a single 8-node 3D solid element. The material was first compressed to a maximum strain $\varepsilon_{yy}^{\text{max}} = -0.05$ and then pulled back to zero strain. The elastic stiffness constants and slip systems were chosen to correspond to the (110) crystallographic plane of CaF$_2$ under ABAQUS analysis coordinate system (Figure 2.1(a)). In the simulation, the reference shear strain rate $\dot{\gamma}_{0}^\alpha$ was taken to be 0.001 s$^{-1}$ and the rate sensitivity exponent $\mu$ was taken to be 0.05. The choice of the values of these two constants are commonly used for the mesoplasticity formulation (see, for instance, [35; 36; 37]). Two sets of the material parameters, 80/120 MPa (initial shear strength/self-hardening coefficient) and 110/100 MPa, were used for comparison. The choice of these material parameters will be further discussed in the following section, where we will demonstrate that such parameters indeed describe the mesoplastic deformation of CaF$_2$.

The stress strain relationships from the numerical simulations are shown in Figures 3.2 and 3.3. For both cases, the relations between axial stress $\sigma_{yy}$ and axial strain $\varepsilon_{yy}$ are displayed. It can be observed that the material behaves harder for the case of constrained compression due to the surrounding material constraining the deformation. Since the material is anisotropic, the transverse terms of stress and strain (if they exist) will be different. For simplicity, in the case of free compression ($\sigma_{xx} = \sigma_{zz} = 0$), only the transverse strain $\varepsilon_{zz}$ versus the axial strain is displayed. Similarly, for constrained compression ($\varepsilon_{xx} = \varepsilon_{zz} = 0$), only the transverse stress $\sigma_{xx}$ versus the axial strain is shown. Mathematica computations
were used to verify that the FEM results were in strong agreement with easily derived analytical solutions.

3.3 Numerical Results for Nano-indentation

Before applying the user material subroutine to the nano-indentation problems, the simulation of (100) plane indentation using one-eighth (45 degrees) of the indented body and full (360 degrees) indented body were compared to verify that the FEM models can capture the material symmetries. To investigate the sensitivity of mesh size on the convergence of the numerical solution, the three additional mesh lengths of 0.1 micron, 0.15 micron, and 0.25 micron were tested for the model of (100) plane indentation and compared to the result of the mesh length of 0.125 micron. The deviations of the load-displacement curves from the 0.1 micron and 0.15 micron cases were within 5% of the curve obtained from the 0.125 micron case. For the 0.25 micron mesh size, the deviation of the results was 11%.

The combined FEM-nano-indentation approach was then used to determine the material properties for CaF$_2$. Appropriate values of the initial shear strength and self-hardening coefficients $h_{\alpha}$ in the mesoelastic constitutive relations for the corresponding crystallographic planes of CaF$_2$ were obtained after multiple simulations by correlating the FEM results with the experimental loading-deflection curves. The experimental tests and the finite element results for nano-indentation with a maximum load of $10 \text{ mN}$ are shown in Figures 3.4-3.6. It can be seen that parameters of 74/180 MPa (initial shear strength/self-hardening coefficient), 80/120 MPa, and 110/100 MPa provide a reasonable numerical approximation to the experimental tests for the (100), (110), and (111) plane indentations, respectively. For a further comparison, the numerical results of plane (100) indentation with parameters of 80/120 MPa and 110/100 MPa, the plane (110) indentation
with parameters of 110/100 MPa, and the plane (111) indentation with parameters of 80/120 MPa are also displayed.

Here we will also observe that the high optical quality of the CaF$_2$ surfaces used (surface roughness in range 0.18-0.35 nm RMS) imply minimal, if any, subsurface damage induced by the polishing process. Subsurface damage is estimated to be less than (2-5) $\times$ the surface microroughness, i.e., less that 0.4-2.0 nm. On the other hand, the penetrations used in the nano-indentation experiments are of order 50-150 nm. We have assumed, therefore, that any initial surface damage induced by the polishing process cannot significantly alter the measured nano-indentation results.
3.4 Data Analysis

3.4.1 Measurable Indentation Parameters

Once the finite element models with the appropriate material parameters for (100)/(110)/(111) crystallographic planes of CaF$_2$ were obtained, they were then implemented to examine the nano-indentation behavior of CaF$_2$. Simulations with maximum loads of 5 mN, 10 mN, and 15 mN were carried out for the (100) and (111) plane indentations. For (110) plane, indentations with maximum loads of 5 mN and 10 mN were simulated.

The elastic/mesoplastic load-deflection relations for three planes of CaF$_2$ are shown in Figure 3.7. The result reveals that, for the same indentation load, the indentation depth of (111) plane is the largest while the depth of the (100) plane is the smallest. This is partially due to the fact that, for CaF$_2$, the $<100>$ direction is the stiffest and the $<111>$ direction is the least stiff.

The deformed surfaces at maximum indentation load and after fully unloading for each of the three planes of CaF$_2$ are displayed in Figures 3.8 and 3.9. It was observed that for the (100) and (111) plane indentations, the contact profiles on surfaces II and III are the same. However, for the (110) plane indentation, this is not the case. This is because the (110) plane has two-fold rotational symmetry, while the (100) and (111) planes have four- and three-fold rotational symmetry, respectively. In addition, all three plane indentations exhibit pile-up after fully unloading, see Figure 3.9. Figure 3.10 shows the maximum pile-up heights for three planes under different indentation loads obtained from the deformation curves. It was found that the pile-up for the (100) plane indentation is slightly higher than that of the (111) plane. For the (110) plane indentation, pile-up is higher on surface III than that on surface II.

The fact that the contact profiles on surfaces II and III are the same for the
(100) and (111) plane indentations indicates that their projected contact areas are circular. On the other hand, the variation in the contact profiles for the (110) plane indentation suggests that its projected contact area is elliptical with semi axes lying in the symmetry planes (surfaces II and III). Figure 3.11 shows the contact radii of three crystallographic planes under different indentation loads obtained from the deformation curves. It can be observed that the contact radii of the (111) plane indentations are larger than those of the (100) plane indentations and the contact radii on surface III of the (110) plane indentations are larger than those on surface II.

### 3.4.2 Spherical Hardness

Hardness represents the resistance of a material to permanent penetration. It is measured after the indenting force has been removed and some of the elastic deformation is recovered. For this reason, hardness is important in understanding a materials finishing process in which abrasive particles are pressed into the sample surface. Experimentally, hardness is calculated by dividing the maximum external force by the residual projected contact area. Table 3.1 shows the numerical radii of the residual projected indent areas for three plane indentations of CaF$_2$, where the indented radii $a_0$ and $a_m$ are indicated in Figure 3.12 and were obtained from the deformation curves after fully unloading. Table 3.2 shows the calculated spherical hardness of CaF$_2$ at the corresponding maximum indentation loads and the residual projected indent areas. Notice that for (110) plane indentation, the residual projected indent area is elliptical. Because of the axisymmetric nature of the spherical indenter, the anisotropy of the hardness is merely due to the material anisotropy. The numerical spherical hardness of CaF$_2$ is compared with the experimental spherical hardness results of Ladison et al. [7] in Figure 3.13. The individual hardness value was found at the associated d/D, which represents the ratio of the indent diameter (residual projected indent diameter for numerical
results) to the spherical indenter diameter. Their data are within the range of the results in this work.
Figure 3.1 Experimental load-displacement curves for (100)/(110)/(111) plane indentations of CaF$_2$. 
Figure 3.2. Numerical stress strain relations of free uniaxial compression for plane (110) of CaF$_2$ (coordinates x, y, and z are in the crystallographic direction [110], [110], and [001], respectively). Two sets of material parameters are 80/120 MPa (initial shear strength/self-hardening coefficient) and 110/100 MPa.
Figure 3.3 Numerical stress strain relationships of constrained uniaxial compression for plane (110) of CaF$_2$ (coordinates x, y, and z are in the crystallographic direction [110], [001], and [001], respectively). Two sets of material parameters are 80/120 MPa (initial shear strength/self-hardening coefficient) and 110/100 MPa.
Figure 3.4 Comparison between numerical and experimental load-displacement curves for (100) plane indentation of CaF$_2$ (coordinates x and z are in the crystallographic direction [001] and [010], respectively). Three sets of material parameters are 74/180 MPa (initial shear strength/self-hardening coefficient), 80/120 MPa, and 110/100 MPa.
Figure 3.5 Comparison between numerical and experimental load-displacement curves for (110) plane indentation of CaF$_2$ (coordinates x and z are in the crystallographic direction [1\bar{1}0] and [001], respectively). Two sets of material parameters are 80/120 MPa (initial shear strength/self-hardening coefficient) and 110/100 MPa.
Figure 3.6 Comparison between numerical and experimental load-displacement curves for (111) plane indentation of CaF$_2$ (coordinates $x$ and $z$ are in the crystallographic direction [01T] and [2T'T'], respectively). Two sets of material parameters are 80/120 MPa (initial shear strength/self-hardening coefficient) and 110/100 MPa.
Figure 3.7 Elastic/mesoplastic load-deflection relations for (100)/(110)/(111) plane indentations of CaF$_2$. 
Figure 3.8 Numerical deformed surfaces at maximum indentation loads for (100)/(110)/(111) plane of CaF₂.
Figure 3.9 Numerical deformed surfaces after fully unloading for (100)/(110)/(111) plane of CaF$_2$. 
Figure 3.10 Numerical maximum pile-up heights for (100)/(110)/(111) plane indentations of CaF$_2$. 
Figure 3.11 Numerical contact radii for (100)/(110)/(111) plane indentations of CaF₂.
Figure 3.12 Schematic of indentation showing the residual projected indent radius.
Figure 3.13 Comparison between numerical and experimental spherical hardness of CaF$_2$. 
Table 3.1 Numerical radii (μm) of residual projected indent area of (100)/(110)/(111) planes for CaF₂ (a₀ and aₘ are indicated in Figure 3.12).

<table>
<thead>
<tr>
<th>CaF₂</th>
<th>5mN</th>
<th>10mN</th>
<th>15mN</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>a₀=1.002, aₘ=1.252</td>
<td>a₀=1.253, aₘ=1.720</td>
<td>a₀=1.503, aₘ=2.002</td>
</tr>
<tr>
<td>(111)</td>
<td>a₀=1.200, aₘ=1.506</td>
<td>a₀=1.600, aₘ=2.012</td>
<td>a₀=1.920, aₘ=2.271</td>
</tr>
<tr>
<td>(110)</td>
<td>a₀ = 1.502(II)/1.004(III), aₘ = 1.752(II)/1.253(III)</td>
<td>a₀ = 2.004(II)/1.257(III), aₘ = 2.254(II)/1.505(III)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2 Spherical hardness (GPa) of (100)/(110)/(111) planes for CaF₂ (H₀ and Hₘ are calculated from a₀ and aₘ indicated in Figure 3.12).

<table>
<thead>
<tr>
<th>CaF₂</th>
<th>5mN</th>
<th>10mN</th>
<th>15mN</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>H₀=1.585, Hₘ=1.015</td>
<td>H₀=2.027, Hₘ=1.076</td>
<td>H₀=2.114, Hₘ=1.191</td>
</tr>
<tr>
<td>(111)</td>
<td>H₀=1.105, Hₘ=0.702</td>
<td>H₀=1.243, Hₘ=0.786</td>
<td>H₀=1.295, Hₘ=0.926</td>
</tr>
<tr>
<td>(110)</td>
<td>H₀=1.055, Hₘ=0.725</td>
<td>H₀=1.264</td>
<td>Hₘ=0.938</td>
</tr>
</tbody>
</table>
4 Stress and Residual Stress in CaF$_2$ Indentation

In order to optimize the surface quality (i.e. minimize surface roughness and subsurface damage) in manufactured high precision CaF$_2$ surfaces, one must understand the interaction between abrasive grains used in polishing or grinding with the CaF$_2$ surface. The interaction is described in terms of the stresses induced on the CaF$_2$ surface during the “loading” portion of the abrasive grain-surface interaction, as well as during the “unloading” portion, i.e. the residual stresses remaining at the surface. Indentation testing is a practical means to provide fundamental information on damage modes for brittle solids in manufacturing. During a complete cycle of loading and unloading, the stress redistribution under the indenter tip may lead to the formation of different types of cracks. Experimental observations show three potential crack patterns, namely radial, median, and lateral, for crystalline materials during elastic-plastic indentation [46]. The radial crack is generated parallel to the load axis, and remains close to the surface. It is often used in the measurement of fracture toughness for brittle materials. The median and lateral cracks are generated beneath the plastic deformation zone, propagating parallel and perpendicular to the load axis, respectively. They are considered to relate with the subsurface damage and material removal rate during the finishing process [47]. Moreover, for CaF$_2$, cleavage fracture is also an impor-
tant concern in its surface preparation, when the normal tensile stresses on the cleavage planes (111) crystallographic planes exceed a critical value. The examination of the stress distributions during the indentation loading and unloading process can provide a better understanding of crack formation, i.e. initiation and propagation, and its relation to material anisotropy.
4.1 Stress

The stress distributions $\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$ at the maximum indentation loads for the three plane indentations of CaF$_2$ were obtained from the simulations. Here, the stress component $\sigma_{xx}$ in the 3D indentation problem is analogous to the radial stress in the simplified 2D axisymmetric indentation problem. Therefore we refer to it as the radial stress. Similarly, we refer to the stress terms $\sigma_{zz}$ as hoop stress and $\sigma_{yy}$ as axial stress. Notice that, due to the characteristics of anisotropy each of the radial and hoop directions belongs to distinctive crystal orientations. It is clear that the current coordinate system $(xyz)$ (Figure 2.1(a)) can be used to describe the stress distributions on surface II. For surface III, a coordinate transformation is needed to precisely describe the distributions of radial and hoop stresses. The transformed coordinate system, explicitly $(x'y'z')$, is rotated counter-clockwise about the $y$-axis 45 degrees for plane (100), and 60 and 90 degrees for planes (110) and (111), respectively.

The stress contours of radial, axial, and hoop stresses at the maximum load of 10 mN are shown in Figures 4.1-4.3. These contours indicate that, under maximum applied load, the maximum compressive stresses occur directly beneath the indenter. The values of the axial compressive stresses were found to be largest in the (100) indentation and smallest in the (111) indentation. Again, this is because, for CaF$_2$, the $<100>$ direction is the stiffest which leads to the smallest contact area and the $<100>$ direction is the least stiff which leads to the largest contact area. In addition, for (110) indentation, near the indented surface, the axial compressive stresses were found larger on surface III than those on surface II. This might cause larger contact radii on surface III compared to those on surface II. Moreover, tensile stresses were also found near the indented surface or below the compressive stresses. It can be seen that both radial tensile and hoop tensile stresses are largest in the (111) indentation and least in the (100) plane.
indentation, which indicates that the median and radial cracks will most easily be generated and propagated during the (111) indentation and least likely to occur in the (100) indentation. The magnitudes of axial tensile stresses for all three plane indentations are quite small with relatively larger values in the (111) indentation than those of the other two plane indentations. This suggests that lateral cracks are less likely to occur during the loading portion and will have better chance to happen in the (111) indentation. Figure 4.7 shows the maximum normal stresses among four possible cleavage planes ((111)/(1\overline{1}11)/(\overline{1}1\overline{1}1)/(1\overline{1}\overline{1})). Tensile normal stresses were only observed in the (111) indentation. This implies that, during loading process, cleavage fracture will only be generated in the (111) indentation. Additionally, the stress distributions of the (100) and (110) indentations exhibit much stronger anisotropy than those of the (111) indentation.
4.2 Residual Stress

Residual stresses arise from the mismatch between the deformed plastic zone and the surrounding elastic medium after fully unloading. Residual tensile stresses reduce the mechanical performance of materials by facilitating crack initiation and propagation.

The stress contours of residual radial, residual axial, and residual hoop stresses after fully unloading from the maximum indentation load of 10 $mN$ are presented in Figures 4.4-4.6. The results show that in the (100) and (110) indentations, both residual radial tensile and residual hoop tensile stresses are larger than the corresponding radial tensile and hoop tensile stresses at maximum load. Nevertheless, these two residual tensile stresses in the (111) indentation are slightly smaller than the corresponding tensile stresses at maximum load. This indicates that, during the unloading portion, the median and radial cracks will grow in (100) and (110) indentations, and will be close or stay the same in the (111) indentation. The residual axial tensile stresses in all three plane indentations are much larger than the axial tensile stresses at maximum load. Moreover, the residual axial tensile stresses are largest in the (111) indentation where they occur directly below the indented area and least in the (100) indentation where they occur under the periphery of the indented area. This suggests that lateral cracks will grow during the unloading segment for all three indentations, and the crack size will be largest in the (111) indentation and least in the (100) indentation. Also, the pattern of cracking is markedly different between (100) and (111) indentations. Figure 4.8 shows the maximum residual normal stresses among four possible cleavage planes. The residual normal tensile stresses are more significant than normal tensile stresses at maximum load for all three indentations. In addition, the residual normal tensile stresses are largest in the (111) indentation and least in the (100) plane indentation. This indicates that cleavage fracture will be generated during
the unloading process for all three plane indentations, and the size of the cleavage will be largest in the (111) indentation and smallest in the (100) indentation. Furthermore, the spatial distribution of the normal tensile stress is markedly different for the three orientations: in (100) indentation, the normal tensile stress is shallow and localized near the indented area at the surface; in (110) indentation the normal tensile stress is deeper and still extends to the surface; in (111) indentation, the normal tensile stress is under the surface and very large. Similar to the stresses distributions at maximum load, the residual stresses distributions of (100) and (110) indentations exhibit much stronger anisotropy than those of the (111) indentation.
4.3 Conclusion

Microfractures and crystalline anisotropy are two major factors affecting the surface quality of CaF$_2$ during manufacturing, and ultimately affecting its optical performance. In order to analyze the stresses that are responsible for the damage mode, a finite element analysis of spherical nano-indentation was carried out that considers elastic-mesoplastic deformation for single crystals. In this analysis, indentation of the three main crystallographic planes (100)/(110)/(111) of CaF$_2$ was studied and compared to examine the effects of crystalline anisotropy. We have emphasized stresses at the maximum indenting load and residual stresses after the load has been removed.

Appropriate material parameters were obtained by correlating the FEM results and the corresponding experimental load-displacement curves. The simulations show a value in the range of 74-110 MPa for the initial shear yield strength, and a value in the range of 100-180 MPa for the self-hardening modulus.

It was found that due to the lower rotational symmetry, the projected contact areas are elliptical instead of circular for the (110) indentation. All three plane indentations exhibit pile-up after fully unloading. The pile-up for the (100) indentation is slightly higher than that of the (111) indentation. For the (110) indentation, pile-up is different along two symmetry planes. The hardness of the (111) plane was found the lowest among three planes under spherical indentation. Same observation was also reported for Vickers [10] and Berkovich indentation[48].

Stresses and residual stresses analysis indicate that during the loading cycle, median and radial cracks are more likely to grow than lateral cracks. All three crack modes will most easily be generated in the (111) indentation and least likely to occur in the (100) indentation. This agrees well with the experimental observations that the subsurface damage is largest in the (111) plane and least in the (100) plane under the same grinding conditions [48]. During the unloading
cycle, lateral cracks tend to grow in all three plane indentations, and will be most significant in the (111) indentation and least significant in the (100) indentation. This suggests that the material removal rate is largest in the (111) plane and least in the (100) plane for the same grinding conditions. This prediction was found in accordance with the experimental results of Kukleva et al. [10] that the volume being ground away is largest for (111) surface and least for (100) surface in the same time interval under identical test conditions.

Since CaF$_2$ cleaves along {111} planes, we have also emphasized the calculation of the largest tensile stresses across the {111} planes, namely cleavage stresses. The distributions of the maximum normal stresses and maximum residual normal stresses among four possible cleavage planes show that during the loading cycle, cleavage is expected to happen only in the (111) indentation. During the unloading cycle, all three planes tend to cleave and the cleavage will be most substantial in the (111) indentation and least in the (100) indentation. This suggests that (111) indentation is the most brittle and (100) indentation is the least brittle. Moreover, the spatial distribution of cleavage stresses shows that: in (100) indentation, the fractures are formed and propagated more readily near the indented area at the surface; in (110) indentation, the fractures are also more likely to propagate on the indented surface; in (111) indentation, the fractures are formed and propagated through the material interior. This is consistent with the experimental observations that the surface roughness is highest for grinding the (111) plane and lowest for (100) plane for the same grinding conditions [13; 48].

The predicted spherical indentation hardness also can be compared to the available experimental data by Ladison et al. [7], see Figure 3.13. Our model predictions for (100) indentation underestimate the experimentally measured hardness by 10-20%. We will note, however, that the Ladison experimental work went up to loads of 2 $N$, whereas the nano-indentation data on which our model was
based only reached 15 mN. It is quite possible that at higher loads the more extensive plastic deformation involves not only constant self-hardening (as we have assumed in our model) but also cross-hardening that itself may depend on the amount of plastic strain. Given the relative lack of available experimental data on hardening in CaF$_2$, especially at temperature close to room temperature, we have adopted the simplest approach, i.e. allowed only self-hardening at a constant rate. Such latent hardening has been documented for the case of FCC crystals such as Al and Cu, and may increase from unity to values as high as 1.6 to 2.2 [49]. Clearly, the possibilities that different slip systems in CaF$_2$ harden at different rates or that hardening of one system affects that of another also must be examined. We will also note, however, that for finishing operations, such as polishing, the loads acting on individual abrasives are expected to be small. In that case, the assumption of constant and uniform hardening for all slip system seems reasonable, especially given the fact that, at room temperature, CaF$_2$ is relatively brittle and thus demonstrates a limited amount of ductility.
Figure 4.1 Contour of the radial stresses under maximum indentation load for (100)/(110)/(111) plane of CaF$_2$. 
Figure 4.2 Contour of the axial stresses under maximum indentation load for (100)/(110)/(111) plane of CaF$_2$. 
Figure 4.3 Contour of the hoop stresses under maximum indentation load for (100)/(110)/(111) plane of CaF$_2$. 
Figure 4.4 Contour of the residual radial stresses after fully unloading for (100)/(110)/(111) plane indentation of CaF$_2$. 
Figure 4.5 Contour of the residual axial stresses after fully unloading for (100)/(110)/(111) plane indentation of CaF$_2$. 
Figure 4.6 Contour of the residual hoop stresses after fully unloading for (100)/(110)/(111) plane indentation of CaF$_2$. 
Figure 4.7 Contour of the maximum normal stresses on the cleavage planes for (100)/(110)/(111) plane indentation of CaF$_2$. 
Figure 4.8 Contour of the residual maximum normal stresses on the cleavage planes for (100)/(110)/(111) plane indentation of CaF$_2$. 
5 Load-displacement for MgF$_2$

5.1 Nano-indentation Experiments

5.1.1 Material

Three oriented crystallographic faces of MgF$_2$ (001), (101), and (111) were chosen for the nano-indentation experiments. These faces were grown and cut to specific orientations (ISP Optics, Irvington, N.Y.). Following polishing to optical standards, the samples were examined in a Zygo NewView 5000 white light interferometer (Zygo Corp., Middlefield, C.T.). The RMS (root-mean-square) averaged in 3 measurements each of the (001)/(101)/(111) faces are 0.22 nm, 0.30 nm, and 0.21 nm, respectively, i.e. of high optical finished quality.

5.1.2 Experiment

A nano-indentation Instruments II (Nano Instruments, Inc., Oak Ridge, Tennessee) was used for nano-indentation experiments on the three crystallographic planes (001)/(101)/(111) of MgF$_2$. The experiments were performed at room temperature (23°C). The conical indenter has a 90 degrees included angle and a spherical tip of 10 µm radius. Load-deflection curves for the three planes with
maximum loads of 5 \textit{mN}, 10 \textit{mN}, and 15 \textit{mN} obtained from experiments are shown in Figure 5.1. For the trial with a maximum load of 10 \textit{mN}, the case we simulated using finite elements, the indentation depths of (001)/(101)/(111) crystallographic planes are 70 \textit{nm}, 85 \textit{nm}, and 80 \textit{nm}, respectively.
5.2 Numerical Results for Uniaxial Compression

The explicit relations of the constitutive laws derived in the chapter 2 for the three crystallographic planes of MgF$_2$ were programmed into the user material subroutine UMAT provided by ABAQUS. Two simple cases, free uniaxial compression and constrained uniaxial compression, were used to test the user material subroutine. Both cases were simulated using a single 8-node 3D solid element. The material was first compressed to a maximum strain $\varepsilon_{yy}^{\text{max}} = -0.05$ and then pulled back to zero strain. The elastic stiffness constants and slip systems were chosen to correspond to the (101) crystallographic plane of MgF$_2$ under ABAQUS analysis coordinate system (Figure 2.1(a)). In the simulation, the reference shear strain rate $\dot{\gamma}_0^\alpha$ was taken to be 0.001 s$^{-1}$ and the rate sensitivity exponent $\mu$ was taken to be 0.05. Three sets of the material parameters, 168/220 MPa (initial shear strength/self-hardening coefficient), 216/260 MPa, and 250/270 MPa, were used for comparison. The choice of these material parameters will be further discussed in the following section, where we will demonstrate that such parameters indeed describe the mesoplastic deformation of MgF$_2$.

The stress strain relationships from the numerical simulations are shown in Figures 5.2 and 5.3. For both cases, the relations between axial stress $\sigma_{yy}$ and axial strain $\varepsilon_{yy}$ are displayed. Since the material is anisotropic, the transverse terms of stress and strain (if they exist) will be different. For simplicity, in the case of free compression ($\sigma_{xx} = \sigma_{zz} = 0$), only the transverse strain $\varepsilon_{xx}$ versus the axial strain is displayed. Similarly, for constrained compression ($\varepsilon_{xx} = \varepsilon_{zz} = 0$), only the transverse stress $\sigma_{xx}$ versus the axial strain is shown. Mathematica computations were used to verify that the FEM results were in strong agreement with easily derived analytical solutions.
5.3 Numerical Results for Nano-indentation

The combined nano-indentation-FEM approach was then used to determine the material properties for MgF$_2$ for a nano-indentation load of 10 mN. In the simulation, the reference shear strain rate $\dot{\gamma}_0$ was taken to be 0.001 s$^{-1}$ and the rate sensitivity exponent $\mu$ was taken to be 0.05. The experimental tests and the finite element results for nano-indentation with a maximum load of 10 mN are shown in Figures 5.4-5.6. It can be seen that parameters of 168/220 MPa (initial shear strength/self-hardening coefficient), 250/270 MPa, and 216/260 MPa provide a reasonable numerical approximation to the experimental tests for the (001), (101), and (111) plane indentations, respectively. For a further comparison, the numerical results of plane (001) indentation with parameters of 216/260 MPa and 250/270 MPa, the plane (101) indentation with parameters of 168/220 MPa and 216/260 MPa, and the plane (111) indentation with parameters of 168/220 MPa and 250/270 MPa are also displayed.
5.4 Data Analysis

5.4.1 Measurable Indentation Parameters

The finite element models for (001)/(101)/(111) crystallographic planes of MgF$_2$ with the appropriate material parameters were then used to examine the nano-indentation behavior of MgF$_2$. Simulations with maximum loads of 5 mN, 10 mN, and 15 mN were carried out for the (001), (101), and (111) plane indentations.

The elastic/mesoplastic load-deflection relations for three planes of MgF$_2$ are shown in Figure 5.7. The result reveals that, for the same indentation load, the indentation depth of (101) plane is the largest while the depth of the (001) plane is the smallest.

The deformed surfaces at maximum indentation load and after fully unloading for each of the three planes of MgF$_2$ are displayed in Figures 5.8 and 5.9. It was observed that for the (001) and (111) plane indentations, the contact profiles on surfaces II and III are the same. While for the (101) plane indentation, this is not the case. Moreover, for (111) plane indentation, the contact profiles on the planes perpendicular to the side II and III are different as those on the side II and III. This is because the (001) plane has four-fold rotational symmetry, while the (101) and (111) planes have two- and zero-fold rotational symmetry, respectively. In addition, all three plane indentations exhibit pile-up after fully unloading, see Figure 5.9. Figure 5.10 shows the maximum pile-up heights for these three planes under different indentation loads obtained from the deformation curves. It was found that the side III and side II of (101) plane indentation has the highest and lowest pile-up, respectively, among all three plane indentations.

The fact that the contact profiles on surfaces II and III are the same for the (001) plane indentations indicates that its projected contact area is circular. On the other hand, the variation in the contact profiles for the (101) and (111)
plane indentation suggests that there projected contact area is elliptical with semi axes lying in the symmetry planes. Figure 5.11 shows the contact radii of three crystallographic planes under different indentation loads obtained from the deformation curves. It can be observed that the contact radii of the (001) plane indentation are smallest among three plane indentations. The contact radii on surface III of the (101) plane indentation is larger than those on surface II.
5.4.2 Spherical Hardness

Table 5.1 shows the numerical radii of the residual projected indent areas for three plane indentations of MgF$_2$ with maximum loads of 5 mN, 10 mN, and 15 mN obtained from the deformation curves after fully unloading. Table 5.2 shows the calculated spherical hardness of MgF$_2$ at the corresponding maximum indentation loads by dividing the maximum external loads by the corresponding residual projected contact areas. Notice that for (101) and (111) plane indentation, the residual projected indent areas are elliptical. Because of the axisymmetric nature of the spherical indenter, the anisotropy of the hardness is merely due to the material anisotropy. The results show that the hardness of (001) plane has the largest value among all three plane indentations and the values of the (111) plane is slightly larger than those of the (101) plane indentation. This explains the experimental results that at the same indentation load the indentation depth of the (001) plane is the smallest and the depth of the (101) plane is the largest.
Figure 5.1 Experimental load-displacement curves for (001)/(101)/(111) plane indentations of MgF$_2$. 

![Graphs showing load-displacement curves for MgF$_2$]
Figure 5.2 Numerical stress strain relations of free uniaxial compression for plane (101) of MgF$_2$ (coordinates x, y, and z are in the crystallographic direction [0 0 c], [c 0 a], and [0 0 1], respectively under analysis coordinate system). Three sets of material parameters are 168/220 MPa (initial shear strength/self-hardening coefficient), 216/260 MPa, and 250/270 MPa.
Figure 5.3 Numerical stress strain relations of constrained uniaxial compression for plane (101) of MgF$_2$ (coordinates x, y, and z are in the crystallographic direction[π 0 c], [c 0 a], and [010], respectively under analysis coordinate system). Three sets of material parameters are 168/220 MPa (initial shear strength/self-hardening coefficient), 216/260 MPa, and 250/270 MPa.
Figure 5.4 Comparison between numerical and experimental load-displacement curves for (001) plane indentation of MgF$_2$ (coordinates x and z are in the direction [\(\bar{T}00\)] and [010], respectively under analysis coordinate system). Three sets of material parameters are 168/220 MPa (initial shear strength/self-hardening coefficient), 216/260 MPa, and 250/270 MPa.
Figure 5.5 Comparison between numerical and experimental load-displacement curves for (101) plane indentation of MgF$_2$ (coordinates x and z are in the direction $[\overline{1} \; 0 \; c]$ and $[0 \; 1 \; 0]$, respectively under analysis coordinate system). Three sets of material parameters are 168/220 MPa (initial shear strength/self-hardening coefficient), 216/260 MPa, and 250/270 MPa.
Figure 5.6 Comparison between numerical and experimental load-displacement curves for (111) plane indentation of MgF$_2$ (coordinates x and z are in the direction [\(\overline{1}0\overline{2}2\overline{c}\)] and [1010], respectively under analysis coordinate system). Three sets of material parameters are 168/220 MPa (initial shear strength/self-hardening coefficient), 216/260 MPa, and 250/270 MPa.
Figure 5.7 Elastic/mesoplastic load-deflection relations for (001)/(101)/(111) plane indentations of MgF$_2$. 
Figure 5.8 Numerical deformed surfaces at maximum indentation loads for (001)/(101)/(111) plane of MgF$_2$ ("⊥" represents the plane perpendicular to the side II and side III).
Figure 5.9 Numerical deformed surfaces after fully unloading for (001)/(101)/(111) plane of MgF$_2$ ("⊥" represents the plane perpendicular to the side II and side III).
Figure 5.10 Numerical maximum pile-up heights for (001)/(101)/(111) plane indentations of MgF₂.
Figure 5.11 Numerical contact radii for (001)/(101)/(111) plane indentations of MgF₂.
Table 5.1 Numerical radii (µm) of residual projected indent area of (001)/(101)/(111) planes for MgF₂ (a₀ and aₘ are indicated in Figure 3.12 and “⊥” represents the plane perpendicular to the side II).

<table>
<thead>
<tr>
<th>MgF₂</th>
<th>5mN</th>
<th>10mN</th>
<th>15mN</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>a₀=0.751</td>
<td>a₀=1.005</td>
<td>a₀=1.220</td>
</tr>
<tr>
<td></td>
<td>aₘ=1.001</td>
<td>aₘ=1.252</td>
<td>aₘ=1.503</td>
</tr>
<tr>
<td>(101)</td>
<td>a₀ = 1.502(II)/1.000(III)</td>
<td>a₀ = 2.005(II)/1.256(III)</td>
<td>a₀ = 2.506(II)/1.508(III)</td>
</tr>
<tr>
<td></td>
<td>aₘ = 1.752(II)/1.252(III)</td>
<td>aₘ = 2.504(II)/1.505(III)</td>
<td>aₘ = 3.005(II)/1.757(III)</td>
</tr>
<tr>
<td>(111)</td>
<td>a₀ = 1.501(II)/1.003(⊥)</td>
<td>a₀ = 2.002(II)/1.256(⊥)</td>
<td>a₀ = 2.253(II)/1.509(⊥)</td>
</tr>
<tr>
<td></td>
<td>aₘ = 1.751(II)/1.253(⊥)</td>
<td>aₘ = 2.502(II)/1.506(⊥)</td>
<td>aₘ = 3.003(II)/1.758(⊥)</td>
</tr>
</tbody>
</table>

Table 5.2 Spherical hardness (GPa) of (100)/(110)/(111) planes for MgF₂ (H₀ and Hₘ are calculated from a₀ and aₘ indicated in Figure 3.12).

<table>
<thead>
<tr>
<th>MgF₂</th>
<th>5mN</th>
<th>10mN</th>
<th>15mN</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>H₀= 2.822</td>
<td>H₀= 3.152</td>
<td>H₀= 3.208</td>
</tr>
<tr>
<td></td>
<td>Hₘ= 1.588</td>
<td>Hₘ= 2.031</td>
<td>Hₘ= 2.114</td>
</tr>
<tr>
<td>(101)</td>
<td>H₀= 1.056</td>
<td>H₀= 1.264</td>
<td>H₀= 1.263</td>
</tr>
<tr>
<td></td>
<td>Hₘ= 0.726</td>
<td>Hₘ= 0.845</td>
<td>Hₘ= 0.904</td>
</tr>
<tr>
<td>(111)</td>
<td>H₀= 1.057</td>
<td>H₀= 1.266</td>
<td>H₀= 1.404</td>
</tr>
<tr>
<td></td>
<td>Hₘ= 0.725</td>
<td>Hₘ= 0.846</td>
<td>Hₘ= 0.905</td>
</tr>
</tbody>
</table>
6 Stress and Residual Stress in MgF$_2$ Indentation

6.1 Stress

The stress distributions $\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$ at the maximum indentation loads for the three plane indentations of MgF$_2$ were obtained from the simulations. Similar as before, we refer to the stress terms $\sigma_{xx}$ as radial stress, $\sigma_{zz}$ as hoop stress and $\sigma_{yy}$ as axial stress. Notice that, due to the characteristics of anisotropy each of the radial and hoop directions belongs to distinctive crystal orientations. The current coordinate system ($xyz$) (Figure 2.1(a)) can be used to describe the stress distributions on surface II. For surface III, a coordinate transformation is needed to describe the distributions of radial and hoop stresses. The transformed coordinate system, explicitly ($x'y'z'$), is rotated counter-clockwise about the $y$-axis 45 degrees for plane (001), and 90 and 180 degrees for planes (101) and (111), respectively.

The stress contours of radial, axial, and hoop stresses at the maximum load of 10 mN are shown in Figures 6.1-6.3. These contours indicate that, under maximum applied load, the maximum compressive stresses occur directly beneath the indenter. The values of the axial compressive stresses were found to be largest in the (001) indentation and smallest in the (111) indentation. In addition, for (101) indentation, near the indented surface, the axial compressive stresses were
found larger on surface III than those on surface II. This might cause larger contact radii on surface III compared to those on surface II. Moreover, tensile axial stresses were found near the indented surface and tensile radial and hoop stresses were found below the compressive stresses. It can be seen that radial tensile stresses are largest in the (101) indentation and least in (001) indentation, while hoop tensile stresses are largest in the (111) indentation. This indicates that the median cracks will most easily be generated and propagated during the (101) indentation and least likely to occur in the (001) indentation, while radial cracks will most easily be generated during the (111) indentation. The magnitudes of axial tensile stresses for all three plane indentations are quite small with relatively larger values in the (101) indentation than those of the other two plane indentations. This suggests that lateral cracks are less likely to generate during the loading portion and will have better chance to happen in the (101) indentation.
6.2 Residual Stress

The stress contours of residual radial, residual axial, and residual hoop stresses after fully unloading from the maximum indentation load of 10 mN are presented in Figures 6.4-6.6. The results show that in the (001) and (101) indentations, both residual radial tensile and residual hoop tensile stresses are larger than the corresponding radial tensile and hoop tensile stresses at maximum load. Nevertheless, these two residual tensile stresses in the (111) indentation are nearly the same as the corresponding tensile stresses at maximum load. This indicates that, during the unloading portion, the median and radial cracks will grow in (001) and (101) indentations, and will be close or stay the same in the (111) indentation. The residual axial tensile stresses in all three plane indentations are much larger than the axial tensile stresses at maximum load. Moreover, the residual axial tensile stresses are largest in the (111) indentation where they occur directly below the indented area and smaller in the (001) indentation where they occur under the periphery of the indented area. For (101) indentation, the residual tensile stresses are only observed on surface III under the periphery of the indented area. This suggests that lateral cracks will grow during the unloading segment for all three indentations, and the crack size will be largest in the (111) indentation and least in the (101) indentation. Also, the pattern of cracking is markedly different between (101) and (111) indentations.
6.3 Plastic Zone

The plastic zones for (001)/(101)/(111) plane indentations of MgF$_2$ were also examined. This is performed by comparing the resolved shear stresses with the initial shear strength for the corresponding six slip systems \{110\}/<001> at the maximum indentation load. The initial shear strength is assumed to be the same for all slip systems and has the value of 168 MPa, 250 MPa, and 216 MPa for the (001), (101), and (111) plane indentation, respectively obtained from the simulation results. The resolved shear stresses were calculated using equation (2.19). Figures 6.7-6.12 show the contour of the normalized resolved shear stresses with the initial shear strength of individual slip systems for the three plane indentations of MgF$_2$. Five out of six slip systems for all three plane indentations are found have positive normalized values. In the simulation, crystalline slip happens where these normalized values are larger than one and these areas are considered to have plastic deformation. The results show that for (001) plane indentation, the slip systems (110)/[001] and (011)/[100] are the major contribution to the plastic deformation, and for (101) plane indentation, these slip systems are (110)/[001] and (101)/[101]. For (111) plane indentation, all six slip systems have decent amount of crystalline slip. The results also suggest that the size of the plastic zone is largest for (001) plane indentation and least for (101) plane indentation.
Figure 6.1 Contour of the radial stresses under maximum indentation load for (001)/(101)/(111) plane of MgF$_2$. 
Figure 6.2 Contour of the axial stresses under maximum indentation load for (001)/(101)/(111) plane of MgF$_2$. 
Figure 6.3 Contour of the hoop stresses under maximum indentation load for (001)/(101)/(111) plane of MgF$_2$. 
Figure 6.4 Contour of the residual radial stresses after fully unloading for (001)/(101)/(111) plane indentation of MgF₂.
Figure 6.5 Contour of the residual axial stresses after fully unloading for (001)/(101)/(111) plane indentation of MgF₂.
Figure 6.6 Contour of the residual hoop stresses after fully unloading for (001)/(101)/(111) plane indentation of MgF$_2$. 
Figure 6.7 Contour of the normalized resolved shear stresses with initial shear strength of slip systems (110)<001> and (101)<010> under maximum load for (001) plane indentation of MgF₂.
Figure 6.8 Contour of the normalized resolved shear stresses with initial shear strength of slip systems (011)<100> under maximum load for (001) plane indentation of MgF₂.
Figure 6.9 Contour of the normalized resolved shear stresses with initial shear strength of slip systems (110)<001> under maximum load for (101) plane indentation of MgF$_2$. 
Figure 6.10 Contour of the normalized resolved shear stresses with initial shear strength of slip systems (101)/<010> and (011)/<100> under maximum load for (101) plane indentation of MgF$_2$. 
Figure 6.11 Contour of the normalized resolved shear stresses with initial shear strength of slip systems (110)/<001> and (101)/<010> under maximum load for (111) plane indentation of MgF$_2$. 
Figure 6.12 Contour of the normalized resolved shear stresses with initial shear strength of slip systems (011)/<100> under maximum load for (111) plane indentation of MgF₂.
7  Load-displacement for KDP

nano-indentation experiments on the two crystallographic planes (001) and (100) of KDP were performed by Kucheyev et al. with a Hysitron Tribo-Scope nanoindentation system [24]. The tests were performed at room temperature (23°C) with an 1 micron radius spherical indenter and under maximum load of 1 mN. The corresponding load-deflection curves obtained from these experiments are shown in Figure 7.1. It shows that, the indentation depths of (001) and (100) crystallographic planes are 90 nm and 112 nm, respectively.

7.1  Numerical Results for Uniaxial Compression

The explicit relations of the constitutive laws derived in the chapter 2 for the two crystallographic planes of KDP were programmed into the user material subroutine UMAT provided by ABAQUS. Two simple cases, free uniaxial compression and constrained uniaxial compression, were used to test the user material subroutine. Both cases were simulated using a single 8-node 3D solid element. The material was first compressed to a maximum strain $\varepsilon_{yy}^{max} = -0.05$ and then pulled back to zero strain. The elastic stiffness constants and slip systems were chosen to correspond to the (100) crystallographic plane of KDP under ABAQUS analysis coordinate system (Figure 2.1(a)). In the simulation, the reference shear
strain rate $\dot{\gamma}_0^\alpha$ was taken to be 0.001 $s^{-1}$ and the rate sensitivity exponent $\mu$ was taken to be 0.05. Two sets of the material parameters, 265/380 MPa (initial shear strength/self-hardening coefficient), and 450/600 MPa, were used for comparison. The choice of these material parameters will be further discussed in the following section, where we will demonstrate that such parameters indeed describe the mesoplastic deformation of KDP.

The stress strain relationships from the numerical simulations are shown in Figures 7.2 and 7.3. For both cases, the relations between axial stress $\sigma_{yy}$ and axial strain $\varepsilon_{yy}$ are displayed. Since the material is anisotropic, the transverse terms of stress and strain (if they exist) will be different. For simplicity, in the case of free compression ($\sigma_{xx} = \sigma_{zz} = 0$), only the transverse strain $\varepsilon_{xx}$ versus the axial strain is displayed. Similarly, for constrained compression ($\varepsilon_{xx} = \varepsilon_{zz} = 0$), only the transverse stress $\sigma_{xx}$ versus the axial strain is shown. Mathematica computations were used to verify that the FEM results were in strong agreement with easily derived analytical solutions.
7.2 Numerical Results for nano-indentation

The combined nano-indentation-FEM approach was then used to determine the material properties for KDP for a nano-indentation load of $1mN$. In the simulation, the reference shear strain rate $\dot{\gamma}^\alpha$ was taken to be $0.001 \text{s}^{-1}$ and the rate sensitivity exponent $\mu$ was taken to be $0.05$. The experimental tests and the finite element results for nano-indentation with a maximum load of $1mN$ are shown in Figures 7.4 and 7.5. It can be seen that parameters of $450/600 \text{ MPa}$ (initial shear strength/self-hardening coefficient) and $265/380 \text{ MPa}$ provide a reasonable numerical approximation to the experimental tests for the $(001)$ and $(100)$ plane indentations, respectively. For a further comparison, the numerical results of plane $(001)$ indentation with parameters of $265/380 \text{ MPa}$ and the plane $(100)$ indentation with parameters of $450/600 \text{ MPa}$ are also displayed.
7.3 Data Analysis

7.3.1 Measurable Indentation Parameters

The finite element models for (001) and (100) crystallographic planes of KDP with the appropriate material parameters were then used to examine the nano-indentation behavior of KDP.

The load-deflection relations for the two planes of KDP reveal that, for the same indentation load, the indentation depth of (100) plane is larger than that of (001) plane. Since the value of the elastic modulus along <100> direction is higher than that along <001> direction for KDP, the load-deflection curves suggest that more slip systems were activated during (100) plane indentation than those during (001) plane indentation. This explains relatively lower initial shear strength and self-hardening coefficient for (100) plane indentation.

The deformed surfaces at maximum indentation load and after fully unloading for the two planes of KDP are displayed in Figures 7.6 and 7.7. Due to the reason that (001) and (100) plane has four- and two-fold rotational symmetry, respectively, the contact profiles on surfaces II and III are the same for (001) plane indentation and different for the (100) plane indentation. This also indicates that the projected contact area is circular for (001) plane indentation and elliptical for (100) plane indentation with semi axes lying in the symmetry planes. It can be observed that the contact radius of the (100) plane indentation is very close to that of the (001) plane indentation and the contact radius on surface III of the (100) plane indentation is slightly larger than that on surface II. In addition both two plane indentations exhibit pile-up after fully unloading. Figure 7.7 shows that the pile-up for the (001) plane indentation is slightly smaller than that of the (100) plane. For the (100) plane indentation, pile-up is higher on surface II than that on surface III.
7.3.2 Spherical Hardness

Table 7.1 shows the numerical radii of the residual projected indent areas for two plane indentations of KDP at the maximum load of 1mN obtained from the deformation curves after fully unloading. Table 7.2 shows the calculated spherical hardness of KDP by dividing the maximum external loads by the corresponding residual projected contact areas. Notice that for (100) plane indentation, the residual projected indent area is elliptical. Because of the axisymmetric nature of the spherical indenter, the anisotropy of the hardness is merely due to the material anisotropy. The experimental spherical hardness by Kucheyev et al. [24] is also included in the Table 7.2 for comparison. Their data are consistent with the results in this work. Our results show that the hardness of (100) and (001) planes are very close (~15% variation) which suggests small hardness anisotropy among (100) and (001) faces. This was also observed by Fang and Lambropoulos [23]. From our data, it is not obvious which face is relatively harder than the other.

Two opposite conclusions might be drawn based on the choice of the numerical radii. The measurements of Kucheyev et al. [24] suggest that (001) face is slightly harder than the (100) face. Since their radius of the residual impression at the maximum pile up (which is $a_m$ in the present work) for (001) plane indentation at 1mN is 0.5 micron (which is 0.505 micron in our results), it appears that they used $a_0$ for the calculation instead of $a_m$ as the latter should give a hardness value of 1.28 GPa and not the 2.0±0.2 GPa. On the other hand, the Vickers hardness of (100) and (001) faces of KDP measured by Rao and Sirdeshmukh [50] are approximately 1.43 GPa and 1.30 GPa, respectively, which suggests that (100) face is slightly harder than the (001) face. Their data matches our results using the numerical radii of $a_m$. 
Figure 7.1 Experimental load-displacement curves for (001) and (100) plane indentations of KDP. These curves were obtained from the article by Kucheyev et al. [24].
Figure 7.2 Numerical stress strain relations of free uniaxial compression for plane (100) of KDP (coordinates x, y, and z are in the direction [001], [100], and [010], respectively under analysis coordinate system). Two sets of material parameters are 265/380 MPa (initial shear strength/self-hardening coefficient) and 465/600 MPa.
Figure 7.3 Numerical stress strain relationships of constrained uniaxial compression for plane (100) of KDP (coordinates x, y, and z are in the direction [001], [100], and [010], respectively under analysis coordinate system). Two sets of material parameters are 265/380 MPa (initial shear strength/self-hardening coefficient) and 465/600 MPa.
Figure 7.4 Comparison between numerical and experimental load-displacement curves for (001) plane indentation of KDP (coordinates x and z are in the direction [100] and [010], respectively under analysis coordinate system). Two sets of material parameters are 265/380 MPa (initial shear strength/self-hardening coefficient) and 465/600 MPa. The experimental curve was obtained from the article by Kucheyev et al. [24].
Figure 7.5 Comparison between numerical and experimental load-displacement curves for (100) plane indentation of KDP (coordinates x, and z are in the direction [001] and [010], respectively under analysis coordinate system). Two sets of material parameters are 265/380 MPa (initial shear strength/self-hardening coefficient) and 465/600 MPa. The experimental curve was obtained from the article by Kucheyev et al. [24].
Figure 7.6 Numerical deformed surfaces at maximum indentation loads for (001) and (100) plane of KDP.
Figure 7.7 Numerical deformed surfaces after fully unloading for (001) and (100) plane of KDP.
Table 7.1 Numerical radii ($\mu$m) of residual projected indent area of (001) and (100) planes for KDP ($a_0$ and $a_m$ are indicated in Figure 3.12).

<table>
<thead>
<tr>
<th>KDP</th>
<th>1mN</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>$a_0=0.375$</td>
</tr>
<tr>
<td></td>
<td>$a_m=0.505$</td>
</tr>
<tr>
<td>(100)</td>
<td>$a_0 = 0.460(II)/0.336(III)$</td>
</tr>
<tr>
<td></td>
<td>$a_m = 0.604(II)/0.362(III)$</td>
</tr>
</tbody>
</table>

Table 7.2 Spherical hardness (GPa) of (100) and (100) planes for KDP ($H_0$ and $H_m$ are calculated from $a_0$ and $a_m$ indicated in Figure 3.12).

<table>
<thead>
<tr>
<th>KDP</th>
<th>1mN</th>
<th>1 mN (Kucheyev et al. [24])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>$H_0= 2.26$</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>$H_m= 1.28$</td>
<td></td>
</tr>
<tr>
<td>(100)</td>
<td>$H_0= 2.06$</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>$H_m= 1.46$</td>
<td></td>
</tr>
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</table>
8 Stress and Residual Stress in KDP Indentation

8.1 Stress

The stress distributions $\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$ at the maximum indentation loads for the two plane indentations of KDP were obtained from the simulations. As before, we refer to the stress terms $\sigma_{xx}$ as radial stress, $\sigma_{zz}$ as hoop stress and $\sigma_{yy}$ as axial stress and due to the characteristics of anisotropy each of the radial and hoop directions belongs to distinctive crystal orientations. Similar as CaF$_2$ and MgF$_2$, a coordinate transformation is performed to describe the distributions of radial and hoop stresses for surface III. The transformed coordinate system, explicitly $(x'y'z')$, is rotated counter-clockwise about the $y$-axis 45 degrees for plane (001) and 90 degrees for plane (100).

The stress contours of radial, axial, and hoop stresses at the maximum load of 1 mN are shown in Figures 8.1-8.3. These contours indicate that, under maximum applied load, the maximum compressive stresses occur directly beneath the indenter. The values of the axial compressive stresses were found to be larger in the (001) indentation than those in the (100) indentation. This might due to the less plastic deformation during the (001) plane indentation. Moreover, tensile stresses were also found at the periphery of the indented area or below the
compressive stresses. It was observed that both radial tensile and hoop tensile stresses for (001) and (100) plane indentations are comparable. This indicates that during the loading process the median and radial cracks will be generated and propagated in nearly the same lever for these two plane indentations. The magnitudes of axial tensile stresses for both plane indentations are quite small with relatively larger values in the (100) indentation. This suggests that lateral cracks are less likely to generate during the loading portion and will have better chance to happen in the (100) indentation.
8.2 Residual Stress

The stress contours of residual radial, residual axial, and residual hoop stresses after fully unloading from the maximum indentation load of 1 mN are presented in Figures 8.4-8.6. The results show that for (100) indentations, the values of the residual radial tensile and residual hoop tensile stresses are larger than the corresponding radial tensile and hoop tensile stresses at maximum load. While for (001) indentation, these values are nearly stay the same as those at maximum load. This indicates that, during the unloading portion, the median and radial cracks will grow in (100) indentations, and will be close or stay the same in the (001) indentation. This agrees well with the experimental observations that the fracture toughness of indenting the (001) planes is higher than that of indenting the (100) planes [23]. The residual axial tensile stresses in these two plane indentations are much larger than the axial tensile stresses at maximum load. The large residual axial tensile stresses in both plane indentations occur directly below the indented area. This suggests that lateral cracks will grow during the unloading segment for both plane indentations, and the crack size will be larger in the (001) indentation than that in the (100) indentation. Also, the pattern of cracking is similar for these two plane indentations.
Figure 8.1 Contour of the radial stresses under maximum indentation load for (001) and (100) plane of KDP.
Figure 8.2 Contour of the axial stresses under maximum indentation load for (001) and (100) plane of KDP.
Figure 8.3 Contour of the hoop stresses under maximum indentation load for (001) and (100) plane of KDP.
Figure 8.4 Contour of the residual radial stresses after fully unloading for (001) and (100) plane of KDP.
Figure 8.5 Contour of the residual axial stresses after fully unloading for (001) and (100) plane of KDP.
Figure 8.6 Contour of the residual hoop stresses after fully unloading for (001) and (100) plane of KDP.
9 Summary

Calcium Fluoride (CaF$_2$), Magnesium Fluoride (MgF$_2$) and Potassium Dihydrogen Phosphate (KDP) are widely used for optical instrumental applications due to their important chemical, physical, and optical properties. The optical performance of these materials is highly correlated to their surface quality. For this reason, it is important to investigate their mechanical properties during the surface finishing process to produce high quality finished parts. Indentation is a useful tool for evaluating mechanical properties of solids, especially for brittle solids. In addition, surface preparation, for example by grinding or polishing, involves a sequence of micro-indentation and micro-scratching effects [9]. In this thesis, the indentation behavior of CaF$_2$, MgF$_2$, and KDP was investigated in detail by using nano-indentation tests and finite element method with a mesoplastic formulation. Indentation on the main crystallographic planes: (100), (110), and (111) of CaF$_2$; (001), (101), and (111) of MgF$_2$; (100) and (001) of KDP was analyzed to examine the effects of crystalline anisotropy.

Appropriate values of material parameters were determined by fitting the numerical load-displacement curves with the corresponding experimental results. The simulations show that parameters in the range of 74–110 / 100–180 MPa (initial shear strength / self-hardening modulus), 168–250 / 220–270 MPa, and 265–450 / 380–600 MPa provide a reasonable numerical approximation to the
experimental tests for CaF$_2$, MgF$_2$, and KDP, respectively. The finite element models with appropriate material parameters were then used to examine the indentation performance of these materials.

The predicted spherical indentation hardness is based on the projected circular area delineated by the pile-up maximum height or the level of zero vertical displacement. For CaF$_2$, the hardness values are 1.02–2.11, 0.73–1.26, and 0.70–1.30 GPa for (100), (110) and (111) plane indentation, respectively, within the load range of 5–10 mN. The experimental spherical hardness for (111) plane of CaF$_2$ is 1.10–1.40 GPa provided by Ladison et al. [7] at the load of 2 N. The fact that our model for (111) indentation underestimates the experimentally measured hardness might be due to the reason that at higher loads the more extensive plastic deformation involves not only constant self-hardening (as we have assumed in our model) but also cross hardening that itself may depend on the amount of plastic strain. For MgF$_2$, the hardness values are 1.59–3.21, 0.73–1.26, and 0.73–1.40 GPa for (001), (101), and (111) plane indentation, respectively, within the load range of 5–10 mN. For KDP, the values are 1.28–2.26 and 1.46–2.06 GPa for (001) and (100) plane indentation, respectively, at the load of 1 mN. The experimental spherical hardness provided by Kucheyev et al. [24] are 2.0 ± 0.2 and 1.6 ± 0.2 GPa for (001) and (100) plane indentation, respectively. Their data are consistent with our results.

For CaF$_2$, the indentation depth of (111) plane is the largest and that of (100) plane is the smallest under the same load. The projected contact areas for (110) indentation are elliptical instead of circular due to its lower rotational symmetry. All three plane indentations exhibit pile-up after fully unloading. The pile-up for the (100) indentation is slightly higher than that of the (111) indentation. For the (110) indentation, pile-up is different along two symmetry planes. The hardness of the (111) plane was found the lowest among three planes indentation.

Stresses and residual stresses analysis of CaF$_2$ indicate that during the loading
cycle, median and radial cracks are more likely to grow than lateral cracks. All three crack modes will most easily be generated in the (111) indentation and least likely to occur in the (100) indentation. This explains the experimental observations that the subsurface damage is largest in the (111) plane and least in the (100) plane under the same grinding conditions [48]. During the unloading cycle, lateral cracks tend to grow in all three plane indentations, and will be most significant in the (111) indentation and least significant in the (100) indentation. This is in accordance with the experimental results of Kukleva et al. [10], that the material removal rate is largest in the (111) plane and least in the (100) plane for the same grinding conditions.

The distributions of the maximum normal stresses and maximum residual normal stresses on cleavage planes 111 of CaF$_2$ show that during the loading cycle, cleavage is expected to happen only in the (111) indentation. During the unloading cycle, all three planes tend to cleave and the cleavage will be most substantial in the (111) indentation and least in the (100) indentation. This suggests that (111) indentation is the most brittle and (100) indentation is the least brittle. Moreover, the spatial distribution of cleavage stresses shows that: in (100) indentation, the fractures are formed and propagated more readily near the indented area at the surface; in (110) indentation, the fractures are also more likely to propagate on the indented surface; in (111) indentation, the fractures are formed and propagated through the material interior. This is consistent with the experimental observations that the surface roughness is highest for grinding (111) plane and lowest for (100) plane for the same grinding conditions [13; 48].

For MgF$_2$, the indentation depth of (101) plane is the largest while the depth of (001) plane is the smallest at the same load. The projected contact areas for (101) and (111) indentation are elliptical due to their lower rotational symmetry. All three plane indentations exhibit pile-up after fully unloading. The hardness of (001) plane has the largest value among all three plane indentations and the
value of the (111) plane is slightly larger than that of the (101) plane indentation.

Stresses and residual stresses analysis of MgF$_2$ indicate that during the loading cycle, median and radial cracks are more likely to grow than lateral cracks. The median cracks will most easily be generated during the (101) indentation and least likely to occur in the (001) indentation, while radial cracks will most easily be generated and propagated during the (111) indentation. During the unloading cycle, lateral cracks will grow during the unloading segment for all three indentations. The lateral crack size will be largest in the (111) indentation where they occur directly below the indented area and least in the (101) indentation where they occur under the periphery of the indented area. This suggests that (111) indentation is the most brittle and (101) indentation is the least brittle.

Plastic zones for (001)/(101)/(111) plane indentations of MgF$_2$ were also examined by comparing the resolved shear stresses with the initial shear strength for the corresponding six slip systems $\{110\}/<001>$ at the maximum indentation load. The results suggest that the size of the plastic zone is the largest for (001) plane indentation and least for (101) plane indentation.

For KDP, the indentation depth of (100) plane is larger than that of (001) plane. The projected contact area for (100) indentation is elliptical due to its lower rotational symmetry. Both plane indentations exhibit pile-up after fully unloading. The pile-up for (001) plane indentation is slightly smaller than that of (100) plane. For (100) plane indentation, pile-up is higher on surface II than that on surface III. The hardness of (100) and (001) planes are very close ($\sim 15\%$ variation) which suggests small hardness anisotropy among (100) and (001) faces. This was also observed by Fang and Lambropoulos [23].

Stresses and residual stresses analysis of KDP indicate that during the loading cycle, median and radial cracks are more likely to grow than lateral cracks. The median and radial cracks will be generated and propagated in nearly the same level for these two plane indentations. During the unloading cycle, lateral cracks will
grow during the unloading segment for both plane indentations. The crack size will be larger in the (001) indentation than that in the (100) indentation. Also, the pattern of cracking is similar for these two plane indentations. This suggests that (001) plane indentation is more brittle than (100) plane indentation.
Bibliography


