2010

Nanomechanics of muscovite subjected to nanoindentation and the pertinent indentation size effect

Hang Yin
Louisiana State University and Agricultural and Mechanical College, yinhang@tsinghua.org.cn

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses

Part of the Civil and Environmental Engineering Commons

Recommended Citation
Yin, Hang, "Nanomechanics of muscovite subjected to nanoindentation and the pertinent indentation size effect" (2010). LSU Master's Theses. 3857.
https://digitalcommons.lsu.edu/gradschool_theses/3857

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master's Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
NANOMECHANICS OF MUSCOVITE SUBJECTED TO NANOINDENTATION
AND THE PERTINENT INDENTATION SIZE EFFECT

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering

in

The Department of Civil and Environmental Engineering

By
Hang Yin
B.S., Tsinghua University, 2003
December, 2010
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor Dr. Guoping Zhang for his insight instructions, continuous encouragement, and academic discussions. Second, I would like to thank other thesis committee members, Dr. Khalid Alshibli and Dr. Robert P. Gambrell, for their guidance, encouragement, and valuable suggestions. I am also indebted to Dr. Stephen J. Guggenheim of University of Illinois at Chicago and Dr. Ray E. Ferrell of Louisiana State University for providing the muscovite samples. Finally thanks would also go to Dr. Z. Wei who prepared the samples for testing.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS ............................................................................................................ ii

LIST OF TABLES .................................................................................................................... iv

LIST OF FIGURES .................................................................................................................. v

ABSTRACT ............................................................................................................................... vii

CHAPTER 1. INTRODUCTION ................................................................................................. 1

CHAPTER 2. LITERATURE REVIEW ....................................................................................... 3
  2.1 Structural Properties of Muscovite .............................................................................. 3
  2.2 Techniques for Determining the Physical Properties of Muscovite ......................... 4
  2.3 Theory of Kink Bands – Surface Deformation under Nanoindentation .................... 6
  2.4 Physical Properties of Muscovite Based on Indentation Technique ......................... 10
  2.5 Nanoindentation Size Effect ....................................................................................... 11

CHAPTER 3. MATERIALS AND METHODS ........................................................................... 14
  3.1 Sample Preparation ..................................................................................................... 14
  3.2 Nanoindentation Testing ............................................................................................ 16
  3.3 Determination of Elastic Modulus and Hardness ....................................................... 20

CHAPTER 4. EXPERIMENTAL RESULTS ............................................................................. 23
  4.1 Indentation Load-Displacement Curves ..................................................................... 23
  4.2 The Relationship between Maximum Load and Maximum Displacement .............. 29
  4.3 Hardness ..................................................................................................................... 31
  4.4 Elastic Modulus .......................................................................................................... 33
  4.5 Contact Stiffness ......................................................................................................... 34

CHAPTER 5. DISCUSSIONS OF RESULTS ............................................................................. 37
  5.1 Nanoscale Deformation under Nanoindentation ......................................................... 37
  5.2 Influence of Loading Methods on the Determination of Material Properties ............ 39
  5.3 Indentation Size Effect ............................................................................................... 41

CHAPTER 6. CONCLUSIONS ................................................................................................. 51

CHAPTER 7. RECOMMENDATIONS ...................................................................................... 52

REFERENCES ........................................................................................................................ 53

VITA ......................................................................................................................................... 57
LIST OF Tables

Table 3.1. Summary of the seven nanoindentation tests and their control parameters............... 16
Table 4.1. Comparison of loading rate for all tests at different load levels............................ 33
LIST OF FIGURES

Figure 2.1. Schematic illustration of the ideal crystal structure of muscovite................................. 4

Figure 2.2. The formation, development and movement of kink bands due to applied shearing force (Frank and Stroh 1952). .................................................................................................................... 7

Figure 2.3. Schematic of surface deformation under spherical indenter (Barsoum et al. 2004b). . 9

Figure 2.4. Geometrically necessary dislocations created by a rigid conical indentation ........... 12

Figure 3.1. The size, shape, and surface topography of the tested muscovite fragment: .......... 15

Figure 3.2. The loading profile for (a) the MTS standard method and (b) repeated loading method modified from the MTS standard method............................................................... 17

Figure 3.3. The CSM loading and unloading profile used as a monotonic loading test. ........... 19

Figure 3.4. Schematic of load-displacement curve for an instrumented nanoindentation test under DCM. .......................................................................................................................... 20

Figure 4.1. The load-displacement curves for Test 1 performed using the MTS standard method. Insets show the entire curve of 5 L/U cycles for all 4 indents (Inset (a)) and each individual indent (other insets).................................................................................................................. 23

Figure 4.2. The load-displacement curves of Test 5 and Test 6 (Table 1) performed under repeated loading: (a) Fmax = 0.05 mN and (b) Fmax = 0.1 mN................................................................. 25

Figure 4.3. The load-displacement curves of Tests 2-4 (Table 3.1) performed under repeated loading: (a) Fmax = 0.5 mN, (b) Fmax = 1.0 mN, and (c) Fmax = 2.0 mN. ................................. 27

Figure 4.4. The load-displacement curves of Test 7 (Table 3.1) performed using the CSM method................................................................................................................................. 29

Figure 4.5. The relationship between maximum load and maximum displacement for all repeated loading tests. .................................................................................................................. 30

Figure 4.6. The hardness of the muscovite derived from all tests. Only one H-h curve obtained by the CSM method is shown as an example. Also shown is the F-h curve averaged on the 7 CSM indents (Figure 4.4). ................................................................. 31

Figure 4.7. The elastic modulus of the muscovite derived from all tests. Only one E-h curve obtained by the CSM method is shown as an example................................................................. 33

Figure 4.8. Comparison of the unloading curves of all indentation tests: (a) 5 unloading sections from one indent of the MTS standard loading test (Test 1) and (b) ~ (f) 6 unloading sections from one indent of 5 repeated loading tests (Test 2 to 6 with Fmax = 2.0 mN, 1.0 mN, 0.5 mN, 0.1 mN and 0.05 mN seperately). ................................................................. 35
Figure 5.1. Continuous hardness measured from test 7 in Table 3.1........................................43
Figure 5.2. Model Regression of Hardness..................................................................................44
Figure 5.3. Four major pop-ins of the 7th indent in test ID 7 in Table 3.1.................................47
Figure 5.4. Illustration for simulating the indentation size effect using both regression relationship and modified model ..........................................................48
Figure 5.5. Regional magnification of the first pop-in in Figure 5.4..............................................49
ABSTRACT

Two groups of nanoindentation experiments, including repeated loading tests and monotonic loading tests, were performed on muscovite with a sharp indenter tip and loading direction normal to the basal plane. By varying the maximum load in the first group of repeated experiments, influences of the load level can be examined on the modes of nanoscale deformation and the resulting estimation of hardness and elastic modulus. The incipient kink band concept was employed to interpret the observed dispersed loading-unloading hysteresis loops by considering formation and annihilation of IKBs. Furthermore, the material’s contact stiffness behavior was characterized by comparing the normalized unloading section of the loading-unloading loops of each test. Then a group of strain rate controlled monotonic loading tests was conducted for further comparison and evaluation of strain hardening effects of muscovite introduced by previously cyclic loading process. The second objective of these experiments was to discuss the indentation size effect, which usually occurred in micro scale indentation tests, and propose a proper model that can simulate the occurrence of pop-ins as well as its degrees.
CHAPTER 1. INTRODUCTION

Muscovite is a true mica clay mineral consisting of continuous 2:1 layers. As a result of isomorphous substitution in the tetrahedral sheets, negative layer charges are usually generated and balanced by the incorporation of unhydrated interlayer K\(^+\) cations that tightly hold together adjacent layers. These interlayer cations introduce strong electrostatic bonds or Coulomb forces which in turn control the complex physical characteristics (elasticity, hardness, plasticity, etc.) of the naturally occurring nanostructured multilayer muscovite. For example, Baker et al. (2002) have noticed that the stretching, rearrangement or breakage of those kink bonds lead to the deformation of the minerals during loading/unloading cycles.

Muscovite is the most abundant form of micas, which are 2:1 phyllosilicate minerals with tightly held, non-hydrated, interlayer cations balancing a high layer charge \(x\) ranging from \(x = 0.5\) to \(x = 1.0\) based on an anion framework of [O\(_{10}\)(OH)\(_2\)]. Owing to their high uniformity in mineral composition and micro crystal structure, micas have the reputation of the most suitable analog material for the study of the nanomechanics of synthesized or manufactured nanostructured multilayers (Chen et al. 2010, Li et al. 2004, Podsiadlo et al. 2007, Rubner 2003, Tang et al. 2003).

Since phyllosilicate minerals are ubiquitous in the Earth’s crust and represent a major portion of soils and rocks, understanding their mechanical properties (e.g., hardness, elastic modulus) are of essential relevance to geomechanics, geophysics, and other disciplines related to subsurface explorations and the design and construction of foundations for civil infrastructure. In this study, muscovite was chosen as a representative mineral of the mica group to examine the
physical responses, e.g., elastic modulus and hardness, of this mineral subjected to various types of indentation tests, including repeated loading experiments and displacement controlled experiments.

The investigation of the nanoindentation behavior of muscovite carried out in this experimental study employed a very sharp indenter tip, which typically resulted in higher contact stress and lead to different modes of elastic and plastic deformation than a spherical indenter tip, with the loading direction normal to the basal plane and a varied maximum load ($F_{\text{max}}$) ranging from 0.05-2.0 mN. Particular objectives of the thesis include:

1) Examine the influence of load level on the modes of nanoscale deformation;
2) Examine the influence of repeated loading at different load levels on the determination of hardness and Young’s modulus;
3) Compare between monotonic loading tests using the continuous stiffness measurement (CSM) method and the repeated loading measurement for further discussion and evaluation of contact stiffness in accordance with indentation size effects;
4) Investigate nanoscale deformation mechanisms at different load levels for muscovite, and
5) Propose a regression model to simulate the unique deformation behavior of clay minerals. For example, to illustrate and predict the occurrence of pop-ins, and the corresponding hardness drop and stiffness restoration observed during indentation tests.
CHAPTER 2. LITERATURE REVIEW

2.1 Structural Properties of Muscovite

Phyllosilicates are a group of peculiar minerals consisting of either discrete or mixed-layered sequences of fundamental, continuous 1:1 layers of 0.7 nm or 2:1 layers of 1.0 nm in thickness, with distinctive sub-nanometer thick interlayers. They are usually platy in shape with high aspect ratios (e.g., >10:1-100:1), possess complex layer structure, and are characterized by different permanent layer charges resulting from the isomorphous substitutions in the tetrahedral or octahedral sheets of the 1:1 or 2:1 layers. Thus, these minerals can be treated as naturally occurring nanostructured layered materials.

Micas are 2:1 phyllosilicate minerals with tightly held, non-hydrated, interlayer cations balancing a high layer charge. According to the Clay Minerals Society (CMS) Nomenclature Report (Martin et al. 1991), the negative charge for this group caused by the isomorphous substitutions variable from $x = 0.5$ to $x = 1.0$ based on an anion framework of $[\text{O}_{10} \text{(OH)}_2]$. To gain an overall charge neutrality of the crystal structures, the positive charge of the interlayer cations must counterbalance the negative layer charge $x$. In micas, this neutrality is satisfied by the incorporation of $\text{K}^+$, or other non-hydrated monovalent cations in the interlayer. Micas may occur naturally as macro crystals with excellent uniformity in both composition and crystal structure, thus rendering them a suitable analog material for the study of the nanomechanics of synthesized or manufactured nanostructured multilayers (Chen et al. 2010, Li et al. 2004, Podsiadlo et al. 2007, Rubner 2003, Tang et al. 2003).

Muscovite is a non-expandable dioctahedral 2:1 phyllosilicate mineral with an ideal crystal formula $\text{K}(\text{Si}_3\text{Al})\text{Al}_2\text{O}_{10}(\text{OH})_2$ (Fanning et al. 1989). Its 2:1 layers typically possesses a
negative layer charge of $\sim 1.0$ per formula unit, primarily due to the isomorphous substitutions of one out of each of four $\text{Si}^{4+}$ in the pyrophyllite formula, $\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$, with an $\text{Al}^{3+}$ in the tetrahedral sheets of the 2:1 layer. The high negative layer charges are counterbalanced by non-hydrated or unsolved interlayer $\text{K}^+$ cations that tightly hold adjacent layers together. As such, the layers are bonded by primarily electrostatic or Columbic forces introduced by the “electrostatic cement” of cations (most commonly $\text{K}^+$) located between the basal oxygen planes of adjacent layers. Owing to this strong electrostatic force, $\text{H}_2\text{O}$ or other polar molecules cannot enter the interlayer space, which makes the muscovite or other mica minerals nonexpendable. Muscovite is the most abundant form of mica, and it possesses one other extremely mechanical behavior: high flexibility and high strength in its basal plane (Caslavsk and Vedam 1970). Figure 2.1 shows a schematic illustration of the crystal structure of muscovite.

![Figure 2.1. Schematic illustration of the ideal crystal structure of muscovite](image)

2.2 Techniques for Determining the Physical Properties of Muscovite

Micas are the third most extensive group of minerals (after feldspars and quartz) in granite, and they serve as precursors for expandable 2:1 minerals by replacing the non-
exchangeable interlayer cations by hydrated exchangeable cations. In order to distinguish these minerals from others where mica is interstratified, several techniques and instruments have been employed by geotechnical engineers and researchers among which the most widely used is X-ray Diffraction (XRD) analysis. Since muscovite is an Al-rich dioctahedral mica with nonexpendable interlayers, its XRD patterns are identified by three intense peaks in the region of 1.0, 0.5 and 0.33 nm. (Fanning, et al 1989). For decades, the measurement of stiffness and elasticity of muscovite or other phyllosilicates has been extended from macro scales down to micro or even nano scales.

Ultrasonic techniques were first introduced to measure the elastic modulus of muscovite in five directions (Aleksandrov and Ryzhova 1961) out of the thirteen independent elastic moduli caused by crystal monoclinic symmetry. Their results varied from 12.2 GPa to 178 GPa with the maximum one obtained from $C_{11}$ which was primarily dependent on the strong covalent bonding within the layers while the small ones were governed by the weaker interlayer bonding. They also utilized this technique to measure the modulus of other rock-forming materials as well as pyrite and pyroxenes.

Previous researchers have also employed classical bending experiments (pure flexure) for determining the Young’s modulus of muscovite in macro scale (Caslavsk and Vedam 1970). Based on numerous carefully prepared experiments carried out in the basal plane but various directions (e.g., [100], [010], [310] and [001]), they figured out that the results obtained on a number of specimens exhibited considerable scatter about the mean value, and a correlation between the corrugation topology and Young’s modulus could be related where corrugation lowered the Young’s modulus value. In this case, the 010 orientation exhibited the lowest bending resistance around 88 GPa with a overall average value at about 159 GPa.
Brillouin scattering measurement was another method that has been used to estimate the elastic modulus of muscovite (Mcneil and Grimsditch 1993, Vaughan and Guggenheim 1986). Vacher and Boyer (1972) have made a systematic analysis of the theorem of transportation of Brillouin lines which have frequency shifts when travelling through mediums, and made attempt to select conditions that allowed the most accurate determination of the elastic and photoelastic constants of all crystal systems including cubic, tetragonal, trigonal and orthorhombic. Vaughan and Guggenheim (1986) first introduced this method into measuring the elastic stiffness modulus of natural muscovite of all the thirteen values, and concluded that significant acoustic anisotropy was expected due to the weak interlayer bonding in the velocity patterns. The maximum value they obtained was also the measured $C_{11}$ which was around 181 GPa. Mcneil and Grimsditch (1993) conducted a series of tests based on Brillouin scattering technique, and used two scattering geometries (backscattering and platelet) to determine the natural muscovite elasticity. Their results yielded that the maximum stiffness generated from $C_{22}$ ~ around 179.5 GPa while $C_{11}$ was nearly the same ~ 176.5 GPa.

2.3 Theory of Kink Bands – Surface Deformation under Nanoindentation

In the article named “On the Theory of Kinking” which was published in 1952, Frank and Stroh (1952) first introduced the concept of kink band, which was proposed based on the kinking theory (Orowan 1942) on the crystals’ deformation mechanism, to describe the phenomenon that a critical shear angle would exist at the edges of paired dislocation walls that were formed when crystalline material suffered from uniform applied stress. Once the shearing angle applied on the material exceeded the critical angle, the energy concentration for shearing generated at the edges of the tilt walls would cause the crack of the existed walls and form new dislocation pairs or
loops. They concluded that generation, development and breakage of the kink bands would properly illustrate the experimentally observed results.

Figure 2.2. The formation, development and movement of kink bands due to applied shearing force (Frank and Stroh 1952).

Figure 2.2 redrawn from the original article shows the process of how these dislocation walls develop under applied shearing stress. According to their concept, a kink band is defined as “a region between two approximately plane parallel ‘walls’ of edge dislocations” and “the dislocations in these two walls are of opposite signs, so that the walls are forced in opposite
directions, away from each other, by the applied stress; but the walls are of finite extent, and their edges attract each other.”

First, when a shearing force is applied on the specimen, stress will be concentrated at the edges of unspecified obstacles such as a cavity or other stress raiser, therefore a pair of horizontal slip planes is generated and first pair of kink bands commences (Figure 2.2a, b). When the kink bands extend to the free surface, the attraction between the edges of the tilt walls disappears and they should become parallel planes (Figure 2.2c). A continuing shear force would then broaden the width of the pair walls and further be able to initiate a second kink band between the first walls (Figure 2.2d). This process keeps going on as long as the shearing force is applied and consequently causes the kink bands moving outwards until a critical width is reached (Figure 2.2e, f). This sequel generally illustrates the typically observed kinks caused by shearing done by prior workers, and provides a fundamental concept for further discussion and analysis on the surface deformation behavior of materials under nanoindentation.

Barsoum et al. (2004a, 2004b, 2003) has further expended Frank and Stroh’s two-dimensional kink bands model to a three-dimensional condition and applied it to the field of nanoindentation tests to illustrate the surface deformation of phyllosilicate materials and their identical physical responses under a spherical indenter tip. In their modified model, a new term named “incipient kink band” or IKB was defined to describe the initially generated, fully reversible and un-dissociated parallel walls with opposite sign dislocations. They considered this IKB as the key micro-structural hysteretic element which can be employed to explain the hysteretic elastic deformation behavior under indenters subject to the subcritical stress.
While Frank and Stroh’s model simply used the repetition of process illustrated in Figure 2.2 to describe the deformation caused by the shearing force, Barsoum et al.’s illustration divided this process into two stages: first, IKBs were initialed under the indenter and two opposite polarized dislocation walls were formed which had high restoring force; then the continuing...
force caused these walls to be mobile and move outside, resulting in the formation of kink boundaries and rupture of basal planes which had no restoring force but possible relaxation potentials (Figure 2.3, redrawn from Barsoum et al. (2004b)).

The mechanism of kink bands together with incipient kink bands mentioned above will be employed in this research to illustrate the surface deformation behavior of muscovite under a series of nanoindentation tests.

2.4 Physical Properties of Muscovite Based on Indentation Technique

Prior researchers (Barsoum et al. 2004b, Basu et al. 2009, Zhang et al. 2009a, b) have found that muscovite exhibits interesting and distinct mechanical and deformational behaviors under nanoindentation. For example, Barsoum et al. (2004b) observed the occurrence of fully reversible, superimposed stress-strain hysteresis loops when a muscovite single crystal was subjected to indentation repeated loading, and associated the nonlinear elastic hysteresis with the formation and annihilation of incipient kink bands. They further pointed out that muscovite and other layered minerals and materials (e.g., graphite, layered ceramics) belonged to a group of kinking nonlinear elastic solids. Zhang et al. (2009a, b, 2010) observed, based on a series of nanoindentation experiments conducted on muscovite and other phyllosilicate minerals with a sharp indenter tip, that both the hardness and elastic modulus of muscovite exhibited apparent indentation size effects. That was, the hardness and elastic modulus decreased with indentation depth and a maximum indentation load increased. Furthermore, muscovite behaved more like a brittle material under sharp indentation compared with other layered minerals with hydrated interlayer cations (e.g., rectorite), and kink band formation, radial cracking, lateral cracking, layer delamination, and even spallation may all occur during nanoindentation (Zhang et al.
In particular, the phenomenon that the elastic modulus decreased with indentation depth was not typically observed for metals or other stereotypical crystalline materials. Apart from these work, the influence of repeated loading on determining the hardness and elastic modulus of muscovite has not been studied in detail.

2.5 Nanoindentation Size Effect

According to the aforementioned kink band theory on phyllosilicate materials, the surface deformation under the indenter tip is comprised of two stages: the initiation of incipient kink bands and the development and movement of kink bands. These two distinct processes exhibit totally different physical behaviors: the IKB is fully reversible elastic deformation while the moveable KB is a kind of irreversible plastic deformation. Since the IKB is primarily governed by angstrom scale (Å) interaction factors such as the crystallographic lattice constants (e.g., layer bonds in phyllosilicate minerals), the elastic deformation usually has virtually no size dependence in an ideal specimen (no preexisting defects) (Choi et al. 2003).

However, the latter deformation response exerts a high dependence on the physical and microstructure length scales of the material. This plastic property of materials has been related to the indentation size effect (ISE) which is termed to describe the phenomenon that measured hardness increases as indentation depth decreases, even for tests of homogeneous materials. The indentation size effect in nanoindentation tests has been experimentally observed during the surface hardness testing of materials from several microns down to a few nanometers, especially in the field of describing plastic deformation in metals (Choi et al. 2003, Ma and Clarke 1995, Zong and Soboyejo 2005).
In order to establish a relationship between the measured decreasing hardness and the microelectronic thin film structures, much research has addressed this issue. Nix and Gao (1998) first developed a strain gradient plasticity law to describe these effects based on geometrically necessary dislocations concept for copper. Afterwards, the concept for the size effect based on strain energy releasing has been proposed by Lam et al. (2004). For amorphous materials such as polymers, kink bands and chains/springs theory (kinking model) have been used to simulate the nanoindentation size effect (Chong and Lam 1999, Han and Nikolov 2007, Lam and Chong 1999).

The Nix and Gao model has made two assumptions. The first one was that the indentation was accommodated by circular loops of geometrically necessary dislocations with Burgers vectors normal to the plane of the surface; the other one was that all of the injected loops remained within the hemispherical volume defined by the contact radius $a$ (Figure 2.4). Geometrically necessary dislocation is one of the two major dislocations that are generated when plastic deformation occurs, as pointed out by Fleck et al. (1994). It is the main process that leads to the gradients of plastic shear when the materials under the indenter moving towards the crystal surface forming slip lines. The other dislocation, called statistically stored dislocation, is stored to harden the material and forms randomly inter-trapped patterns (Bortoloni and Cermelli 2004).

![Figure 2.4. Geometrically necessary dislocations created by a rigid conical indentation](image-url)
Based on these two assumptions and von Mises flow rule, Nix and Gao’s model can be expressed as:

\[ H = H_0 \sqrt{1 + \frac{h^*}{h}} \]  \hspace{1cm} (2.1)

Where \( H_0 \) is the hardness that would arise from the statistically stored dislocations alone; \( h^* \) is the characteristic length; \( h \) is the indented depth.

This model fits the observed experimental results of crystalline materials very well at the stable stage of plastic deformation (indentation depth greater than approximate 100 nm), and has been referred to widely as a fundamental concept for modeling the indentation size effect.

The other kinking model is derived from the molecular theory of yield and nucleation energy for a loop of critical loop size formed under the combine influence shear stress and thermal energy (Lam and Chong 1999). Compared with equation (2.1), the kinking model has a regression expression as:

\[ H = H_0 \left( \frac{h^*}{h} + 1 \right) \]  \hspace{1cm} (2.2)

Where \( H_0 \) is the hardness at infinite indent depth; \( h^* \) contains the material and temperature dependencies; \( h \) is the indented depth.
CHAPTER 3. MATERIALS AND METHODS

3.1 Sample Preparation

The muscovite sample chosen for this study was collected from Panasqueira, Portugal. Its chemical composition and crystal structure were well analyzed previously by Guggenheim et al. (1987). It is a $2M_1$ mica polytype and has a layer charge of -1.05 with a chemical formula $(K_{1.00}Na_{0.03}Ca_{0.01})(Al_{1.93}Fe^{2+}_{0.01}Mg_{0.01}Mn_{0.01})(Si_{3.09}Al_{0.91})O_{10}(OH)_{1.88}F_{0.12}$. A carefully selected small fragment with an in-plane dimension of $> 2$ mm and a thickness of $> 0.1$ mm was gently cleaved off the muscovite rock chip and then used for subsequent sample mounting.

A piece of single-crystal silicon wafer (100) (MTI Corporation, Richmond, CA) with a dimension of $10 \times 10 \times 0.6$ mm (length × width × thickness) was used as the substrate that provides the atomically flat surface for sample mounting. A regular aluminum puck was first heated to 130 °C on a hot plate and then a thin layer of Crystalbond 509 amber resin (Aremco Products, Inc., New York), which melts at the temperature of 130 °C or higher, was applied to the puck surface. This was followed by carefully placing the silicon wafer substrate onto the puck surface where the resin was applied. To avoid trapping air between the resin and wafer interface, the wafer was gently pressed into the melted resin with a continuous rotation along one straight edge. Sufficient time was allowed for the wafer to be heated to 130 °C. Then another thin layer of amber resin was applied onto the silicon wafer surface, followed by carefully placing the muscovite sample onto the silicon wafer in a similar manner. Again, during mounting, extremely special care was taken to avoid trapping air between the resin and muscovite interface and to keep the muscovite basal plane as parallel to the wafer surface as possible. Moreover, to prevent overheating the muscovite sample, immediately after the sample placement, the entire sample set
(i.e., including alumina puck, silicon wafer, and muscovite) was removed off the hotplate to a leveling table for cooling. Finally, a very thin layer was cleaved off the top of the muscovite sample with a razor blade so that a fresh and intact surface was exposed for nanoindentation loading.

![Image](image_url)

Figure 3.1. The size, shape, and surface topography of the tested muscovite fragment: (a) optical image and (b) AFM image.

Before indentation testing, the sample was first examined under an optical microscope to check the sample dimension and quality of sample mounting. Figure 3.1a shows an optical micrograph of the sample. The cleaved fragment has a hexagonal shape with all six straight edges. It has a minimum dimension of 2 mm. No cracks are observed within the sample, indicating that this fragment is most likely a single crystal. The surface topography of the sample was further characterized using an Agilent 5500 atomic force microscope (AFM) (Agilent Technologies, Inc., Chandler, AZ). Figure 3.1b shows a typical AFM micrograph for an area of 100 × 100 μm on the muscovite surface. It is normal that an air-cleaved mica may not yield the
atomically flat surface due to surface contamination by the atmosphere and the reaction of interlayer $K^+$ with atmospheric water and $CO_2$ (Ostendorf et al. 2008). The blurred lines, divided into several parallel sets, are either very tiny scratches caused by a cotton swap during sample surface cleaning or the edge and screw dislocations that are previously present in the crystal or newly introduced by cleaving (Amelinckx 1952, Amelinckx and Delavignette 1960, Hull and Bacon 2001). Again, no cracks are observed in the scanned area.

3.2 Nanoindentation Testing

An MTS Nano XP indenter (MTS Nano Instruments, Inc., Oak Ridge, TN) was employed for all nanoindentation experiments. Totally seven tests, which used three different loading methods including the MTS standard method, the repeated loading modified from the MTS standard method, and the CSM method, were performed with a dynamic contact module (DCM) head equipped with a diamond Berkovich tip of < 20 nm in tip radius. The DCM head has a load resolution of 1.0 nN and displacement resolution of < 0.01 nm. For each test, typically 2-7 duplicate indents at a spacing of 100 $\mu$m were performed to ensure measurement repeatability. All tests were run at an allowed thermal drift rate of < 0.05 nm/s. Table 3.1 summarizes the control parameters for all the tests. Further details are given below.

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Loading method</th>
<th>Maximum load $F_{max}$ (mN)</th>
<th>Loading time $t_L$ (s)</th>
<th>Number of L/U cycles</th>
<th>Number of duplicate indents</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MTS Standard</td>
<td>2.0</td>
<td>30.0</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Repeated</td>
<td>2.0</td>
<td>30.0</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Loading</td>
<td>1.0</td>
<td>15.0</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>modified from the MTS</td>
<td>0.5</td>
<td>5.0</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>Standard</td>
<td>0.1</td>
<td>2.0</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.05</td>
<td>2.5</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>CSM*</td>
<td>~2.8-3.8</td>
<td>Varied</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 3.1. Summary of the seven nanoindentation tests and their control parameters.
The MTS standard method applies indentation load at a constant loading rate under load control mode. Figure 3.2a depicts the loading sequences for this method. The maximum load ($F_{\text{max}}$) and loading time ($t_L$) were preset to 2.0 mN and 30 s, respectively. It took 5 cycles of loading and unloading (L/U) to reach the $F_{\text{max}}$. For the $i$-th cycle (where $i = 1, 2, \ldots, 5$), the peak load $F_{P,i}$ and loading rate to peak load $\dot{F}_i$ are given by:

Figure 3.2. The loading profile for (a) the MTS standard method and (b) repeated loading method modified from the MTS standard
where $N$ is the total number of L/U cycles or 5 for this test. For the unloading section of each cycle, the same unloading rate was used as that of loading section in that particular cycle, and the load was reduced to 90% of the peak value of that cycle. Also, at the peak load, the holding time ($t_h$) of 10 s was allowed in all L/U cycles. At the end of the 5th cycle unloading, a holding time of 100 s was allowed for thermal drift correction.

This MTS standard method was modified to perform repeated loading tests (Figure 3.2b). Three modifications were made, including keeping the peak load of each cycle the same as $F_{\text{max}}$; reducing the holding time to zero at all peak loads; and changing the percentage of unloading from 90% in the MTS standard method to 100% in the repeated loading method. All other parameters remained the same. Totally 5 tests (i.e., Tests 2 to 6) with different $F_{\text{max}}$ and loading time $t_L$ (Figure 3.2) were performed.

The CSM method was conducted under strain or deformation control mode using a constant indentation strain rate ($\dot{h}/h$) of 0.05 s$^{-1}$, where $h$ is indentation depth. The CSM mode involved the superimposing of a displacement-controlled harmonic loading with a frequency of 75 Hz and amplitude of 1.0 nm. A five-step loading procedure depicted in Figure 3.3 was employed: (1) increase load at a constant indentation strain rate of 0.05 s$^{-1}$ to a pre-selected maximum indentation depth ($h_{\text{max}}$) of 200 nm; (2) hold the maximal load $F_{\text{max}}$ constant for a given holding time ($t_h$) of 10 s; (3) decrease load under load control mode using the same loading rate ($\dot{F}$) as that at $F_{\text{max}}$ of loading section to 10% of $F_{\text{max}}$; (4) hold the load (at 10% of $F_{\text{max}}$) constant for 100 s to record the thermal drift for correction; and (5) decrease load linearly to zero.

\[
F_{P,i} = F_{\text{max}} \frac{2^i}{2^N} \tag{3.1}
\]

\[
\dot{F}_i = \frac{F_{P,i}}{t_L} = \frac{F_{\text{max}}}{t_L} \frac{2^i}{2^N} \tag{3.2}
\]
For each of the tests shown in Table 3.1, a rigorous four-step testing scheme was employed to ensure high reliability and accuracy of the results: (1) tip cleaning by indenting (nine indents) on a piece of Scotch double-sided sticky tape; (2) pre-testing of tip by indenting on standard fused silica to calibrate the tip and check the instrument working status; (3) making multiple indents (typically 2-7 indents, depending on the size of an available clean and intact area) with a spacing of 100 μm on a smooth region of the muscovite sample surface selected under the optical microscope installed with the nanoindenter; and (4) post-testing of the tip by checking indentation of the same standard fused silica used prior to the test. If the hardness and elastic modulus of the fused silica measured in Steps 2 and 4 deviated from the standard values significantly, the results obtained in Step 3 were discarded and a new measurement was performed starting from Step 1.
3.3 Determination of Elastic Modulus and Hardness

Determination of the elastic modulus \( E \) and hardness \( H \) of the sample were derived by the Oliver and Pharr method (Li and Bhushan 2002, Oliver and Pharr 1992, 2004). For the MTS standard and modified MTS standard methods, determination of \( E \) and \( H \) requires estimating the contact stiffness defined as the slope of the initial unloading curve at the maximum indentation depth \( h_{\text{max}} \). For the CSM method, a harmonic contact stiffness continuously determined over the indentation depth is required to derive the \( E \) and \( H \) values. The above analysis requires the elastic constants of the indenter tip and the sample. For all tests, a diamond tip was used with a Young’s modulus and Poisson’s ratio of 1141 GPa and 0.07, respectively. The Poisson’s ratio of the muscovite sample was assumed to be 0.25 (Mavko et al. 1998), since previous studies suggested that the Poisson’s ratio of the tested materials had little significant influence on the Young’s modulus (Mencik et al. 1997). Finally, because the loading direction is normal to the basal plane of the phyllosilicate mineral, the derived elastic modulus and hardness are referred to the [001]° direction.

![Figure 3.4. Schematic of load-displacement curve for an instrumented nanoindentation test under DCM.](image-url)
As shown in Figure 3.4, the DCM head measures the hardness \( (H) \) and the reduced Young’s Modulus \( (E_r) \) of the sample at each initials of unloading, which can be described as:

Reduced modulus of elasticity:

\[
E_r = \frac{1}{\beta} \frac{\sqrt{\pi} S}{2 \sqrt{A(h_c)}}
\]  
(3.3)

Hardness at maximum loading:

\[
H = \frac{F_{\text{max}}}{A_r}
\]  
(3.4)

Here \( \beta \) is a dimensionless correction factor if the indenter tip is not axisymmetric, e.g., a circular contact where \( \beta = 1 \). For a triangular cross section like the Berkovich indenter, \( \beta = 1.034 \) is recommended; \( A(h_c) \) is the projected contact area calculated by evaluating an empirically determined area function at the contact depth \( h_c \); \( S \) is the unloading stiffness and has a power law relationship with the displacement (Oliver and Pharr 1992) as shown below:

\[
S = \left. \frac{dF}{dh} \right|_{h=h_{\text{max}}} = \frac{Bm(h - h_f)^{m-1}}{h}
\]  
(3.5)

\[
F = B(h - h_f)^m
\]  
(3.6)

The tip function \( A(h_c) \) associates the projected contact area with the contact depth and can be approximated by a fitting polynomial function proposed by Oliver and Pharr (1992) for a Berkovich tip:

\[
A_c = C_0 h_c^2 + \sum_{j=1}^{8} C_j h_c^{(2j-1)}
\]  
(3.7)

Where the contact depth is obtained by:
\[ h_c = h - \varepsilon \frac{F}{S} \quad (3.8) \]

Here, \( h \) is the total penetration depth, and \( \varepsilon \) is the indenter geometry constant (0.75 for a Berkovich tip). The leading terms \( C_j \) are reflections of the tip wearing condition. For a perfect Berkovich indenter, equation 3.8 can be calculated using \( A_c = 24.5 \cdot h_c^2 \) only. As the indent size decreases the error caused by tip rounding increases. And other terms of \( C_j \) should be added into the function. The value of them were determined through tip calibration indentation tests on standard fused silica with a Young’s modulus \( E \) of 72 GPa.

On obtaining the reduced Young’s modulus, the elastic modulus of the sample is derived by (Doerner and Nix 1986, Johnson 1985):

\[ \frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (3.9) \]

Here \( \nu \) and \( \nu_i \) are the Poisson’s ratios of the sample and indenter, and \( E \) and \( E_i \) are the Young’s modulus of the sample and indenter, respectively.
CHAPTER 4.  EXPERIMENTAL RESULTS

4.1 Indentation Load-Displacement Curves

Figure 4.1 shows the load-displacement curves for Test 1 performed using the MTS standard method. The four curves from four duplicate indents exhibit similar behavior. The L/U cycles generate hysteresis loops, which are very small for the initial three L/U cycles and become more pronounced for the 4th and 5th L/U cycles. Another striking feature is the presence of multiple, randomly occurring pop-ins in the loading section of these curves, whose magnitude varies but typically tends to increase with load, while the unloading section is much smoother. Small pop-ins with an extension of \(~1.0\) nm can occur as early as at a depth of 8-10 nm and a load of \(~0.03-0.04\) mN. In general, for duplicate indents, the greater the pop-in extends, the
deeper the indentation depth under the same load reaches, reflecting apparent overall reduction in the material’s resistance to penetration. Moreover, once pop-ins occur, these curves start to separate away from each other, leading to the dispersion of the loading section of the curves. It appears that pop-ins are likely the major cause for the dispersion of the curves. Careful observation can find that the width of the L/U hysteresis loops is also affected by pop-ins. For instance, due to pop-ins, the 5th L/U loop of Indent 1 and 4th L/U loop of Indent 4 are relatively wider than the corresponding loops of other indents.

Figure 4.2 shows the load-displacement curves for two tests (Tests 5-6 in Table 3.1) performed using the repeated loading method at small $F_{\text{max}}$ of 0.05-0.1 mN. In Figure 4.2a, for all four duplicate indents, each with 20 L/U cycles, all 20 hysteresis loops are nearly fully superimposed. Both the loading and unloading sections of the loops are smooth, and no pop-ins are discernable. All loops are also fully closed, completely repeatable, and fully stabilized, indicating that no permanent or plastic deformation occurs. Similar phenomenon can be observed in Figure 4.2b. As discussed later, the occurrence of these completely closed, fully reversible, and superimposable L/U hysteresis loops can be interpreted by a nanoscale deformation mechanism: the formation, movement, and annihilation of incipient kink bands (Barsoum et al. 2004a, Barsoum et al. 2004b).

In spite of the different $F_{\text{max}}$ (i.e., 0.05 vs. 0.1 mN), the width of the loops for these two tests are nearly the same, about 2-3 nm measured for a given indentation load. The small difference in the L/U loops between these two tests may be caused by the different loading rates (i.e., 0.02 vs. 0.05 mN/s). It is worth pointing out that the pseudo holding periods at zero and maximum loads are caused by the indenter’s capability of accurate control of loading. Because the loading time is very short for these two tests (Table 3.1) and the switch of loading and
unloading direction also takes time, a very small holding period (≈0.2-0.4 s) was found from the directly recorded data for load and time measurements.

Figure 4.2. The load-displacement curves of Test 5 and Test 6 (Table 1) performed under repeated loading: (a) $F_{\text{max}} = 0.05$ mN and (b) $F_{\text{max}} = 0.1$ mN.
Figure 4.3 shows the load-displacement curves for the other three tests (Tests 2-4) performed using the repeated loading method. These tests exhibit nearly the same behavior. First, pop-ins of varying extension occurs randomly in all curves. The first pop-ins of typically small extension take place above 0.1 mN and 20 nm, and larger pop-ins take place at higher loads. With these pop-ins, the curves from different indents and the L/U hysteresis loops from individual indents start to disperse and move faster toward the right. The phenomenon that the width of the L/U loops increases with pop-in extension observed in Figure 4.1 is further manifested here. Second, an interesting phenomenon common to all three tests is that the L/U loops tend to converge to a stabilized one, after a few L/U cycles. Such a phenomenon has been referred to as “shakedown” by previous researchers (Cross et al. 2006, Johnson 1985, Williams et al. 1999). It refers to the process, under repeated loading, whereby the plastic deformation caused by initial L/U cycles introduces a system of residual protective stresses which make the steady cyclic state purely elastic (Johnson 1985) or cyclically plastic (Williams et al. 1999), leading to elastic shakedown or plastic shakedown, respectively (Williams et al. 1999). In general, three mechanisms contribute to the apparent shakedown process: the protective residual stress induced by plastic deformation of initial L/U cycles; the increased contact area along with accumulated plastic deformation, leading to the reduced contact stress; and the strain-hardening of the material. For the tested muscovite, the former two mechanisms may be dominant. As discussed later, the increase in contact stiffness with the number of L/U cycles also suggests that the muscovite exhibits cyclic strain hardening. Finally, during the process of shakedown, the occurring frequency and extension of the pop-ins also tend to decrease and even disappear as the number of L/U cycles increase. This also suggests that pop-ins are the major cause of non-recoverable or permanent deformation during nanoindentation loading for the tested mineral.
This observation is also in accordance with the observed increment of the width of L/U loops with pop-in number and occurring frequency. In other words, if pop-ins or non-recoverable permanent deformation occurs, the L/U loops are not fully closed or shakedown cannot take place.

Figure 4.3. The load-displacement curves of Tests 2-4 (Table 3.1) performed under repeated loading: (a) Fmax = 0.5 mN, (b) Fmax = 1.0 mN, and (c) Fmax = 2.0 mN.
Figure 4.4 shows the load-displacement curves of Test 7 performed using the CSM method. Although the small harmonic sinusoid loading is superimposed, these curves are monotonic loading and unloading (i.e., just 1 L/U cycle). Some phenomena related to what has been discussed above are clearly identifiable: random occurrence of pop-ins of varied extension in the loading section of the curves; dispersion and separation of the curves after the occurrence of pop-ins; and increment in the width of the L/U loops with the total extension of all pop-ins. Moreover, although the initial pop-ins are small and the extension of pop-ins tends to increase with increasing load, this is not always true. Smaller pop-ins may still take place after a giant pop-in occurs.
By comparing Figure 4.2 with Figure 4.3, one can easily see that muscovite responds quite differently to repeated loading at different load levels. It appears that a critical maximum load, \( (F_{\text{max}})_{\text{crit}} \), exist between 0.1-0.5 mN. Below this value, the L/U loops are completely closed, fully reversible, and muscovite behaves as a kinking nonlinear elastic solid (Barsoum et al. 2004a). Otherwise, the L/U loops are not closed and permanent deformation accumulates with the number of L/U cycles increasing. However, muscovite will reach a state of plastic shakedown after a number of L/U cycles, characterized by smooth, closed, and thinner L/U loops. Further testing is required to determine the exact value of this critical maximum indentation load.

### 4.2 The Relationship between Maximum Load and Maximum Displacement

Figure 4.5 collectively summarizes the relationship between the \( F_{\text{max}} \) and \( h_{\text{max}} \) for all tests performed by repeated loading, including the one by the MTS standard method. Interestingly, the data can be divided into two groups according to the load level. When \( F_{\text{max}} \) is \( \leq 0.25 \) mN, the
points for all L/U cycles at a given $F_{\text{max}}$ are superimposed over each other, indicating that the maximum displacement remains the same in spite of multiple L/U cycles; When $F_{\text{max}}$ is $\geq 0.5$ mN, the points for all L/U cycles at a given $F_{\text{max}}$ form a band, whose width increases with the load level. This indicates that the variations in the maximum indentation depth increases with $F_{\text{max}}$. Apparently, this variation is associated with the pop-ins whose accumulative extension usually increases with $F_{\text{max}}$.

![Figure 4.5. The relationship between maximum load and maximum displacement for all repeated loading tests.](image)

As discussed below, the most obvious influence of this band or variation of $h_{\text{max}}$ is on the determination of the material’s hardness $H$ and elastic modulus $E$. Because even a fixed $F_{\text{max}}$ may cause different $h_{\text{max}}$ and the latter is used to estimate the projected contact area and contact stiffness in the Oliver and Pharr method (Oliver and Pharr 1992, 2004), the derived hardness and
elastic modulus will vary significantly. Based on Figure 4.5, \( (F_{\text{max}})_{\text{crit}} \) can be further refined to be between 0.25-0.5 mN.

4.3 Hardness

Figure 4.6. The hardness of the muscovite derived from all tests. Only one \( H-h \) curve obtained by the CSM method is shown as an example. Also shown is the \( F-h \) curve averaged on the 7 CSM indents (Figure 4.4).

Figure 4.6 summarizes the hardness values derived from all tests. The continuous \( H-h \) curve was obtained by the CSM method (Test 7), while the discrete data points by the MTS standard and repeated loading methods. Several striking features can be observed, which are discussed as follows:

- The first phenomenon is the significant variation of hardness with indentation depth, the maximum load (even at the same indentation depth), and the method of loading (i.e., repeated loading vs. CSM). The derived hardness values range widely from 3.0 to 12.2 GPa. The hardness decreases significantly with indentation depth for both monotonic
CSM loading and repeated loading at a given $F_{\text{max}}$, indicating that the apparent indentation size effect exists for this mineral. For repeated loading at the same $F_{\text{max}}$, the $H$ values also decrease with the number of cycles.

- At small maximum loads ($\leq 0.25$ mN), the hardness values obtained by repeated loading methods all lie above the continuous $H-h$ curve by the CSM method. However, at relatively larger loads ($\geq 0.5$ mN), the majority of the $H$ values lie below that continuous $H-h$ curve, although some values lie above it. This may be attributed to the random occurrence of pop-ins of varied extension, which affects determination of the projected contact area used in hardness estimation.

- It is also interesting to compare the load values on the CSM curve at the points where the series of points from repeated loading at a given $F_{\text{max}}$ intersect with the continuous $H-h$ curve from the CSM method. Table 4.1 compares these two series of load values (i.e., the 1st vs. 4th column). Surprisingly, at these intersecting points, the load values from the CSM method are nearly equal to the $F_{\text{max}}$ of the repeated loading tests. Furthermore, based on the obtained load values, the loading rate $\dot{F}$ at each load can be found from the recorded data according to Figure 3.3, which is also summarized in Table 4.1 (the 5th column). The difference in the loading rate may contribute to the variation of the hardness at a given $F_{\text{max}}$, although the major factor contributing to the hardness variation appears to be the multiple, randomly occurring pop-ins.

- For the $H-h$ curve by the CSM method, the general trend is that the hardness decreases with $h$. However, unlike some crystalline metals, the $H-h$ curve is not smooth, but characterized by many abrupt drops, which typically correspond to pop-ins.
Table 4.1. Comparison of loading rate for all tests at different load levels.

<table>
<thead>
<tr>
<th>$F_{\text{max}}$ (mN)</th>
<th>Repeated loading method: Constant loading rate (mN/s)</th>
<th>MTS standard method: Constant loading rate (mN/s)</th>
<th>Corresponding load from CSM (mN)</th>
<th>CSM method: Loading rate at this load (mN/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.02</td>
<td>0.00418</td>
<td>0.03</td>
<td>0.0024</td>
</tr>
<tr>
<td>0.1</td>
<td>0.05</td>
<td>0.00835</td>
<td>0.06</td>
<td>0.004</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0625</td>
<td>0.0167</td>
<td>0.43</td>
<td>0.023</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0667</td>
<td>0.0333</td>
<td>0.95</td>
<td>0.044</td>
</tr>
<tr>
<td>2.0</td>
<td>0.0667</td>
<td>0.0667</td>
<td>1.9</td>
<td>0.095</td>
</tr>
</tbody>
</table>

4.4 Elastic Modulus

![Graph](image)

Figure 4.7. The elastic modulus of the muscovite derived from all tests. Only one $E$-$h$ curve obtained by the CSM method is shown as an example.

Figure 4.7 summarizes the elastic modulus obtained from all tests. Some features similar to Figure 4.6 can be observed. The $E$ values vary from 55 to 155 GPa. For low maximum loads ($\leq 0.25$ mN), the $E$ values obtained by the repeated loading method lie above the continuous $E$-$h$
curve by the CSM method. For high maximum loads (> 0.5 mN), the majority of the $E$ values lie below the continuous curve. Moreover, for a given large maximum load (> 0.5 mN), the $E$ values fall inside a wide, scattered band, but not a line compared with the hardness values shown in Figure 4.6. The large scattering of the $E$ values at a given $F_{\text{max}}$ may be caused by the change in both the projected contact area and contact stiffness. The latter is further discussed below.

4.5 Contact Stiffness

Figure 4.8 compares the unloading curves of all the indentation tests. In this figure, $F_u$ and $h_u$ are the indentation load and displacement recorded during unloading process, respectively. It is worth noting that, although the MTS standard method unloads to 10% of $F_{\text{max}}$ and $F_{\text{max}}$ varies for different L/U cycles (Figure 3.2a), the normalization of $F_u$ and $h_u$ by $F_{\text{max}}$ and $h_{\text{max}}$ respectively, makes it easy for the comparison of the unloading curves. In Figure 4.8a, all 5 unloading curves have very similar shapes after normalization, but the contact stiffness defined as the initial slope of the unloading curves clearly increases with the L/U cycles.

In Figure 4.8e and Figure 4.8f, owing to the small indentation loads which did not exceed the critical value (0.25 ~ 0.5 mN) mentioned before, the unloading curves for all the L/U cycles are completely superimposed on each other. The measured contact stiffness remained the same during all the L/U process, which means that the cyclic hardening effect could not be expected when the compression load is so small that no plastic shakedown happens.

In Figure 4.8b~d for truly repeated loading where load is exceeding the critical value (0.25 ~ 0.5 mN), both the shape and initial slope of the unloading curves are altered with the number of L/U cycles increasing: the contact stiffness increases with the L/U cycle number, and the curve becomes more elbow-shaped when the load decreases to 80-90% of $F_{\text{max}}$. Furthermore, the
last three unloading curves (i.e., from the 4th to 6th) are nearly superimposed. This is highly consistent with the observed shakedown of the full L/U hysteresis loops. These observations,
when interpreted together with the decrease in the areas encompassed by the L/U loops, are clear evidence that muscovite exhibits cyclic hardening, which eventually leads to a plastic shakedown of repeated loading. Similar phenomena have also been observed on mica and other layer materials (e.g., Ti$_3$SiC$_2$) (Barsoum et al. 2004a, Murugaiah et al. 2004). At this point, all three mechanisms, protective residual stresses, increased contact area, and strain hardening, may work together to cause the plastic shakedown observed in the repeated loading tests.
5.1 Nanoscale Deformation under Nanoindentation

The experimentally observed responses of muscovite to both monotonic and repeated loading and unloading under nanoindentation are complex, and understanding the relevant modes of nanoscale deformation is of particular importance to the appreciation of this material’s behavior. In principle, the responses differ in varied load levels. The following discussion attempts to interpret the muscovite’s indentation behavior according to the load level.

When the maximum indentation load is smaller than \( (F_{\text{max}})_{\text{crit}} \), muscovite behaves as the kinking nonlinear elastic material. This type of load-displacement or stress-strain response is attributed to the formation, movement, and annihilation of incipient kink bands (IKBs). Similar phenomena have been observed on an array of other materials, such as graphite (Barsoum et al. 2004b) and Ti\(_3\)SiC\(_2\) (Murugaiah et al. 2004). An IKB is a thin ellipsoidal band bounded by two near parallel dislocation walls of opposite polarities that attract each other (Barsoum et al. 2004a, Basu et al. 2009, Frank and Stroh 1952). The dislocation walls are kept apart by the applied load and annihilate completely when the load is removed. This results in fully reversible L/U hysteresis loops. In addition, the process of formation, propagation, and annihilation of IKBs is of a continuous nature. As such, the load-displacement curves are smooth, and no pop-ins occur during the formation and movement of IKBs. Whether IKBs can take place depends on the material’s intrinsic crystal structure. As pointed out earlier, muscovite has a pronounced layer-type crystal structure where the binding forces between atoms in the layers are much stronger than the binding forces between atoms in adjacent layers (Zhang et al. 2010). Slips occur only in parallel to the layers and are almost impossible in non-layer planes, and the dislocation
arrangements and movement are confined mainly to the layer planes. Therefore, IKBs tend to generate the first deformation response to loading.

When the maximum load is greater than the \((F_{\text{max}})_{\text{crit}}\), higher stress forces the IKB walls to separate further, and the IKBs eventually become regular irreversible kink bands (KBs). This transition is expectedly associated with plastic deformation and hence pop-ins in the load-displacement curves. Again, owing to the layer structure, occurrence of KBs is inherently and simultaneously accompanied with layer delamination (or lateral cracking) and basal plane rupture. These modes of deformation are reflected by the macroscopically observed pop-ins. With the \(F_{\text{max}}\) increasing further, more KBs are formed, which progressively lead to cracking and even spallation (Zhang et al. 2009a, b). Again, the experimentally observed response to these deformations is pop-ins. Different modes of nanoscale deformation may be the major reason why pop-ins of varied extension occur randomly in the load-displacement curves.

The phenomenon that the contact stiffness increases with the number of L/U cycles in Figure 4.8 is also interesting. Cyclic hardening has also been observed on graphite (Barsoum et al. 2004b). Two major reasons may contribute to this phenomenon. First, because of layer delamination and basal plane rupture, some delaminated, fractured chips may spall off the indentation site, while some may still exist and compressed under the indenter tip. Unloading allows the rebounding and further layer separation of these fractured chips. As such, some of these delaminated chips act as tiny cantilevers that recover elastic bending deformation upon unloading. Similar phenomena were also observed in the nanoindentation unloading on silicon and germanium, two highly brittle semiconducting materials (Oliver et al. 2007, Oliver et al. 2008). Apparently, the stiffness of elastic unbending of cantilevers should be much smaller than
that of true elastic modulus of the muscovite, while the combined effect is the reduced contact stiffness.

Subsequent reloading to the same maximum load can easily push the chips away from the indenter tip, leaving a cleaner, undamaged, and fresh surface for indenting. Since the maximum loads of the two L/U cycles are the same, the damage of reloading would not be as much as that of first loading. Thus, the indented surface is more of the original undamaged solid, and higher contact stiffness results. Second, the residual stress, which can be introduced during each of the L/U cycles, gradually accumulates and increases, leading to a stiffer response to unloading at later L/U cycles.

In summary, muscovite with particular layer structure exhibits complex and multiple modes of nanoscale deformation in response to different levels of the indentation load. A critical maximum load exists that distinguishes the kinking nonlinear elastic deformation (i.e., due to IKBs) from the plastic kink bands (KBs) formation. With increasing the maximum load, KBs, layer delamination or lateral cracking, basal plane rupture, radial cracking and even spallation may occur, and these observed, randomly occurring pop-ins of varied extension may originate from these different modes of deformation.

5.2 Influence of Loading Methods on the Determination of Material Properties

Both the hardness and elastic modulus shown in Figure 4.6 and Figure 4.7 exhibit drastic variations, manifesting the dependence of the determination of these two material properties on the method of indentation loading, indentation depth, and maximum load. The obtained hardness value varies from ~3.0 to 12.2 GPa, while the elastic modulus from 55.0 to 115.0 GPa. The apparent indentation size effects were observed on both hardness and elastic modulus. Obviously,
this leads to the difference between the macro-scale hardness and nano-scale hardness, as well as the question that at what scale the muscovite’s hardness should be measured and used. Moreover, the variation of the two properties with the method of indentation loading and maximal load provides a need to decide what the mica’s true hardness and elastic modulus are and how to measure these values using nanoindentation. As repeated loading tends to decrease the hardness and elastic modulus as the number of cycle increases, neither the hardness nor elastic modulus can be determined by repeated loading, or at least by the latter L/U cycles. The CSM method, by determining the harmonic contact stiffness, tends to eliminate the rate dependence or the viscous effect on property determination. Therefore, this loading method is expected to yield more accurate results. However, as discussed above, the layer structure of muscovite leads favorably to the KBs formation, layer delamination, basal plane rupture, radial cracking, and spallation, resulting in multiple pop-ins during loading. These pop-ins in turn cause an apparent indentation size effect. Therefore, the maximum \( H \) and \( E \) values obtained by CSM are more representative and reflect the truly intrinsic properties of the muscovite. From this study, the true nanoscale \( H \) and \( E \) are 10-12 and 83 GPa, respectively; and the obtained nanoscale \( E \) value agrees with the reported true Young’s modulus of muscovite based on compressibility measurements in macro scale pretty well (Chen and Evans 2006, Faust and Knittle 1994, Pavese et al. 1999, Smyth et al. 2000).

The hardness and elastic modulus determined from the low load repeated loading (i.e., \( F < (F_{\text{max}})_{\text{crit}} \)) in Figure 4.6 and Figure 4.7 are greater than those determined by the CSM method. Apparently, since no plastic deformation occurs during the kinking nonlinear elastic loops, the hardness values are not the true material property, but the artifact introduced by the employed data analysis method. For the elastic modulus, the reason why the values obtained by the
repeated loading are much greater than those by the CSM method is unclear. Although the IKBs clearly affect the elastic unloading stiffness, it is unknown whether this effect increases or decreases the elastic modulus and how to separate the effects between truly elastic unloading and the kinking nonlinear elastic unloading.

5.3 Indentation Size Effect

Seven curves indicating hardness versus indentation depth using CSM are plotted in Figure 5.1a–g; while Figure 5.1h is plotted from averaged values of the seven indents. The descending hardness measured with the increasing depth can be obviously recognized from all these plots, which indicates that the indentation size effect does exist in measuring the stiffness of muscovite using nanoindentation techniques. Several identical features can be easily identified from the figures, including:

- At the beginning stage of each tests (e.g., displacement less than approximate 12 nm), the calculated hardness increases linearly with increasing indent depth. Theoretically, the deformation behavior of this stage of the material under applied load exhibits elastic properties and hardness could not be defined on this part. For the reason that indentation hardness is employed to examine the resistance of a sample to permanent plastic deformation due to a constant compression load from a sharp object;

- The major trend after the hardness peak occurs is the decreasing hardness with the increasing indent depth. Generally, this hardness decreasing phenomenon is described as the nanoindentation size effect as mentioned in the literature review section;

- The occurrence of giant pop-ins results in a sudden drop in the measured hardness. As pointed out before, the determination of hardness is by dividing the applied force with
the projected contacting area, which is obtained from the contact depth $h_c$. Pop-ins are exhibited as flat steps on the $P$-$h$ curves which means increasing of the indent depth without increasing the applied load. So this would cause a sudden drop in the hardness calculation;

- After giant pop-ins are encountered, the hardness may slightly increase with the increasing indent depth. This period may last for a few indent depth increases or even until next pop-in occurs. This phenomenon is unique in clay materials, and has never been reported in metal material studies;

- All the seven tests reach a final indent depth around 180 to 190 nm, which is almost the same as test ID 2 in Table 3.1. However, when we compare the hardness results from these two measurements, it can be noticed that repeated loading tests would lead to a final but much smaller hardness at 2.95 GPa, while the CSM method yields a relative higher value at 5.74 GPa (averaged value of 7 tests) at the same final indent depth. This higher hardness is mainly produced by the “strain hardening” process when performing indentation tests continuously. However, the repeated loading tests could effectively reduce this effect and give a strainless hardness result; and this conclusion has been experimentally proved on the study of metals (Harris 1922, Tabor 2000);

- It is important to note that the strain-hardening of the mineral only exists at the larger indent depth, while with the smaller indentation, it is negligible. As in Figure 4.6, a critical indent depth or load may exist to determine whether this effect appears or not.
Figure 5.1. Continuous hardness measured from test 7 in Table 3.1.
According to Nix and Gao’s concept, we can establish a relationship between the measured hardness with the indent depth to simulate the indentation size effect, by defining the statistically stored dislocations produced hardness $H_0$ and the characteristic length $h^*$, when the indent depth exceeds 100 nm. For the reason that all the seven CSM tests subjected to a controlled indent depth around 180-190 nm, here the hardness measured from test ID 2 in Table 3.1 (2.95 GPa) is adopted as $H_0$, and a regression based on the averaged value in Figure 5.1 is calculated to find $h^*$. On the other hand, for the points that have indent depths less than 100 nm, we may consider that kinking dominates the major mineral deformation trend other than the plastic deformation of the broken or delaminated kink bands and layers. In this case, we can assume a kinking relationship between the hardness and the indent depth based on the kinking theory mentioned before to establish the regression model. One should notice that to keep consistence, we adopt the statistically stored dislocations produced hardness $H_0$ as the infinite indent hardness used in regressing the kinking model, so that the interception of this model is no longer 1.0. Instead, it is an experiment dependent parameter.

![Figure 5.2. Model Regression of Hardness.](image)
Figure 5.2 shows the regression results based on Nix and Gao’s model for deeper indent, and Kinking model for the smaller indent depth. The yielded high R-squared values indicate acceptable regressions for both models and they fit the hardness variation trends with the indent depth very well. However, neither of these two models can be used to simulate the hardness drop caused by pop-ins or the slight increase in hardness after the appearance of pop-ins. So, further discussion and modification of the models are still necessary.

The aforementioned equation for calculating the hardness $H$ is based on the ratio between the applied force $F$ and the contact area $A_c$; and the latter is directly proportionally to the contact depth $h_c$, which means the measured hardness is sensitive to the reverse of the contact depth. Here we first use the Kinking regression equation for interpreting, and rewrite it by substituting $h$ with $h_c$ to emphasize that it is the contact depth measured by the indentation instrument:

$$H = H_0 \left( \frac{h_k^*}{h_c} + C \right)$$

(5.1)

Where $h_k^*$ is the characteristic length defined in the Nix and Gao model, and has a regressed value at 0.4819 in this study. As we know that the sudden drop in the hardness measurement is caused by a sudden increase in the contact depth, we can introduce another indent depth named the virtual indent depth $h_v$ and relate it with $h_c$ by:

$$h_c = h_v + h_s$$

(5.2)

Here $h_s$ stands for the depth of a sudden drop of the indent tip. So this equation relates the sudden decrease of the contact depth by subtracting $h_v$ by the observed value $h_c$.

By assuming that the total measured hardness of the mineral is composed of two parts: the deformation resistance $H_v$ raised from the continuous indent depth $h_v$, and the deformation...
resistance change $\Delta H_s$ raised from the sudden indent depth increasing $h_v$, we can express the hardness by summing these two terms:

$$H = \text{sum}(H_v, \Delta H_s)$$  \hfill (5.3)

The first component of equation 5.3 can be simulated using the kinking model when the indent depth is small:

$$H_v = H_0 \left( \frac{h_k^*}{h_v} + C \right)$$  \hfill (5.4)

This equation is the true regression result obtained by kinking model regression, based on changes of its continuous indent depth. It predicts the hardness of the mineral at a given indent depth affected by the indentation size.

With a sudden penetration into the mineral, the contact depth changes correspondingly, while the virtual indent depth increases continuously. So the calculated hardness based on the contact indent depth presents a sudden drop in value from the virtual hardness obtained from equation 5.4. After the pop-ins occur, the second component in equation 5.3 contributes to the contact hardness being measured. For the reason that increasing indent depth would decrease the resistance, $H_s$ should have a negative effect on the overall measured hardness.

$$\frac{\Delta H_s^2}{H_0^2} = h_N^* \left( \frac{1}{h_c} - \frac{1}{h_v} \right)$$  \hfill (5.5)

If we fit this negative effect of pop-ins using the Nix and Gao’s regression relationship (slope only) empirically (equation 5.5), it will give an acceptable regression result over the whole data series. In other words, by interpreting the hardness drop with the sudden geometrically
necessary dislocations raised deformation resistance around the indenter tip, the experimental results with pop-ins can be illustrated very well.

Furthermore, for the reason that the sudden drop of the indenter tip will introduce a fresh intact interlayer surface beneath it, which would generate elastic deformation and then attribute to an artificial increment in measured hardness, we can employ the original hardness-depth relationship (the linear regressed slope in Figure 5.1h) to simulate the hardness restoration process.

![Figure 5.3. Four major pop-ins of the 7th indent in test ID 7 in Table 3.1.](image)

Here is an example using the modified regression model to interpret the pop-ins and gradually restoration in hardness calculation occurred when performing the indentation tests. Here we select the 7th indent in test ID 7 in Table 3.1 to examine the model in details. Four major drops are picked up from Figure 5.3 marked by 1/2/3/4 consequently.
First, the two original regression models (kinking model for the smaller indent depth and Nix and Gao’s model for the deeper depth) obtained from the averaged result series (Figure 5.2) are plotted to show the general trends that related to the indentation size effect (dash line in Figure 5.4). Then a calibrated solid line is generated by modifying the dash line with the occurrence of four major pop-ins and hardness restoration process using equation 5.5 and the elastic deformation relationship. By comparing these two lines, it can be clearly seen that the combination of two models can simulate the indentation size effect on muscovite mineral over the indent depth pretty well and generally illustrate how the indent depth affects the measured indentation hardness. When the indent depth is relatively small, the measured hardness slowly decreases with the indent depth increment; while as the indenter penetrates deeper, the depth effect becomes significant which presents a stiffer slope in the figure.

![Figure 5.4. Illustration for simulating the indentation size effect using both regression relationship and modified model](image-url)
Meanwhile, the calibrated relationship (solid line) between the indentation hardness and the indent depth fits the experimental points in such a good manner that it almost overlaps the experimental data and predicts the hardness drops over giant pop-ins, especially when the pop-ins are encountered at the small indent depth (Kinking model zone, e.g., the 1/2/3 pop-ins).

Another important feature associated with the calibrated regression result is that the elastic deformation raised stiffness resistance beneath the indenter tip can generally be used to illustrate the recovery of indentation hardness after the occurrence of pop-ins empirically. Especially when the pop-ins are small and happen in the early stage of the indentation test. Figure 5.5 is a regional magnification of Figure 5.4 when the indent depth is less than 20 nm. The solid line here shows the calibrated model regression result, which can simulate the hardness variance due to the occurrence of small pop-ins perfectly. In this figure, both the drop and
restoration of the indentation hardness can be modeled and predicted by the proposed model as long as the pop-in happens and the degree of the sudden indent depth increasing are known.

However, when the pop-ins are relatively large or last over several steps (e.g., number 2 and 3 in the figure), the slope of the calibrated model is slightly greater than the experimental points at the hardness restoration proportion. This exhibits as a faster restoration rate in the model than the observed values. This phenomenon may be illustrated by the indentation hardness testing process itself. As the indent tip gets deeper, the geometrically necessary dislocation raised deformation resistance begins to take more effect over the kinking resistance and the elastic resistance. Interestingly, this conclusion is consistent with the previous results discussed in section 5.1, which points out that no real pop-ins that affects the hardness measurement are identified when the indent depth is less than 20 nm under a very small load.
CHAPTER 6. CONCLUSIONS

As a result of the study of the nanomechanics of muscovite subjected to nanoindentation and the pertinent indentation size effect, the following conclusions can be drawn:

- Muscovite with particular layer structure exhibits complex and multiple modes of nanoscale deformation in response to different levels of the indentation load. A critical load \((F_{\text{max}})_{\text{crit}}\) exists that leads to distinct load-displacement curves: when \(F_{\text{max}}\) is greater than this load, after a few initial cycles, the observed curves exhibit characteristic closed hysteresis loops, suggesting that shakedown process occur quickly in muscovite; otherwise, muscovite behaves as a kinking nonlinear elastic material;

- Loading methods affect the determination of material properties. Based on experimental results, the CSM method yields more accurate, representative results and reflect the truly intrinsic properties of the muscovite, which is also consistent with previous macroscale compressibility measurement results;

- Cyclic loading will introduce extra shakedown process when the maximum load is greater than the critical value. This process can lead to a three dimensional confinement around the indenter tip at relatively large depth and result in a reduction of the measured elastic modulus, which is associated with a transition from Young’s modulus to bulk modulus;

- The size effect on muscovite subjected to nanoindentation can be simulated by a combination of Nix and Gao model and Kinking model.
CHAPTER 7. RECOMMENDATIONS

Since muscovite is a naturally occurred phyllosilicate mineral, its properties vary from sample to sample. However, only one carefully prepared sample was used in this study to examine the nanomechanics of muscovite and the pertinent indentation size effect, and derive the new model. In this case, more experiments should be finished to obtain more confident model parameters before applying the new model to other muscovite samples.
REFERENCES


VITA

Hang Yin was born on March 5, 1980 in Liaoning Province, China. After completing high school in her hometown, she was admitted into Tsinghua University, Beijing, China. She graduated from Tsinghua University with a bachelor of science in Hydraulic and Hydropower Engineering in 2003, and a master of science in Civil Engineering in 2006 with interest in hydrology and water resources management.

She joined the Department of Civil Engineering at Louisiana State University in August of 2008 as an M.S. candidate in geotechnical engineering group, Civil Engineering. She is going to receive her master’s degree in December 2010 and continue her Ph.D. study in the same program.