Role of Elastic Anisotropy in the Development of Deformation Microstructures in Zircon

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ABSTRACT

The deformation of zircon by various mechanisms, including brittle fracture, dislocation creep, twinning, and transformation to a high-pressure polymorph (reidite), is preceded by elastic behavior. This study presents new visualizations of the anisotropy of elastic properties of zircon as a function of radiation damage and pressure, and investigates the links between elastic properties and deformation microstructures in zircon. Zircon is highly anisotropic in Young’s modulus (E), shear modulus (G), and Poisson’s ratio (ν) elasticity. Anisotropy of E, G, and ν decreases by radiation damage and increases with pressure from 0 to 24 GPa, with a peak in elastic stiffness at ~8 GPa. A switch in dislocation line energy factor K could indicate that ⟨001⟩<100> dislocations are energetically more favorable than ⟨100⟩<010> above ~17 GPa. Shock twinning of zircon occurs via plane of invariant shear K₁ = {112} and shear direction η₁ = <111>, which corresponds to the lowest values of G₁₁₁₁ (~98 GPa) and ν(=0) in zircon. Minima in G₁₁₁₁ at ~4 and ~16 GPa could indicate favorable pressures for twinning. Reduction of E and G associated with radiation damage inhibits propagation of reidite lamellae during shock metamorphism because sufficient pressures to permit phase transformation cannot be supported.

8.1. INTRODUCTION

Zircon is very important for geochronology, and recent work has shown that deformation microstructures can act as fast-diffusion pathways that facilitate trace element mobility and resetting of the U-Pb isotopic system [e.g., Reddy et al., 2006; Timms et al., 2006, 2011; Moser et al., 2009; Nemchin et al., 2009; Timms and Reddy, 2009; Grange et al., 2013; Cavosie et al., 2015b; Piazolo et al., 2016]. Consequently, it is important to understand the mechanisms by which zircon can deform, and conditions required for zircon deformation. Deformation of minerals via brittle fracture, dislocation creep, twinning, and phase transformations are often strongly controlled by crystal structure. Minerals respond elastically before brittle or ductile yield, and elastic behavior influences the nature of inelastic strain in many materials. All minerals exhibit directional variations (anisotropy) of elasticity that is governed by their intrinsic lattice structure, the same crystal structure that governs crystal-plastic deformation. In this study, we investigate the effects of anisotropic elasticity on the formation of various types of deformation microstructure along specific crystal planes {hkl} in zircon (ZrSiO₄).
Figure 8.1 Conceptual diagrams of elasticity moduli and their directional anisotropy in crystals. (a) Young’s modulus, $E$, is a measure of longitudinal stiffness, and defines the slope on a plot of normal stress ($\sigma_n$) versus normal strain ($\varepsilon_n$). A scalar value for $E$ can be plotted for any crystallographic direction as a color-coded pole plot. (b) Shear modulus, $G$, is a measure of stiffness in shear, and defines the slope on a plot of shear stress ($\sigma_s$) versus normal strain ($\varepsilon_s$). Any given plane contains directional differences in $G$. The minimum scalar value ($G_{\text{min}}$) and maximum scalar value ($G_{\text{max}}$) for any plane can be plotted as two separate color-coded pole plots, respectively. (c) Poisson’s ratio, $\nu$, is the ratio of lateral strain to longitudinal strain, and is positive in most materials. Perfectly compressible materials have $\nu = 0$, whereas negative $\nu$ can occur in some crystalline solids, and is a property known as auxeticity. The minimum scalar value ($\nu_{\text{min}}$) and maximum scalar value ($\nu_{\text{max}}$) for planes in any orientation can be plotted in the same way as for $G$. (d) Hypothetical scenarios that relate elastic moduli to failure controlled by (i) critical yield strain, (ii) critical yield stress, (iii) yield as a function of stress and strain.
8.2. ELASTIC ANISOTROPY OF MINERALS

In continuum mechanics, three fundamental measures of elasticity are the Young’s modulus, $E$, which relates longitudinal stress to longitudinal strain; the shear modulus, $G$, which relates shear stress to shear strain; and Poisson’s ratio, $\nu$, which relates longitudinal strain to lateral strain (Fig. 8.1). The elasticity of many minerals has been quantified either experimentally by ultrasonic resonance [e.g., Bass, 1995; van Westrenen et al., 2004] and/or by first-principles calculations using density functional theory [e.g., Dutta and Mandal, 2012a]. Young’s modulus, shear modulus, and Poisson’s ratio are all derived from elastic stiffness (or compliance) tensors that are used to predict seismic anisotropy through the Christoffel equation [e.g., Lloyd and Kendall, 2005; Mainprice et al., 2008; Tatham et al., 2008; Healy et al., 2009]. Young’s modulus varies with crystallographic orientation in a relatively straightforward way (Fig. 8.1a) so that directions on pole figures can be color-coded for scalar values of $E$. However, shear modulus and Poisson’s ratio are more complex in that they are directionally scalar values of $E$.

Yielding and shear stress in minerals, $\tau$, is related to shear strain, $\gamma$, by the shear modulus, $G$, according to the equation $\tau = G \gamma$. Yeasting and shear stress in minerals, $\tau$, is related to shear strain, $\gamma$, by the shear modulus, $G$, according to the equation $\tau = G \gamma$. However, shear modulus and Poisson’s ratio are directionally scalar values of $E$, and so horizon azimuths can be visualized in $G$ or $\nu$ is to color-code pole to planes on pole figures for either the minimum or maximum value of $G$ or $\nu$ (i.e., $G_{\text{min}}$, $G_{\text{max}}$, $\nu_{\text{min}}$ or $\nu_{\text{max}}$) along the plane. Alternatively, directional anisotropy in $G$ or $\nu$ can be visualized for projection-specific planes on polar plots.

Plastic deformation of crystals (either brittle or ductile, in extension or shear failure) can be controlled by a critical yield strain, a critical yield stress, or some function of both stress and strain (Fig. 8.1d). Each yield scenario predicts a different relationship between the initial or pre-cursory elastic response and the ultimate plastic yield. In classical dislocation/plasticity theory, $G$ and $\nu$ exert first-order influences on the stresses required to mobilize dislocations, the so-called Peierls-Nabarro stress [Peierls, 1940; Nabarro, 1947; Nye, 1957], and twin nucleation stress [Orowan, 1954; Christian and Mahajan, 1995; Kibey et al., 2007]. Subsequently, anisotropic plasticity has been incorporated into dislocation theory [Eshelby et al., 1953; Stroh, 1958; Steeds, 1973; Hirth and Lothe, 1982; Joós and Duesbery, 1997]. Anisotropy of elasticity has also been shown to be important for brittle fracture and microcrack development, and the relocation and interpretation of associated focal mechanisms of acoustic emissions [Stroh, 1958; Timms et al., 2010].

8.3. ZIRCON: PROPERTIES, DEFORMATION MECHANISMS, AND MICROSTRUCTURES

Zircon is one of the most refractory and least compressible silicate minerals known, and it owes its physical durability to its crystal structure. Zircon has a body-centered tetragonal crystal structure (space group I41/amd), with chains of alternating edge-sharing SiO$_4$ tetrahedra and ZrO$_6$ triangular dodecahedra parallel to $<100>$ [Finch and Hanchar, 2003]. Natural zircon typically incorporates impurities and trace elements, with hafnium the most abundant at ~1 wt%, and other elements such as uranium, thorium, rare earth elements (REEs), titanium, and aluminum typically incorporated at one to hundreds of parts per million [Hoskin and Schaltegger, 2003]. Whilst these low abundances are probably insufficient to have any significant effects on elasticity, $\alpha$-particle recoil associated with radioactive decay of U and Th causes localized damage to the crystal structure [e.g., Nasdala et al., 2005]. This “radiation damage,” also known as metamictization, accumulates over time and can change physical properties of zircon, such as density, and also permits chemical alteration above threshold $\alpha$-doses due to the formation of interconnected porosity [Salje et al., 1999]. Metamictization inhibits cathodoluminescence (CL), and so growth zones in crystals with different initial actinide contents are commonly visible on CL images [e.g., Corfu et al., 2003].

Crystal plasticity, that is, the accommodation of strain via dislocation glide and climb, occurs in zircon in a range of tectonic and impact environments, and can result in the formation of planar deformation bands (PDBs) [e.g., Nemchin et al., 2009; Kovaleva et al., 2015], networks of subgrains with low-angle boundaries [e.g., Reddy et al., 2006, 2009; Timms et al., 2006, 2011, 2012; Timms and Reddy, 2009; Kaczmarek et al., 2011; Moser et al., 2011; Erickson et al., 2011a; MacDonald et al., 2013; Kovaleva et al., 2014], and strain-free recrystallized subdomains (neoblasts) [Piazolo et al., 2012; Cavosie et al., 2015b; Timms et al., 2017]. Such microstructures can be readily identified using electron backscatter diffraction (EBSD) analysis because they comprise changes in crystallographic orientation [Prior et al., 1999]. Crystal plasticity results in systematic and often incremental rotation of the crystal structure, which can be quantified by EBSD mapping. The misalignment between two parts of crystal can be expressed as a rotation angle and rotation axis that would result in crystallographic realignment; this is known as misorientation [Wheeler et al., 2001]. The angle/axis pair corresponding to the minimum rotation required for realignment is known as disorientation. Disorientation axes associated with crystal-plasticity commonly coincide with rational low-index directions, and are a consequence of one or more dislocation slip systems involving a slip plane and slip direction. The most common slip systems in zircon in both tectonic and impact environments include {100} $<010>$, {100} $<001>$, and {001} $<100>$, which result in disorientation around $<001>$ or $<100>$ [Reddy et al., 2006, 2009; Kaczmarek et al., 2011; Moser et al., 2011; Piazolo et al., 2012; Timms et al., 2012; MacDonald et al., 2013; Kovaleva et al., 2014]. These slip systems involve Burgers vectors $b <100> \sim 6.61\AA$.
and $b_{<001>}$, having a slightly lower dislocation line energy [Reddy et al., 2007]. Furthermore, it has been suggested that the $<001>$ slip could also be achieved by slip via two conjugate partial dislocations with $b_{<112>}$, which is potentially more energetically favorable [Reddy et al., 2007]. Whilst the stability of dislocations and the stress required for migration (the Peierls stress) is governed by the elastic anisotropy of a crystal, calculation of the Peierls stress requires atomistic simulation due to the breakdown of elasticity in the dislocation core [Joós and Duesbery, 1997] and is beyond the scope of this study.

So far, $\{100\}$-parallel PDBs, which result from $\{100\}<010>$ slip, have only been identified in zircon grains within pseudotachylites (frictional melt rocks) and lunar samples (presumably impact-related deformation) [Nemchin et al., 2009; Kovaleva et al., 2015], which could indicate that these types of microstructure require very high (seismogenic) strain rates for their formation. Consequently, it is inferred that $\{100\}<010>$ is the easiest slip system to activate in zircon. However, there are very few published constraints for the activation stresses of any slip systems in zircon [Reddy et al., 2007].

Mechanical twinning has only been recorded in terrestrial and lunar impact-shocked zircon, and is thought to be diagnostic of shock conditions [Moser et al., 2011; Timms et al., 2012; Thomson et al., 2014; Crow et al., 2015; Cavosie et al., 2015a, 2015b; Erickson et al., 2013a, 2013b, 2016; Montalvo et al., 2017]. Twin lamellae form along $\{112\}$ in zircon, and twin domains have strict $65^\circ/\langle110\rangle$ disorientation relationships with the host, resulting in up to four distinct, symmetrical equivalent twin orientations [Timms et al., 2012; Erickson et al., 2013a]. Typically, sets of multiple twin lamellae up to a few micrometers wide (sometimes referred to as “microtwins”) form within shocked zircon grains. Neither the kinematic twin mechanism nor exact conditions at which twinning can occur in zircon have been systematically quantified. However, twinning has been reported in a static pressure laboratory experiment in a sample compressed up to 20 GPa [Morozova, 2015].

The transformation of zircon to reidite (a tetragonal (I4/1/a) high-pressure ZrSiO$_4$ polymorph only reported in nature from impact environments) is diagnostic of shock conditions [Glass and Liu, 2001; Glass et al., 2002; Guesik et al., 2004; Wittmann et al., 2006; Chen et al., 2013; Cavosie et al., 2015a, 2016b; Reddy et al., 2015; Erickson et al., 2017; Timms et al., 2017]. Reidite typically forms sets of lamellae up to a few micrometers across, and in some instances occurs as microgranular aggregates within and surrounding host zircon grains [Cavosie et al., 2015a; Reddy et al., 2015; Erickson et al., 2017]. Lamellar reidite can form in various nonrational habit planes in zircon, yet it consistently forms with a strict orientation relationship with close alignment ($<5^\circ$ misorientation) of a $\{100\}$$_{\text{zircon}}$ with a $\{112\}$$_{\text{reidite}}$ and good alignment of a $\{112\}$$_{\text{zircon}}$ with a different $\{112\}$$_{\text{reidite}}$ [Erickson et al., 2017]. A geometric consequence of this orientation relationship is an approximate alignment ($<10^\circ$ misorientation) of $\{110\}$$_{\text{reidite}}$ with (001)$_{\text{zircon}}$, which has been reported in earlier studies [Leroux et al., 1999; Cavosie et al., 2015a; Reddy et al., 2015]. The tetragonal symmetry of both phases means that up to eight distinct yet symmetrically equivalent reidite orientation variants can form in a single zircon grain [Erickson et al., 2017]. The exact transformation mechanism is debated, and possibilities include deviatoric and reconstructive mechanisms [Kusaba et al., 1985; Leroux et al., 1999; Marqués et al., 2008; Du et al., 2012]. Nevertheless, it has been observed in several studies that reidite lamellae are primarily hosted in highly cathodoluminescent, crystalline domains, and do not penetrate into adjacent metamict zones [Cavosie et al., 2015a; Reddy et al., 2015; Erickson et al., 2017]. This suggests that the intrinsic crystallinity of zircon plays a key role in zircon-reidite transformation dynamics and the subsequent stability field of reidite. However, the precise relationship is yet to be established.

8.4. Elastic Properties of Zircon

Elastic properties have been measured experimentally for zircon with different degrees of crystallinity (and densities) [Özkan, 1976; Özkan and Jamieson, 1978; Hearmon, 1984] and computed from first principles as a function of pressure [Dutta and Mandal, 2012a]. Like many minerals, zircon is highly anisotropic in its elasticity. Natural radiation damage in zircon is accompanied by significant reduction in the elastic moduli $E$ and $G$ (and density), both of which approach elastic isotropy with common saturation values of 150 and 49 GPa, respectively [Özkan, 1976; Safie, 2006]. These effects are consistent with the formation of randomly oriented and distributed nonspherical defect clusters and nano-pores from α-recoil damage due to metamictization [Özkan, 1976]. Pressure and temperature derivatives calculated from the elastic constants have revealed elastic “softening” with increased pressure associated with a negative pressure derivative of the $c_{66}$ shear modulus in zircon, which has also been linked to a phase change to the high-pressure polymorph, reidite [Özkan, 1976; Özkan and Jamieson, 1978; Dutta and Mandal, 2012a]. All other elastic constants (and the anisotropy of elastic moduli) show a positive relationship with pressure, with shear modulus being relatively sensitive to pressure [Dutta and Mandal, 2012a]. The anisotropy of $E$ and one component of $G$ have been visualized for zircon [Timms et al., 2012]. However, neither the “shape” of the full anisotropy of elastic moduli $E$, $G$, and $\nu$ nor their variability with intrinsic...
physical properties or environmental parameters has been described. The ability to visualize and compute directional variations (i.e., anisotropy) of elasticity is important given that elastic properties control and influence the microstructures that are both used as shock indicators and those that disrupt the isotopic systematics of this otherwise robust geochronometer.

8.5. APPROACH AND METHODS

This study uses published elasticity data for zircon to visualize the full anisotropy of \( E, G \), and \( \nu \) for the first time in order to investigate the effects of intrinsic properties [radiation damage, Özkan, 1976; Özkan and Jamieson, 1978; Hearmon, 1984] and environmental parameters [pressure, Dutta and Mandal, 2012a] on zircon’s elasticity. We use these data to quantify the stresses required to activate different processes and produce different microstructures in zircon.

8.5.1. EBSD Measurements

Three examples of zircon grains are shown to illustrate different types of deformation microstructures: a lunar zircon from an Apollo 17 clast-rich impact melt breccia 72215, in the thin section 72215, 195 [Nemchin et al., 2009; Timms et al., 2012]; a detrital zircon (sample 09VD42, mount 1, grain 110) that was sourced from the giant Vredefort impact structure and collected from the Vaal River, 674 km downriver from the Vredefort Dome, South Africa (28°42.473’S, 24°04.478’E) [Erickson et al., 2013b]; and a zircon grain from a clast in suevite breccia from a depth of 498 m in the Nördlingen 1973 borehole, which is located near the center of the 24 km-wide Ries impact structure in southern Germany (48°51.0’N, 10°30.0’E) [Bauberger et al., 2011; Erickson et al., 2017]. Electron microscopy was done on colloidal silica polished samples [Prior et al., 1999] using a Zeiss NEON dual beam FIB-SEM (lunar zircon grain) and a Tescan MIRA3 FE-SEM (Vredefort and Ries zircon grains) fitted with an Oxford Instruments’ Flamenco EBSD and AzTEC combined energy-dispersive X-ray (EDX)/EBSD acquisition systems, respectively, at Curtin University, Perth, Western Australia, using established settings and protocols [Timms et al., 2012; Cavosie et al., 2015a, 2015b; Reddy et al., 2015]. Secondary electron (SE), backscatter electron (BSE), CL images, and EBSD maps with step sizes between 200 and 500 nm were collected from each grain. Indexing of EBSD patterns included a choice of match units for zircon and reidite, with a mean angular deviation rejection threshold of 1.2°. Oxford Instruments’ Channel 5.10 software was used to remove isolated, erroneous EBSD data points (wildspike correction), calculate angle/axis pairs that describe the disorientation between adjacent data points of the same phase [see Wheeler et al., 2001], and produce thematic EBSD maps and pole figures [Timms et al., 2012; Cavosie et al., 2015a; Reddy et al., 2015]. Raman spectra were collected using a Horiba LabRAM HR Evolution using a 600 g/mm grating and a synapse visible detector at CSIRO Energy, Australian Resources Research Centre.

8.5.2. Calculation of Elastic Properties

Elastic stiffness data (\( c_{ij} \)) were taken from published papers [Özkan, 1976; Özkan and Jamieson, 1978; Hearmon, 1984; Dutta and Mandal, 2012a]. Using the equations provided in Nye [1957], values for \( E, G \), and \( \nu \) have been calculated for all directions around the unit sphere, and then visualized as representation surfaces in three dimensions (3D) and stereograms (equal area, lower hemisphere projections) in two dimensions (2D). In addition, from published values of the lattice parameters for zircon, we have also calculated \( E, G \), and \( \nu \) for specific crystallographic directions relating to known deformation microstructures, and plotted these as polar plots projected on to a convenient reference plane. These calculations were performed in MATLAB using a script developed by the authors (available on request). In detail, the procedure is as follows: working around a unit sphere in 3D space, we take a unit vector in a specific direction. This then becomes the \( i \) direction for the subsequent calculations of \( E_i^r = 1/s_{ii}^r, G_i^r = 1/(4 s_{ij}^i s_{ji}^i) \), and \( \nu_i^r = -s_{ij}^i/s_{ii}^i \) where the prime denotes a value in the rotated reference frame. The value of \( j \) is taken normal to \( i \) and rotated through \( 2\pi \) to generate the directional variations of \( G \) and \( \nu \). Note that whereas \( E_i^r \) is a scalar value for each direction \( i \), depending only on coaxial stress and strain values, the situation for \( G \) and \( \nu \) is more complex (Fig. 8.1b and c). For \( G \), a shear couple can be directed along the \( i \) direction and vary azimuthally about it, or the shearing can occur in the plane normal to \( i \) and vary within it. A similar issue exists for \( \nu \) as the ratio of a transverse to a longitudinal strain. We calculate values for \( G \) and \( \nu \) in relation to each given direction \( i \) in increments of 1°, and extrema are selected from the full set of calculations and the maximum and minimum values are reported for each elastic constant [see Tan et al., 2015 for further examples]. The calculations of anisotropic elastic properties with tetragonal symmetry were benchmarked against published values for the zeolite ZIF-zi [Tan et al., 2015], with complete agreement between our results and theirs for multiple planes and directions (Appendix Fig. A1).

We also calculate the Voigt-Reuss-Hill (VRH) average (\( \approx (M_v + M_r)/2 \), where \( M_v \) is the Voigt upper bound, and \( M_r \) is the Reuss lower bound), as a useful measure of the “average” elastic property over all directions (equations in Mavko et al., 2009). The VRH average is plotted as a
semitransparent sphere in the top row of Figure 8.5, and labeled for each of the stereograms below. The effect of variations in elastic constants as functions of pressure and metamictization on dislocation activity is investigated by calculating the energy factor for common slip systems in zircon using the approach detailed in Reddy et al. [2007] based on Foreman [1955]. The energy factor (K) is the dislocation line energy in a specific direction along a specific plane irrespective of Burgers vector, and dislocation lines with lower energy factors will be energetically more favorable. Calculation of the Peierls-Nabarro stress requires knowledge of the interatomic and interplanar spacing of dislocations, which is not known or reported for zircon, and so Peierls-Nabarro stress is not currently resolvable using available data.

8.5.3. Results/Deformation Microstructures

The lunar zircon grain clearly shows two sets of {100}-parallel PDBs, both of which result in dispersion of crystallographic poles around the pole to (001) (which is parallel to [001]), with a total cumulative disorientation across the grain of 12° (Fig. 8.2a–d). This is consistent with dislocation creep via {100} <010> slip (Fig. 8.2e) [Nemchin et al., 2009; Kovaleva et al., 2015]. The zircon grain from the Vredefort impact structure contains four sets of twin lamellae (Fig. 8.3a). All twin lamellae are parallel to {112} and have a 65° disorientation around <110> relative to the host grain, which is consistent with mechanical twins in zircon reported elsewhere [Timms et al., 2012; Erickson et al., 2013a; Thomson et al., 2014]. The zircon grain from the Ries impact structure contains a single set of reidite lamellae that are restricted to the bright CL growth domains in the rim of the grain (Fig. 8.4a–c). Raman spectroscopy shows that the reidite-bearing rim of the grain has a narrow, high amplitude (SiO) peak (spot 1 in Fig. 8.4), whereas this peak has shifted position and broadened in the reidite-absent core (pot 2 in Fig. 8.4). Using equation 6 of Nasdala et al. [2004], the α-dose within the core of the zircon is calculated to be ~0.9 × 10⁶/µg, consistent with moderately metamict zircon, whereas α-dose in the rim is ~0.14 × 10⁶/µg, indicating a higher degree of crystallinity.

8.6. ELASTIC ANISOTROPY OF ZIRCON

8.6.1. Non-Metamict Zircon at 1 atm

Non-metamict zircon is highly anisotropic in E (88%), G (74%), and ν (130%) (Özkan and Jamieson [1978] data, Fig. 8.5). Zircon is longitudinally stiffest (i.e., highest E value) parallel to <001>, closely followed by <100> (Figs. 8.5 and 8.6). Girdles of high E lie along {100}, and values decrease monotonically to minima parallel to <110> (Fig. 8.5). An inverse of this pattern is almost mimicked by the minimum shear modulus G<sub>min</sub>, where lowest G<sub>min</sub> values are along {100} and {001}, whereas {110} contains the highest G<sub>min</sub> values (Fig. 8.5). Zircon is stiffest in shear (i.e., highest G<sub>max</sub> values) in directions along {110} (Fig. 8.5). Values for Poisson’s ratio ν range from <0.1 up to ~0.7 with a complex anisotropy “form” (Fig. 8.5). The lowest values of ν are along {110}, {111}, and {112} where ν<sub>min</sub> approaches zero; however, non-metamict zircon does not show auxetic behavior (ν < 0) in any direction (Fig. 8.5). The highest values of ν<sub>max</sub> in zircon lie along {110}, {111} and {112} (Fig. 8.5).

8.6.2. The Effects of Radiation Damage

The elasticity of several zircon grains with different degrees of radiation damage, as indicated by shifts and broadening of peak in XRD spectra, was measured by Özkan [1976]. A systematic relationship between the positions and full width half maximum (FWHM) of peaks in XRD spectra and radiation damage has permitted quantification of α-dose of the three grains from Özkan [1976] used in this study [Murakami et al., 1991; Ellsworth et al., 1994] (Table 8.1). Using the FWHM of the 112 peak (at ~35 2θ), grains 1, 2, and 3 have α-doses of ~0.62, ~0.64, and ~0.7 × 10⁶/µg, respectively [Ellsworth et al., 1994]. These doses lie between those of the core and rim domains of the Ries zircon grain (Fig. 8.5).

A significant reduction in values of E and G, and a change in the “shape” and strength of their anisotropy correspond with the degree of metamictization (grains 1–3, Özkan [1976] data, Fig. 8.5). This is primarily achieved by “softening” of E along {100}, G<sub>max</sub> and G<sub>min</sub> along {110} and {001} (Fig. 8.5). Radiation damage also decreases the strength of the ν anisotropy significantly, involving tendency for the convergence of extreme ν<sub>min</sub> and ν<sub>max</sub> values toward the Voigt, Ruess, and Hill average of ~0.3 (Fig. 8.5). Plots derived from the elasticity data from a metamict zircon of Hearmon [1984] show a markedly different geometry of anisotropy for E, G, and ν (Fig. 8.5). Highs in E and G<sub>max</sub> are centered around <111> and <100>, respectively, whereas this effect is not seen in any of the data sourced from Özkan [1976] or Özkan and Jamieson [1978] (Figs. 8.5 and 8.6).

The anisotropy of E, G, and ν along specific crystallographic planes varies significantly with metamictization (Fig. 8.7). Again, Özkan and Jamieson [1978] and Özkan [1976] data show systematic relative changes, whereas the Hearmon [1984] data are anomalously different (Fig. 8.7). In general, the shape of the anisotropy in the planes shown remains constant but becomes less extreme with increasing metamictization.
Figure 8.2 A lunar zircon grain that preserves two sets of (100)-parallel planar deformation bands (PDBs). (a) SE image. (b and c) EBSD maps colored for crystallographic disorientation from reference point (red cross). (d) Pole figure of data shown in (c). Lower hemisphere projection in the x-y-z reference frame of the EBSD map. (e) Schematic pole figure in the crystal reference frame showing the relationship between PDBs and causative dislocation slip system. The alignment of the disorientation axis along the PDB plane is consistent with a tilt boundary geometry resulting from {100} <010> slip.
8.6.3. Pressure Dependence of Elastic Properties of Zircon

With increasing pressure, zircon develops a systematic increase in $E$ anisotropy from 88 to 108% at 24 GPa, without any significant changes to the “form” of anisotropy of $E$ (Fig. 8.8). This is primarily achieved by increases in $E$ in <100> and <001> (Figs. 8.8 and 8.9). Young’s modulus in <100> is more sensitive to pressure than <001> and zircon becomes more stiff in <100> than in <001> over ~4 GPa (Fig. 8.9). Anisotropy of $E$, $G$, and $\nu$ change non-linearly with pressure, with dips in anisotropy strength at ~8 GPa (Figs. 8.8 and 8.9). Overall stiffening of $G_{\text{min}}$ and increase in $\nu_{\text{min}}$ in all directions is observed at this pressure (Fig. 8.10). The lowest values of $G$ in zircon (i.e., $G_{\text{min}}$) are in $G <111>$ along {112} (Appendix Table A1), and this varies non-linearly with pressure, with a peak at ~8 GPa and saddles at ~4 and ~16 GPa (Fig. 8.9).

The anisotropy of $E$, $G$, and $\nu$ along specific planes in zircon in the pressure range 1 atm to 24 GPa are illustrated in Figure 8.10. Whilst pressure does not change the overall “shape” of the elastic anisotropy along specific planes in zircon, it is clear that some directions are more sensitive to pressure variations than others (Fig. 8.10). For example, $E$ parallel to <100> in {001} varies significantly, yet $E$ parallel to <110> remains almost unchanged (Fig. 8.10a). This will be discussed in more detail in the next section.

The dislocation energy factor ($K$) for {100}<010> and {001}<100> edge dislocations have been calculated using the approach detailed in Reddy et al. [2007] as a function of radiation damage and pressure using elasticity and unit cell/bond length data from Özkan [1976] and Dutta and Mandal [2012a] (Figs. 8.11 and 8.12). Using elasticity values from zircon with low levels of radiation damage, {100}<010> dislocations have a lower energy factor than {001}<100> (Fig. 8.11). The energy factor of both
Figure 8.4 A zircon grain from the Ries impact structure, Germany, preserving a set of reidite lamellae. (a) CL image. Dark concentric growth zones have higher U and Th contents and higher levels of radiation damage than the pale domains. Reidite is non-luminescent. (b) BSE image. (c) EBSD map colored for crystallographic orientation phase. White dashed lines delimit dark CL zones in (a). (d) Raman spectra from spots 1 and 2 shown in (c). (e) Schematic pole figure in the crystal reference frame showing orientation relationship between host zircon (black symbols) and reidite (green symbols). The other seven possible reidite orientation variants are shown by gray symbols.
Figure 8.5 Plots of the anisotropy of elastic moduli $E$, $G_{\text{max}}$, $G_{\text{min}}$, $\nu_{\text{max}}$, and $\nu_{\text{min}}$ in zircon as 3D visualizations (top row) and lower hemisphere equal area projections (subsequent rows). Poles to significant planes in zircon are shown on top left projection. Gray spheres in the 3D plots are the calculated VRH averages of each attribute. Strength of anisotropy (A) and VRH averages for each attribute are shown below pole plots. O&J’78 = non-metamict Australian grain data, Özkan and Jamieson [1978]; O’76 = data for varying degrees of radiation damage, grains 1–3, Özkan [1976]; and H’84 = metamict zircon data, Hearmon [1984]. (See insert for color representation of the figure.)
dislocation types is significantly reduced with increasing radiation damage (Fig. 8.11). Unlike radiation damage, the effects of pressure scale up from the unit cell to bulk crystal scales. Both dislocation types show significant increase in energy factor $K$ with pressure (Fig. 8.12). However, the increase is nonlinear; both dislocation types have a positive deviation from a linear trend at $\sim 8$ GPa (Fig. 8.12). Furthermore, the relationships of $K$ with pressure have different slopes for each slip system, such that $\{001\}<100>$ have lower $K$ than $\{100\}<010>$ above $\sim 17$ GPa (Fig. 8.12).

8.7. DISCUSSION

8.7.1. New Approaches to the Visualization of Elastic Anisotropy of Zircon

The stereograms and polar plots of elastic anisotropy presented in this study permit the visualization of different components of elasticity, for example, moduli, Poisson’s ratio, and other factors derived from the tensor data, allowing their key aspects and complexity to be readily assessed and compared. The plane-specific polar plots are effective in allowing comparative assessment of elastic anisotropy as a function of different parameters (in this case, radiation damage and pressure). These kinds of visual representations of large number of variables are therefore suitable for future studies involving elastic anisotropy data.

8.7.2. Crystal Plasticity in Zircon

Analyses of the energetics of slip systems in zircon (Figs. 8.11 and 8.12) show that dislocations have lower energies with increasing levels of metamictization. However, these results should be interpreted with caution; the empirical elasticity measurements of Özkan [1976] were made for a bulk sample at the grain scale, exhibiting spatially heterogeneous radiation damage domains lie within pristine lattice. Dislocations operate at the unit-cell scale, and so will interact with pristine and damaged lattice domains differently.

<table>
<thead>
<tr>
<th>Grain</th>
<th>Peak</th>
<th>Peak Centre ($2\theta$)</th>
<th>Peak Shift ($2\theta$)</th>
<th>Peak Intensity (a.u.)</th>
<th>Change in Intensity (a.u.)</th>
<th>Peak FWHM ($2\theta$)</th>
<th>$\alpha$-Dose $\times 10^{15}$/mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>112</td>
<td>35.77</td>
<td>0</td>
<td>19.5</td>
<td>0</td>
<td>0.19</td>
<td>6.2</td>
</tr>
<tr>
<td>2</td>
<td>112</td>
<td>35.51</td>
<td>0.26</td>
<td>12.7</td>
<td>6.8</td>
<td>0.21</td>
<td>6.4</td>
</tr>
<tr>
<td>3</td>
<td>112</td>
<td>35.15</td>
<td>0.62</td>
<td>9.8</td>
<td>9.7</td>
<td>0.31</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Source: $\alpha$-Dose calculated from FWHM using relationship in Ellsworth et al. [1994].
Figure 8.7 Plots to show the anisotropy of $E$, $G$, and $\nu$ along specific planes in zircon as a function of direction in that plane. Colors show values for zircon with different levels of radiation damage. Data from Özkân and Jamieson [1978], Özkân [1976], and Hearmon [1984].
Figure 8.8 Lower hemisphere equal area projections of the anisotropy of $E$, $G_{\text{max}}$, $G_{\text{min}}$, $\nu_{\text{max}}$, and $\nu_{\text{min}}$ in zircon as a function of pressure in the range 1 atm to 24 GPa. Data from Dutta and Mandal [2012a]. Poles to significant planes in zircon are shown on top left projection.
The energy factors for (100)<010> and (001)<100> dislocation lines are strongly pressure dependant, and the lowest energy dislocation line type switches above ~17 GPa from (100)<010> to (001)<100> (Fig. 8.12). Whilst there may be a similar, if not greater, dependence of energy factor on temperature, these effects have not been resolved, and therefore their general applicability may be limited. One particular scenario where the results shown in Figure 8.12 may be applied is that of shock deformation, in which extreme changes in pressure are accompanied by (at least initially) relatively small changes in temperature [e.g., Wackerle, 1962; Kieffer et al., 1976; Holland and Ahrens, 1997]. If energy factor is used as a proxy for dislocation stability, our calculations predict that the presence of lines of (001)<100> edge dislocations may be energetically more favorable than lines of {100}<010> edge dislocations above 17 GPa, which we speculate may be manifested in microstructural changes such as subgrain boundary geometries. However, the energetics associated with the migration of the dislocation line (i.e., dislocation slip) in zircon are not understood, and are not considered further in this paper. Rigorous atomistic simulations are required to fully understand the dynamics and kinematics of dislocation slip systems in zircon, which is beyond the scope of this paper. Nevertheless, the quantification of directional elasticity terms presented in this paper will be useful for future studies of dislocation creep in zircon. Further work is also required to characterize the velocity dependence of dislocation energetics in zircon under shock conditions [e.g., Hirth et al., 1998].

8.7.3. Twinning in Zircon

The geometry of shock twinning in zircon (i.e., lamellae along {112} with 65° disorientation around <110>) is compatible with the twin mode \( K_1 = \{112\}, \eta_1 = <111> \), where \( K_1 \) is the plane of invariant shear and \( \eta_1 \) is the shear direction [Christian and Mahajan, 1995]. The conjugate \( K_2 = \{112\}, \eta_2 = <111> \) are also contained within the plane of shear, P, which is \{110\}. This twin mode occurs in other tetragonal accessory phases, such as xenotime [Cavosie et al., 2016a].

The shear modulus and Poisson’s ratio along <111> (\( G_{<111>} \) and \( \nu_{<111>} \), respectively) in zircon have been resolved as a function of pressure and radiation damage (Figs. 8.7 and 8.10; Appendix Table A1). This shows that in all cases, \( G_{<111>} \) is anisotropic in zircon (e.g., 98.5–155 GPa for non-metamict zircon at 1 atm), and that the lowest value of \( G_{<111>} \) can be found along \{112\}. Conversely, the lowest G along \{112\} is in <111>. Furthermore, some of the lowest values of \( \nu \) are in <111> in zircon, and zircon is perfectly compressible in <111> along {112} (i.e., \( \nu_{<111>} = 0 \)). This suggests that elastic softness in shear (low \( G \)) and a lack of lateral strain in the shear plane (\( \nu \approx 0 \)) are favorable conditions for twinning.

According to Orowan [1954], the theoretical twin nucleation stress can be calculated using

\[
\tau = \gamma \frac{G}{2\pi}
\]

where \( \tau \) is the twin nucleation stress, \( \gamma \) is the shear strain in the shear direction \( \eta_1 \), and \( G \) is the shear modulus in the shear direction \( \eta_1 \) along the shear invariant plane \( K_1 \).

Given that \( \gamma \) is a function of bonds lengths, which have approximately linear dependence on pressure (Appendix Fig. A2), and do not vary significantly with...
Figure 8.10 Plots to show the anisotropy of $E_i$, $G_{ij}$, and $\nu_{ij}$ along specific planes in zircon as a function of direction in that plane. (a) Projection of (001). (b) Projection of (100). (c) Projection of (110). (d) Projection of (112). Colors show values for zircon at different pressures. Data from Dutta and Mandal [2012a].
radiation damage, then twin nucleation stress is primarily controlled by $G_{\langle 111 \rangle}$ which has a nonlinear dependence on pressure and varies significantly with radiation damage (Appendix Table A1, Figs. 8.7 and 8.9). This means that for $K_1 = \{112\}$; $\eta_1 = \langle 111 \rangle$ twinning in zircon, $\tau$ is lowest at 16 GPa for non-metamict zircon, which is lower than the pressure (20 GPa) at which twins have been formed in laboratory experiments to 20 GPa [Morozova, 2015]. Furthermore, the Orowan [1954] equation predicts that $\tau$ is reduced significantly by radiation damage. However, this approach does not consider the energy barriers for stacking fault nucleation and an unstable transition state twin nucleation, both of which can only be computed from ab initio calculations and are required for rigorous determination of twinning stresses [Kibey et al., 2007]. In other materials (e.g., face-centered cubic metals) where these parameters have been computed, it has been found that twin nucleation energy barrier is larger than that for twin propagation [Kibey et al., 2007]. Once twins are formed, they propagate readily. The energy “overstep” associated with twin nucleation versus propagation is probably the reason why twins form lamellae in most minerals. Nevertheless, values for $G_{\langle 111 \rangle}$ and $\nu_{\langle 111 \rangle}$ along $\{112\}$ calculated in this study will be useful for future studies of twin nucleation parameters in zircon.

### 8.7.4. Effects on the Zircon-Reidite Transformation During Shock Metamorphism

Unlike twinning where the transformation product is isostructural and isochemical with the host, reidite transformation requires high pressure. Therefore, lamellae propagation requires sustained pressure in the vicinity of the lamellae tip. There is clear microstructural evidence that formation of reidite lamellae is inhibited in radiation-damaged domains in zircon [Cavosie et al., 2015a; Reddy et al., 2015; Erickson et al., 2017] (Fig. 8.4). The $\alpha$-dose values determined from the rim and core from the Ries grain (Fig. 8.4) are within the same order of magnitude as that of grains 1 (non-metamict zircon) and 2 (partially metamict zircon), respectively, from Özkan [1976]. Significantly reduced values of $E$ and $G$ toward isotropy due to metamictization reported by Özkan [1976] are also shown by the anisotropy plots (Figs. 8.5 and 8.6).

The fact that the pressure derivative of $c_{66}$ element of the stiffness matrix and the associated mode Grüneisen parameter, $\gamma(c_{66})$ are both negative implies that zircon becomes less stable with increasing pressure due to shear transformation involving $c_{66}$ [Özkan and Jamieson, 1978]. A deviatoric (martensitic or quasi-martensitic) phase transformation involves shear, and will be facilitated by low values of shear modulus in the shear direction of the transformation. However, shear modulus in all directions is reduced with increasing radiation damage, which would intuitively result in...
in a higher propensity for transformation in metamict domains, which is counter to observations. This means that $G$ is probably not the controlling factor in the inhibition of reidite lamellae formation in metamict domains.

High values of $E$ and $G$ can support higher stresses per unit strain. Therefore, the high elastic stiffness of non-metamict zircon means that higher pressures can be attained during the propagation of a shock wave through the zircon. Metamict domains, by comparison, are elastically softer, and may not be able to achieve the pressures required for reidite transformation in the same shock event. Given that $E$ in $<100>$ and $<001>$ and along $\{100\}$, $G_{\text{max}}$ along $\{001\}$, $G_{\text{min}}$ and $G_{\text{min}}$ along $\{110\}$ are the most affected by radiation damage, we propose that the reduction of these parameters are important for the inhibition of reidite transformation in metamict domains. Furthermore, lattice defects associated with metamictization could have two effects on shock microstructures: (i) They could provide sites of nucleation whereby the energy barrier is lowered making nucleation easier. (ii) They are physical obstacles that could impede propagation of lamellae. The effects of impurities in metamict domains could further impede transformation given that ion diffusion is required for a two-stage or reconstructive zircon-reidite phase transformation [Kusaba et al., 1986; Marqués et al., 2008], and metamict domains commonly contain higher abundance of non-native ions (trace elements) [Geisler et al., 2003]. This is supported by experiments where zircon samples with impurities have higher transformation pressures [Knittle and Williams, 1993].

Curiously, a global increase in $G_{\text{max}}$ and $\nu_{\text{min}}$ in non-metamict zircon is observed at ~8 GPa (Figs. 8.8 and 8.9), which is close to the theoretical and experimental zircon-reidite transformation pressure in hydrostatic conditions [Ono et al., 2004; Dutta and Mandal, 2012a, 2012b]. However, the exact relationship between elasticity and reidite lamellae formation is yet to be fully understood.

8.7.5. Future Directions

The dependence of elasticity on temperature and composition in zircon have not yet been determined. However, natural variations in zircon composition are limited to trace levels of impurities, and are not expected to translate to significant effects on elasticity. Effects of temperature are potentially important but may be difficult to quantify experimentally. Quantification of elasticity as a function of pressure with a higher resolution than 4 GPa increments could provide useful insights into the links between elasticity and the zircon-reidite phase transformation. With the twin mode of zircon now established as $K_1 = \{112\}$; $\eta_1 = <111>$, and $G_{<111>}$ along $\{112\}$ determined, there is now a need for ab initio computation of the energy barriers associated with stacking fault formation in order to determine twin nucleation and propagation stresses.

8.8. CONCLUSIONS

- The 3D omnidirectional and 2D \{hkl\}-specific anisotropy of the elastic properties $E$, $G$, and $\nu$ have been visualized for zircon as functions of radiation damage and pressure using available elasticity data, and have been used to derive parameters that are relevant to different plastic deformation mechanisms in zircon.

- Zircon is highly anisotropic in elasticity, with particular longitudinal stiffness (high $E$) in all directions parallel to $\{100\}$, softest in shear in (low $G_{\text{min}}$) some directions along $\{100\}$, and Poisson’s ratio ($\nu_{\text{min}}$) approaching zero parallel to $<111>$.

- Radiation damage leads to significant reduction in longitudinal stiffness in $<100>$ and $<001>$, and shear stiffness in all directions, resulting in a weakening of the anisotropy of $E$, $G$, and $\nu$.

- Longitudinal stiffness in $<100>$ and $<001>$ increase with pressure. The anisotropy of $E$, $G$, and $\nu$ generally strengthens with pressure, but are reduced at ~8 GPa. $G$ changes nonlinearly with pressure, with a peak in stiffness at ~8 GPa.

- The energy factor $K$ of $\{100\}<010>$ and $\{001\}<100>$ edge dislocations increases nonlinearly with pressure, and a cross over in $K$ for $\{001\}<100>$ could indicate that $\{001\}<100>$ slip is energetically more favorable above ~17 GPa in shock scenarios.

- The lowest values of $G$ (~98 GPa) and $\nu$ (=0) align with $<111>$ along $\{112\}$ in zircon, which are key parameters for the twin mode $K_1 = \{112\}$, $\eta_1 = <111>$. A non-linear dependence of $G_{<111>}$ on pressure suggests that twinning may be favored around 4 and 16 GPa where $G_{<111>}$ is low. However, additional data are required to calculate twin nucleation stress.

- Propagation of lamellae of the high-pressure polymorph, reidite, during shock metamorphism is inhibited in partially metamict domains because of the general reduction in longitudinal and shear stiffness ($E$ and $G$) with radiation damage. Consequently, radiation damaged domains are unable to support pressures high enough to allow phase transformation.

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APPENDIX

Figures and tables are available in https://drive.google.com/drive/folders/0B09qsZWFhRukxMkZzdktMS1fU?usp=sharing.

REFERENCES


