Spherical Nanoindentation, Modeling and Transmission Electron Microscopy Evidence for Ripplocations in Ti_3SiC_2

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ABSTRACT

Herein we present experimental and modeling evidence for a new deformation micromechanism operating in layered solids termed a ripplocation. Select Ti_3SiC_2 grains were cyclically indented – either parallel or normal to the basal planes - with spherical tips with radii, R of 21 μm and 100 μm . When the load vs. displacement curves were converted to indentation stress vs. a/R curves, where a is the contact radius, fully and spontaneously reversible hysteresis loops were recorded. The energy dissipated per unit volume per cycle, W_d , was found to be a function of basal plane orientation; W_d was smaller when the basal planes were loaded edge on. Transmission electron microscope images of areas under the indentations revealed the existence of defects that previous work confirmed have a strain component along the c -axis and for which no $g \cdot b$ condition was found that resulted in their disappearance. These defects thus cannot be basal dislocations; their characteristics, however, are consistent with bulk ripplocations, BRs. It is the to-and-from movement of these BRs – and not basal dislocations as previously assumed - that is believed to be responsible for the fully and spontaneously reversible loops in Ti_3SiC_2 and possibly in most other layered solids. Consistent with the need of the basal planes to expand upon the introduction of BRs, the initial friction stress needed to move them was found to be almost three times lower when the basal planes were loaded edge-on. Molecular dynamics simulations on graphite at 10 K faithfully reproduce many features observed below the indenter in this, and previous, work on Ti_3SiC_2 . The existence of BRs will require a revisiting and reassessment of our understanding of how layered solids - from geologic formations to 2D solids – deform.

Key words: ripplocations, MAX phase, deformation of layered solids.

I. INTRODUCTION

Layered solids, defined herein as solids whose deformation is constrained to two-dimensions, 2D, are ubiquitous in nature and our modern world. From the graphite used in nuclear reactors and Li-batteries, to geological formations of layered silicates, composite materials and those comprising the 2D materials, such as graphene and MXenes, that are showing great promise in a host of current and future applications. When the literature of the deformation of crystalline, layered solids is reviewed, however, it is clear that implicitly, or explicitly, the micromechanism responsible for their deformation was in all cases assumed to be the basal dislocation, BD.[1, 2, 3, 4, 5, 6, 7] Another commonality in the deformation of layered solids is their failure mode: when the basal planes are loaded edge-on, they almost always fail by the formation of kink bands, KBs.[3, 4, 5, 6, 7, 8] In 1952 Frank and Stroh put forth a theory to explain how BDs can result in KBs [9]. We modified Frank and Stroh's theory of kinking to explain the deformation of a number of layered solids, including the MAX phases,[10] graphite,[11] and mica [12] among others.[13]

This work deals with the constrained deformation of the $M_{n+1}AX_n$ (MAX) phase, Ti_3SiC_2 . The MAX phases are so called because they are comprised of an early transition metal, M, an A-group element; X is C and/or N, and n ranges from 1 to 3. At room temperature, BDs have been postulated to exist in the MAX phases [14, 15, 16]. These BDs were presumed to be mobile, glide along their basal planes, self-assemble into dislocation arrays/pile-ups or low angle kink boundaries.[16] Non-basal dislocations would require inordinately high Burgers vectors due to their large c/a ratios (typically > 4), which renders their existence nearly impossible. Twins have never been observed in any MAX phase. In short, the MAX phases are layered as per our definition. It is thus not surprising that like other layered solids, kink bands form when the basal

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5 planes are loaded edge-on.[15, 17] Indeed KBs in the MAX phases have been imaged at
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7 multiple lengths scales, from the sub-micrometer [15] to the centimeter.[18] What renders the
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9 MAX phases unique is the fact that the density of states at the Fermi level is substantial and
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11 therefore it is not unreasonable to think of them as layered metals. As discussed herein, this is a
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13 key feature that allowed us to readily image BRs.
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17 When the MAX phases are cyclically loaded in compression, they form fully, and
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19 spontaneously, reversible stress-strain hysteresis loops (Fig. 1a).[19] Since part of the strain is
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21 fully reversible, viz. elastic, but non-linear, and the end result in most cases was the formation of
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23 kink boundaries/bands, we termed these solids kinking non-linear elastic or KNE. The
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25 mechanism invoked to explain these fully reversible stress-strain hysteresis loops was based on
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27 the aforementioned Frank and Stroh paper. In our model, the growth and annihilation of incipient
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29 kink bands, IKBs was postulated.[9, 10, 20] IKBs are BD loops, confined to the basal planes,
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31 that are extended when a load is applied, but shrink and annihilate when the load is removed as
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33 dislocations of opposite sign attract and combine. The to-and-fro motion of the IKB dislocations
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35 was postulated to explain the reversible, but non-linear elastic strain, ϵ_{NL} , and the energy
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37 dissipation per unit volume per cycle, W_d . The latter is given by the area of the fully, reversible
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39 stress-strain loop (hatched area in Fig. 1a). In light of the work shown here, this idea is no longer
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41 considered viable.
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49 To study KNE solids in layered materials, such as the MAX phases,[21] graphite [11] and
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51 mica [12] we developed a nanoindentation, NI, technique [22, 23] wherein hemispherical
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53 indenters with radii, R , were repeatedly indented in the same location, of typically, single
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55 crystals. The load is then converted to a normal stress, σ_{NI} , and plotted vs. a/R , where a is the
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5 contact radius (see Fig. 1b). This technique is used here to study the mechanics of this
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7 phenomenon (see Appendix A).
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10 This is not the first NI study of a MAX phase. In 2003, Molina-Aldareguia et al. used a
11 Berkovich tip to study the deformation of Ti_3SiC_2 epitaxial thin films.[24] When they examined
12 cross-sectional lift outs of the volume under the indentation in a transmission electron
13 microscope, TEM, delaminations and kink bands, KBs, near the indentation edges were
14 observed. In the same year, Kooi et al. [25] compared the response of Ti_3SiC_2 and SiC to
15 Berkovich indenters as a function of basal plane orientation. Like Molina-Aldareguia et al. [24],
16 they found that when the load was normal to the basal planes, a relatively large pileup of material
17 accumulated near the indentation mark edges (Fig. 2a). Tellingly, such pileups were *not* observed
18 when SiC single crystals were indented in any orientation.[25] In 2004, Murugaiah et al.[21]
19 again working with Ti_3SiC_2 , used a combination of electron backscatter diffraction, EBSD, and
20 spherical nanoindenters, to produce the first, fully reversible load-displacement NI curves for the
21 MAX phases. In that study, like here, the loads were applied either parallel, or normal, to the
22 basal planes. For the most part, when the applied load was normal to the basal planes it was
23 difficult to find the post-indentation mark. In contradistinction, when the load was applied
24 parallel to, i.e., edge on to the basal planes, pop-ins and delamination cracks parallel to the basal
25 planes were observed, but only over a threshold stress (see below).
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48 Other studies have suggested that the reversible hysteresis is the result of micro-cracking,
49 [26] or residual elastic lattice strains,[27] which result in part due to the limited number of slip
50 systems. In a series of papers [28, 29, 30], we also argued that microyielding and W_d in
51 hexagonal metals could be ascribed to IKBs. However, recently we showed that it was most
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probably the bowing out of dislocations that was responsible for microyielding and W_d , at least in Mg [31].

In early 2015,[32] evidence for a new micromechanism termed a ripplocation was presented. Ripplocations were defined as surface ripples created when atoms are locally inserted into one layer relative to other adjacent layers (left top inset in Fig. 1b). Kushima et al. [32] made the case that ripplocations are a near surface defect operative during the deformation of 2D van Der Waals solids. We recently extended their idea to all layered solids and showed – by a combined modeling and experimental approach - that *bulk* ripplocations, BRs, formation is essentially an atomic scale buckling phenomenon (top right inset in Fig. 1b).[33] We also showed that BRs are *not* restricted to van der Waals solids and can occur in bulk and thus are not necessarily restricted to surfaces, or near surfaces.[33] Unlike dislocations, BRs have no Burgers vector or polarities. Their energies only depend on the amount of "excess" material that needs to be accommodated. Our molecular dynamic calculations on graphite at 10 K showed them to be quite mobile.[33]

In the same paper, we presented TEM evidence for the existence of BRs in the volume under the indenter when it was loaded normal to the basal planes - i.e. along [0001] – in Ti_3SiC_2 . [33] The TEM evidence presented was threefold: i) Dark streaks - parallel to the basal planes were observed that geometric phase analysis, GPA, of HRTEM images showed were clearly associated with c-axis elastic strain [33]. ii) After Bragg filtering, it was also clear that some atomic layers appeared to undulate in areas surrounding the dark streaks, but not in areas far removed from these streaks.[33] iii) Most importantly there was *no* $g \cdot b$ condition in the TEM that rendered these defects invisible. It follows that these defects were not BDs, but fully consistent with the presence of BRs.

The purpose of this work is to present more direct and indirect evidence for the existence of BRs in Ti_3SiC_2 and to shed more light on their nucleation, growth and motion. This is accomplished by repeatedly indenting - the same location - with spherical indenters with two different indenter radii, R . Like in our previous work, the load was applied either parallel, or normal, to the basal planes. In contrast to our previous work, however, herein the TEM observations focused mainly on a location where the basal planes were loaded *edge-on*. To explain some of the observations made herein and in previous work, we also simulate what occurs in graphite when a cylindrical indenter is loaded normal to the basal planes. The situation when the indenter is loaded normal to the basal planes was dealt with previously.[33]

II: THEORETICAL CONSIDERATIONS

In this work, NI load-displacement curves (Fig. 3) are converted to NI stress, σ_{NI} vs. a/R plots (Figs. 4 and 5) using a procedure described previously [22] and summarized in Appendix A. The fundamental idea of our approach is to estimate the contact radius a from load-displacement curves. Once the latter is estimated, we assume that the non-linear reversible shear strain is given by:

$$\gamma_{\text{R}} \approx \frac{4}{3\pi} \frac{\Delta a_{\text{r}}}{R} \quad (1)$$

where $\Delta a_{\text{r}}/R$ is defined in Fig. 1a. The $4/3\pi$ term comes from Hertzian analysis (see Eq. A1 in Appendix A). This figure plots a highly idealized σ_{NI} vs. a/R plot in which at a maximum stress, σ_{max} , a pop-in event occurs, beyond which the stress drops to a constant value. The deformation then occurs to a maximum strain, γ_{max} . Upon unloading the response follows the γ_{max} to a_0/R trajectory, where a_0 is the contact radius of the residual indentation left when the indenter is

removed. Upon reloading, the response is initially linear elastic, with a slope E resulting in a linear elastic strain, $\varepsilon_{LE} = \Delta a_e/R$. At a critical stress, σ_c , an additional reversible nonlinear shear strain, $\Delta a_r/R$, appears (Fig. 1a). Beyond that stress, the total shear strain (Fig. 1a) is given by:

$$\gamma_{\max} = 4/3\pi (\Delta a_e/R + \Delta a_r/R) \quad (2)$$

When $\gamma_{\max}$ is reached, the load is reduced, and the unloading trajectory follows the $\gamma_{\max}$ to a_0/R path again. All repeat cycles then fall on the fully reversible loops outlined by, $a_0/R - \sigma_c - \gamma_{\max} - a_0/R$ (Fig. 1a). The loop area is a direct measure of W_d .

We now turn our attention to W_d . The latter is equal to $2\tau_f\gamma_r$, where the factor of 2 accounts for the energy dissipated during loading and unloading [34]. In our case, τ_f is the frictional shear stress of whatever defect is moving reversibly. Making use of Eq. 1, and assuming that $\sigma_f \approx \tau_f/\Omega$ – where Ω is a factor of the order of 0.5 that relates the shear stress on the basal planes, τ_f , to the normal stress σ_{NI} – it follows that:

$$W_d \approx 2\Omega\sigma_f \frac{4}{3\pi} \frac{\Delta a_r}{R} \approx \frac{4\pi_f}{3\pi} \frac{\Delta a_r}{R} \quad (3)$$

If τ_f and Ω are not functions of Δa_r , then plots of W_d vs. $\Delta a_r/R$ should yield straight lines with a slope $\approx 4\sigma_f/3\pi$. The slope is thus a *direct* measure of the friction stress of whatever defect is responsible for both ε_{NL} and W_d .

Experimentally (see below) we find that

$$\sigma_{NI} - \sigma_c = K \frac{\Delta a_r}{R} \quad (4)$$

where K is a constant which is a measure of the hardening rate of whatever defect is responsible for the deformation. Combining Eqs. 3 and 4 yields:

$$W_d = K' \sigma_f (\sigma_{NI} - \sigma_c) \quad (5)$$

where K' is another constant. It is crucial here to recognize that since BRs are nucleated in the first cycles, then σ_f should equal σ_c especially at low loads since the latter is nothing but the stress needed to move the defects.

Because, by their very nature, BRs can only nucleate either at free surfaces,[33] or when basal planes are severed (see below), how the basal planes are loaded can have a profound effect on the response observed, especially, as discussed below, as it pertains to the resolved in-plane compressive strain. To illustrate consider the two surface examined in this work: (0001) and (10-10). The latter is easier to visualize. Here, loading the basal planes edge-on results in their buckling by the formation of a series of near-parallel kink boundaries, KBs, of opposite sign that are more or less normal to the basal planes (see Fig. 4a in Ref. [33]). If the buckling is not severe enough to form permanent kink boundaries, upon unloading the buckled layers fully recover, leaving no trace of the indentation.[33] If, however, permanent kinks do form, delamination cracks, parallel to the basal planes, are nucleated, again as observed herein and previously.[21]

The situation when the (0001) surface is indented is less transparent. When loaded in this orientation, permanent KBs, if they form, are again normal to the basal planes (Fig. 2a). Topologically, before moving away from beneath the indenter to the sides, the basal planes must *first rupture*, (Fig. 2a). The situation when the stresses are high enough to cause permanent deformation in the form of KBs, is best depicted in Fig. 2a taken from Movie 1. In this instance,

the basal planes are pushed to the sides with the indenter, resulting in the formation of permanent KBs near the indent edges, together with concomitant delamination cracks. Along the same lines, the situation when the buckling stresses are not high enough to result in permanent KBs, but a dissipative non-linear strain is recorded (Fig. 1a) *necessitates* that some basal planes below the indenter first rupture, allowing them to move back and forth.

From these simple considerations the following predictions can be made: i) It should be easier to nucleate BRs when the basal planes are loaded edge; ii) All else being equal, the critical resolved shear stress, CRSS, needed to move ripplocations must be higher when the load is normal to the basal planes, since in this case the applied normal stress should add to the friction force. iii) If the bending rigidity of the MX layers in the $M_{n+1}AX_n$ phases are a function of n , then, all else being equal, it should be significantly easier to nucleate BRs in a 211 MAX phase than in its 413 counterpart. Here again this is a crucial prediction since the CRSS of basal dislocations would be expected to be a weak function of the number of MX layers for the same M-A combination.

III. EXPERIMENTAL DETAILS

A highly orientated Ti_3SiC_2 polycrystalline sample was synthesized from Ti (99.9% metal basis, Alfa Aesar), Si and graphite (Alfa Aesar) elemental powders mixed in stoichiometric ratios, and hot pressed at 1450° C under a load corresponding to a stress of 25 MPa for 4 h. The sample was further annealed at 1550° C for 72 h in Ar to coarsen the grains. The samples were fully dense and their grain sizes ranged between 200 and 500 μm (inset in Fig.

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5 1a). X-ray diffraction verified that the material was predominantly Ti_3SiC_2 , with a small fraction
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7 of an impurity TiC phase.
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10 The bulk sample was mounted, ground down using 600-1200 SiC grit paper, and polished
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12 down to 0.25 μm diameter diamond particles, suspended in water (Struers Inc., Cleveland, OH).
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14 Lastly, the sample was vibropolished with a 0.05 μm diameter alumina suspension.
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17 A scanning electron microscope, SEM (Philips FEI XL30) - equipped with EBSD - was
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19 used to generate an orientation map of the grains (inset in Fig. 1a). As noted above, two surfaces
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21 were chosen for further study: (0001) and $(10\bar{1}0)$. These surfaces were indented with
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23 hemispherical diamond indenters with R's of 100 μm or 21 μm . A nanoindenter (MTS
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25 Nanoindenter XP system, MTS Corporation, Oak Ridge, TN) equipped with continuous stiffness
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27 mode, CSM, was used. A schematic of a spherical indenter tip on a sample surface is shown in
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29 Fig. 1b. Cyclic NI tests were performed using the CSM mode, which recorded the stiffness
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31 continuously, in addition to the loads and displacements. Each test was programmed to a
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33 targeted strain rate of 0.1 s^{-1} .
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39 Although the results were collected from a number of locations, this study focuses
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41 primarily on 4 locations that were deemed to have the least amount of drift. Their designation,
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43 grain orientations, nanoindenter radii used and maximum loads are listed in Table 1. Other
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45 locations can be found in Ref. [35]. In a typical experiment, a select location was initially loaded
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47 to the maximum load (500 or 550 mN). The load was then decreased to 5 mN, before loading to
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49 the maximum again. This process was repeated 50 times. Typical load-displacement curves –
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51 showing all 50 cycles - are shown in Fig. 3, for both orientations. The reason the same location
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53 was indented 50 times to the same load was to insure that whatever microstructure develops
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55 below the nanoindenter was one that no longer changed significantly with loading. Once the 50
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cycles were terminated, the load was incrementally increased from 20–100% of the maximum load to generate nested loops (not shown) that are the main focus of this work.

As noted above, the load vs. displacement curves were converted into NI stress, σ_{NI} vs. a/R plots (Appendix A).

Table 1: Summary of surface orientations, R , maximum loads, and the K' values (see Eq. 5) obtained from a least squares fits of lines shown in Fig. 6c, and σ_f from Fig. 6b for locations A, B and C. In Fig. 6b, the lines were forced through the origin. All locations were cycled 50 times before the nested loops were generated.

Location	Orientation	R (μm)	Max Load (mN)	K' (GPa)	σ_c (GPa)	σ_f (GPa)
A	(0001)	100	550	112 ± 4	1 ± 0.2	1.4
B	(10 $\bar{1}0$)	100	550	150 ± 2	0.5 ± 0.2	0.6
C	(0001)	21	500	135 ± 5	1.7 ± 0.1	1.8
D	(10 $\bar{1}0$)	21	500	--	--	

A dual beam focused ion beam-scanning electron microscope, FIB-SEM (FEI Dual Beam 235), was used to prepare cross-sectional lift outs of the volumes underneath, and in close proximity, to the indentation marks. The lift outs were examined in a transmission electron microscope, TEM, (JEOL 2100 LaB₆) for further analysis and characterization.

When the indents were clearly visible in the SEM, the contact radii, a_o , of the residual indents were measured. When the craters were too faint for their radii to be accurately measured in the SEM, an atomic force microscope, AFM, (Park NX10), was used instead. In both cases, the a_o values were used to calculate σ_{NI} .

Atomistic simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator, LAMMPS, molecular dynamics, MD, package [36] using the adaptive Intermolecular Reactive Empirical Bond Order, AIREBO, inter-atomic potential [37] to create our graphite system, which includes both covalent and Van der Waals bonding between C

atoms and is therefore well suited to the modeling of graphite. We modeled a cylindrical nanoindenter through a repulsive potential applied to all atoms within a cut-off distance of 10 nm to the center of the indenter. This distance was numerical set to effectively create the indenter radius. The initial atomistic configuration consisted of 48 atomic layers and the nanoindenter was moved sinusoidally perpendicular to the basal planes with an amplitude of 10 nm and a period of 50 ps – 2 complete periods were simulated. The simulation was carried out at a temperature of 10 K, where the amount of material and its volume were conserved. As shown in the bottom right inset in Fig. 2a, the top 8 atomic layers were artificially ruptured before NI, by removing 1 row of atoms in each layer to aid in the nucleation of KBs under the indenter (see below). All atoms in Fig. 2 are colored according to their potential energy, with green being higher than blue.

IV. RESULTS

A. Nanoindentation Results

The entire 50 load vs. displacement cycles for indentations A and B are compared in Fig. 3a; indentations C and D are compared in Fig. 3b. When R was 100 μm (Fig. 3a), the maximum load was 550 mN and the first cycles were open, with a permanent displacement of < 100 nm. Further cycling, resulted in mostly fully reversible load-displacement cycles. The loops for the $(10\bar{1}0)$ surface (blue loops in Fig. 3a) are so reproducible that despite the fact that 50 cycles are superimposed, the center of the loop area is still visible. For the (0001) surface (red loops in Fig. 3a), the loops slowly drifted to the right with cycling. At this time it is not clear whether the drift is thermal or due to a small plastic deformation during every cycle. If it is the latter, then the average displacement per cycle is ≈ 1 nm.

When R was 21 μm , the maximum applied load was 500 mN and the two surfaces behaved quite differently (Fig. 3b). For the (0001) surface (red loops in Fig. 3b), the first cycle

was open, with a permanent displacement of ≈ 150 nm. With increasing cycle number, the loops drifted to the right with cycling, with an average displacement per cycle of ≈ 2 nm. Note the small pop-ins at loads > 400 mN. For the $(10\bar{1}0)$ surface (blue loops in Fig. 3b), there were two, relatively large, pop-ins, and a number of smaller ones. Like our previous work,[21] post-indentation SEM observations of location D confirmed the pop-ins correlated with delamination cracks parallel to the basal planes.

The σ_{NI} vs. a/R curves for locations A to B are shown in Fig. 4a ; the respective curves for locations C and D are shown in Fig. 4b. With the $100\ \mu\text{m}$ indenter, the response of the two surfaces are comparable; in both cases the maximum stresses are ≈ 3 GPa. After the first cycle, the σ_{NI} vs. a/R loops are quite reproducible, with a little more apparent drift in the case of the (0001) surface. In all figures, the slopes of the dashed inclined straight lines correspond to a modulus of 325 GPa as one would expect from Hertzian analysis (Appendix A).

Not surprisingly, given the results shown in Fig. 3b, the σ_{NI} vs. a/R curves for locations C to D could not be more different (Fig. 4b). This is only true, however, *after* the first cycle. For the first cycles, the two curves are almost superimposable (note the results for the $(10\bar{1}0)$ surface were shifted to the right by 0.02 for clarity's sake), where the response initially is linear elastic (Fig. 4b). Both reach maximum stresses around 7 GPa. The small pop-ins occurring when the (0001) surface is indented manifest as small drops in σ_{NI} . The σ_{NI} drops for the $(10\bar{1}0)$ surface are much more severe and ultimately result in much higher penetration depths (compare red and blue curves in Fig. 4b).

The nested loops – after 50 cycles - for indents A and B are shown in Fig. 5a; those for indents C and D are shown in Fig. 5b, respectively. In Fig. 5a, the initial response is again linear elastic up to a critical, or microyielding stress, σ_c , beyond which fully, and spontaneously,

reversible loops emerge. At 0.5 GPa, σ_c for the $(10\bar{1}0)$ planes is roughly half that of the (0001) planes, which is ≈ 0.9 GPa (Fig. 5a). Note that for both surfaces, the maximum stresses are ≈ 3 GPa.

The results shown in Fig. 5b are dramatically different. For the (0001) planes, at ≈ 6 GPa, the maximum stresses were some of the highest recorded for nested loops. Here again, good agreement is obtained between the inclined dashed line (325 GPa) and the initial regime of the nested loops up to $\sigma_c \approx 2.0$ GPa, beyond which the nested loops emerge. Not surprisingly, the shapes of nested loops for the $(10\bar{1}0)$ plane (location D, Fig. 5b) are different than all other loops in that: i) their initial moduli are quite low (compare the slopes of the dashed black line for location D in Fig. 5b to the initial slope of the loops); ii) with increased loading, the nested loops stiffen; iii) the indenter penetrates significantly deeper; iv) at comparable stresses, W_d for location C is higher than location D; v) because of the higher penetration depth, the maximum stresses reached are a fraction of those sustained by the (0001) planes (Fig. 5b); vi) For the $(10\bar{1}0)$ planes, a critical stress is absent and energy is dissipated starting at quite low stresses.

B. Nonlinear Strain

Figure 6a plots W_d vs. $\Delta a_r/R$, for locations A, B and C; Fig. 6b plots the same results over a smaller $\Delta a_r/R$, range. From these results it is clear that for a given $\Delta a_r/R$, the $(10\bar{1}0)$ surface dissipates the least energy, followed by the (0001) surface loaded with the 100 μm indenter. The most energy is dissipated by the (0001) surface loaded with the 21 μm indenter. The differences between the latter two however are small. Figure 6c plots the maximum σ_{NI} values of each of the nested loops - shown in Fig. 5a and those labeled C in Fig. 5b - versus $\Delta a_r/R$. The results fall on straight lines; the y-axis intercepts represent the σ_c 's of each configuration.

C. Surface Topography Results

Typical post-indentation SEM images of indentation marks taken at various locations are shown in Fig. 7. Notably, and in accord with previous work [21], delamination cracks – normal to the c-axis - were present after the 21 μm tip was indented in location D edge-on into the basal planes (Fig. 7a). The nucleation of such cracks explains why this location was so different as compared to the other locations (Fig. 5). This crater radius can also be used to calibrate the values of a_0 calculated using the procedure outlined in Appendix A. The radius of the crater was $\approx 7 \mu\text{m}$, for a a_0/R ratio of 0.33 (see Fig. 5b), a value that is in excellent agreement with the a_0/R ratio of ≈ 0.34 calculated using the procedure outlined in Appendix A. This is an important result because it confirms that our procedure is valid even when the penetration depth of indenter is considerable.

In general, indentations marks made using the 100 μm tip were quite difficult to image and sometimes *no* trace of the indent could be detected. Therefore these values could not be independently verified. In one location, however, the NI penetration was higher than other locations, which resulted in a faintly visible mark (Fig. 7b) only observable by tilting of the sample in the SEM. The length of the mark was $\approx 17.5 \mu\text{m}$, which implies an a_0/R of 0.0875. The a_0/R value for this location (not shown) was 0.08.

Indentations made using the 21 μm tip along [0001], viz. location C, were easier to detect (Figs. 7c and d). Crucially, and in sharp contradistinction of location D, in this direction, delamination cracks were *absent* (Fig. 7c). Furthermore, like in our previous work on other hexagonal solids such as graphite [11] mica [12] and ZnO [38], the indentation mark had a 6-fold symmetry as outlined on the micrograph (Fig. 7c). The length of the near horizontal line shown in Fig. 7c is 8.5 μm . An AFM scan of the same location is shown in Fig. 7d. Here the diameter of

the indentation was closer to 7 μm . Thus a_0/R should be fall somewhere between 0.14 and 0.2. At ≈ 0.17 , the a_0/R value calculated for this location (Fig. 5b) is in reasonable agreement with the aforementioned values. The totality of these results indirectly confirms that our conversion of load/displacement results to NI stress vs. a/R are valid. Another important testament to the robustness of our methodology is the fact that, with the exception of location D, the initial slopes of *all* σ_{NI} vs. a/R (see dashed inclined lines) are parallel to each other and correspond to an elastic modulus of 325 GPa. This result *cannot* be easily dismissed and is consistent with all our previous work.[12]

D. TEM Results

Cross sectional lift outs were made of locations C and D (Table 1) and imaged in a TEM. The former were already presented elsewhere [33]. A cross section of the region directly below indent D is presented in Fig. 8 as a collage of TEM micrographs. In the SEM image of this lift out (not shown), some cracks and voids could be very faintly resolved. Indentation at such high stresses, resulted in the creation a multiplicity of grains of different orientations beneath the indented region (Fig. 9a and b), where different grains appear in contrast. Delamination cracks (Fig. 9c) and KBs and concomitant delamination cracks are also clearly seen in Fig. 9d.

Dark streaks, parallel to the basal planes – identical to those seen under location C in Ref. [33] - were also observed (Fig. 10a). Similar to our previous work [33], there was no $g \perp b$ condition where these dark streaks were out of contrast, as shown by Figs. 10b and c taken with g vectors (top right) orthogonal to each other. A lift out from a pristine region also showed dark streaks (Fig. 11a), that Bragg analysis of an HRTEM image of one streak confirmed. Figures 11b and c highlight the wavy nature of the basal planes, which is a signature of BRs. The streak density, however, was significantly lower than for the region under the nanoindenter.

Figure 12a shows a collage of TEM micrographs of a region near the edge of an indentation mark generated by loading normal to the basal planes, showing clear evidence for kink bands and boundaries. These regions were pushed away from under the nanoindenter during indentation and are shown in greater detail in Fig. 12b.

E. Simulation Results

In our previous work, we simulated what happens when the basal planes in graphite are loaded edge-on with a cylindrical indenter.[33] Here we simulate what happens when the indenter is loaded normal to the basal planes. Preliminary runs indicated that without severing the basal planes directly under the indenter the response was linear elastic (not shown) and no KBs were formed. Therefore to carry out the simulation in this orientation, we ‘severed’ 8 graphitic layers under where the indenter first touched the sample (inset in Fig. 2a). Movie 1 in Supp. Information shows two loading cycles of the simulation. Figures 2a to c show time steps in the microstructure's evolution under the indenter. When the penetration of the indenter is shallow (Fig. 2a) two kink bands, together with concomitant delaminations, form on either side of the indent. When the indenter penetrates further into the surface (Fig. 2b), the deformation - restricted to the topmost 8 severed layers introduced before the simulation was run - moves away from the central region by the creation of a multitude of kink boundaries of opposite polarity, again with concomitant delaminations.

Lastly, Fig. 2c shows the morphology at maximum penetration. By that point highly defective, and severely deformed, atomically thin lamella form near the indent edges. Note that in this simulation the indenter penetrates so fast into the substrate as to generate shock waves that eventually aid in the deformed configuration containing the delaminated layers. The colorful inset in Fig. 2c – reproduced from Ref. [18] - is that of a Ti_3SiC_3 grain that was deformed at

room temperature, under compression. The similarities between the simulations and experiment OM micrographs are striking.

V. DISCUSSION

Before making the case that the defects observed herein are BRs, it is crucial to make the case that they are not basal dislocations. This is important because, as noted in the introduction, the latter have been invoked to explain the deformation of layered solids from graphite [1] to mica [3, 4, 5, 6, 7], to the MAX phases [20] among many other layered solids. A BD, however, cannot result in strain along the c-direction. Evidence for the latter herein, however, can be seen at different lengths scales: i) delamination cracks observed in Fig. 7a; ii) redistribution of material from under the indenter to its sides (Fig. 2a and Figs. 12a and b) and, iii) TEM results shown in Figs. 10b and 11a. More importantly geometric phase analysis, GPA, analysis of dark regions, identical to those shown in Figs. 10a and 11a, provided direct evidence for strain in the c-direction [33]. Since the features shown here are identical to those shown previously, the GPA was thus not repeated here.

Furthermore, the defects cannot be basal dislocations because as shown in Figs. 10b and c, they could *not* be rendered invisible in the TEM. In contradistinction, interstitial dislocation loops in neutron irradiated Ti_3SiC_2 samples with a Burgers vector $1/2[0001]$ were readily rendered invisible [39]. This result is crucial because it eliminates interstitial dislocations loops as the source of the c-axis strain and shows that well-established dislocation-based defects - like interstitial dislocation loops - behave as they should in a TEM.

If not dislocations, then what? It is easy to argue, as we have done previously, that if two atomic layers are to slide relative to each other without breaking the all important in-plane bonds then ripplocations are a topological imperative [33]. In the remainder of this paper we make the

case that the defects observed are indeed BRs. In addition to the aforementioned TEM, the evidence is multifold and includes:

a) Effect of applied stress on CRSS

From Figs. 6a and b it is amply clear that the relationship between W_d and $\Delta a_r/R$ is non-linear; it increases with increasing strain. According to Eq. 3, this in turn implies that the CRSS of the BRs is not a constant, but is itself a function of strain/stress. This general result is not new, and well established in the geologic literature. For example, Kronenberg and coworkers [3, 4, 5] have shown that the compressive strengths of biotite and muscovite micas are strong functions of confining pressure. The same is true of most of the literature on layered solids. In fact the dependence of the failure stresses on confinement can be taken as a good indication that BRs, and not dislocations, are the operative micromechanism.

The last two columns in Table 1 list the values of σ_c and σ_f obtained by two independent methods. The former was obtained from a least squares fit of the W_d vs. $\Delta a_r/R$ plot (Fig. 6c); the latter from a least squares fit of the first 3 points of the σ_{NI} vs. $\Delta a_r/R$ plot (Fig. 6b). The agreement between the columns has to be considered excellent considering the many simplifying assumptions made in deriving Eqs. 3 and 5 and experimental difficulties, such as instrumental drift, and the uncertainty in determining the value of a_0 and hence the stresses. The good correlation between these two values is evidence that the same micromechanism/defect is responsible for ϵ_{NL} and W_d .

b) Effect of orientation on W_d

Table 1 clearly shows that σ_f is a strong *function of orientation*. And while this result would be difficult to rationalize in terms of BDs, it is easier to do so in the BR case. As discussed above, to move BRs the basal planes have to essentially "separate" the basal planes ahead of

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5 them. It follows that when the applied load is normal to the basal planes, this simply increases σ_f
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7 by a force proportional to the applied normal stress.
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10 When the basal planes are loaded edge-on, however, the Poisson expansion would tend to
11 "pry" the basal planes open allowing for easier BR motion, at least initially. However, note that
12 with increasing deformation, σ_f increases faster in the latter case than for the (0001) planes (Fig.
13
14 5b). This may be rationalized by postulating that after an initial deformation, the material around
15 the indentation mark, as a result of the same Poisson-like expansion, starts pushing back and/or the
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17 amplitude of the BRs increases faster (see below).
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24 Along the same lines we showed recently that when highly textured polycrystalline
25 Ti_2AlC samples (a MAX phase) were compressed [20], contrary to expectations, the values of
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27 W_d were greater when the basal planes were loaded along [0001] compared to when they were
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29 loaded edge-on. This result – at the time unexpected - is fully consistent with the aforementioned
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31 discussion.
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36 The fact that the initial W_d values for the (0001) plane indented with the 21 μm and 100
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38 μm indenters are quite close (Fig. 6b) - despite a factor of almost 5 in their radii - is gratifying at
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40 many levels. It is consistent with the fact that σ_f should only be a function of orientation. It also
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42 indirectly confirms that our NI stress/strain analysis is valid over a wide stress range. The fact
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44 that we obtain the results shown in Fig. 6a and b, despite almost a factor of two difference in
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46 maximum stress between the two indenters (compare Figs. 5a and b) is also an indication that
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48 our overall analysis must be valid. This cannot be overemphasized.
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53 c) Amplitude Hardening 54 55

56 In metallurgy, a figure like Fig. 6c reflects the increase in dislocation density with
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58 deformation, i.e. work hardening. Here, the interpretation must be different since the process is
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5 fully reversible and dislocations are not involved. In our previous work on BRs [33] we showed
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7 that when two BRs in graphite are adjacent to each other they tend to spontaneously merge into
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9 one BR with a higher amplitude. Since we did not carry out any simulations on the MAX phases
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11 – for the lack of useful potentials – it is an open question at this time whether the MAX phases,
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13 with their significantly higher c_{33} values, would behave like graphite,
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17 The results shown in Fig. 6c, however, are important in that they can shed some light on
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19 the question. The slopes of the lines shown in Fig. 6c are a measure of "work hardening" (See
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21 Table 1). Said otherwise, with increased deformation it becomes harder for BRs to move. This
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23 resistance implies that as the BRs are pushed away, one or both of the following two scenarios
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25 must play out: i) their amplitude increases, and/or, ii) their motion is impeded by back stresses,
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27 in the same spirit that dislocation pileups do so in metals. Said otherwise, in the absence of these
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29 mechanisms, the lines in Fig. 6c should have remained more or less flat.
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33 The results shown in Fig. 6c suggest that amplitude hardening is not only important but is
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35 also a function of orientation. There is little doubt that the hardening rate is higher when the
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37 basal planes are loaded edge-on than along [0001] (compare K' values in Table 1). Given that in
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39 the former case, the stress on the BRs is directly implicated in their buckling, it is reasonable to
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41 assume that the amplitudes increase faster and are much more severe than in the latter case.
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43 When loaded along [0001], σ_{NI} cannot by itself cause buckling; rather it is penetration of the
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45 indenter that results in the compression of basal planes and ultimately results in their moving out
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47 the way (Figs. 2a and 12). This is presumably why at ≈ 6 GPa delamination cracks nucleated
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49 when the $(10\bar{1}0)$ surface was loaded (Fig. 7a) but not when the (0001) surface was (Fig. 7c)
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51 despite the fact tha the same R was used.
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58 Note that if the BRs propagated *without* an increase in amplitude, then delamination
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5 cracks would have no reason to nucleate and indeed they do *not* when the stress is of the order of
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7 3 GPa (Fig. 5b). Along the same lines, and for exactly the same reasons, if the amplitude of the
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9 BRs in the (0001) orientation did not increase with loading, there would be no driving force to
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11 delaminate the planes, and hence no driving force to cause the kink band and concomitant
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13 delaminations at the edges of the indentation marks clearly seen in Fig. 12. Said otherwise,
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15 delaminations are a manifestation in the increases in amplitude of BRs with stress. Needless to
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17 add, had BDs been the operative micromechanism such delaminations would be impossible to
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19 explain.
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23 24 d) Strain Accommodation

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26 Based on the totality of the results and arguments presented it is now possible to
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28 reconstruct what happens at the atomic scale upon loading a layered solid like the MAX phases.
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30 Since the two orientations are so different we discuss them separately starting with the edge-on
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32 configuration.
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35 36 *Edge-on Loading*

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38 In this case, the applied load – after a linear elastic regime - results in the formation of a
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40 multitude of near parallel kink boundaries that propagate into the bulk of the sample.[33] As the
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42 deformation amplitude increases, the energy needed to move them increases. Beyond a critical
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44 stress – estimated here to be just below 6 GPa (Fig. 4b) – the amplitudes are no longer
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46 sustainable and the material fails by delamination and permanent buckling – i.e. formation of
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48 kink bands - of the layers beneath the indenter. This process, when it occurs suddenly as it did
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50 here, not only results in delaminations parallel to the basal planes, but also a dramatic
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52 reconfiguration and rotation of basal planes presumably by the formation of a multiplicity of
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54 kink bands (see Figs. 8 and 9). The extent of lattice rotation seen in Fig. 9 is noteworthy, and
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consistent with our single crystal graphite [11] and, especially, mica work [12].

Loading along [0001]

In this case, before the slightest nonlinear strain or any plastic deformation can occur, the basal planes *have to* rupture first. (Note this is *not* required when the planes are loaded edge-on.) This rupturing has to occur during the first cycle. Once the planes are ruptured, viz. BRs are nucleated, they can now move back and forth in response to the cyclic stress and their motion results in ϵ_{NL} and W_d . The driving force, reversing their motion, is the elastic energy stored in their crests, i.e. curvature.[40]

Before discussing permanent deformation in this orientation it is instructive to estimate what fraction of basal planes would have to rupture to accommodate ϵ_{NL} . To estimate ϵ_{NL} we start with the fact that the maximum stresses are of the order of 3 to 6 GPa. For an elastic modulus of 325 GPa, this translates to a linear elastic strain, ϵ_{LE} , between 0.01 and 0.02. Since from Fig. 5a, $\epsilon_{NL} \approx 1/2 \epsilon_{LE}$, it follows that the ϵ_{NL} 's are of the order of 0.005 and 0.01 at 3 and 6 GPa, respectively. Hence only one BR need be nucleated for every 100 planes to account for what we observe. A perusal of the TEM micrographs shown in Fig. 3c in Ref. [33] and Fig. 10 here, suggest that this crude estimate is quite reasonable.

When loaded along [0001], the stresses were sufficient to move the BRs but not cause permanent kink banks to form right below the indenter. TEM of the region just below the indenter in this orientation were free of kink bands/boundaries and only dark streaks parallel to the basal planes were imaged.[33]

This is only true for the volume directly below the indenter, however, and does not imply that permanent damage does not occur. In this orientation permanent damage, in the form of KBs, only occurs near the indentation periphery, as shown in Figs. 12a and b. Such kink bands -

ubiquitous in all layered solids, in general, and in early nanoindentation work on Ti_3SiC_2 [25], graphite [11] and mica [12] - can now be explained. The fact that our simulations on graphite in that direction (Fig. 2a) results in their spontaneous formation supports this idea (Fig. 2b) and again suggests that our simulations are indeed mimicking nature. Interestingly even in this orientation and for reasons that are not clear, lattice rotations are also observed. Selected area diffraction, SAD (not shown), of regions I and II in Fig. 12a, showed little if any difference. SAD of regions I and III, on the other hand, showed that an almost 90° rotation of the basal planes below and above the crack shown.

Lastly we turn our attention to the fantastical structures observed in the simulations at higher penetration depths seen in Fig. 2b and especially in Fig. 2c. That similar structures (see inset in Fig. 2c) were indeed observed near the corners of Ti_3SiC_2 cubes, with grains of the order to 2 mm, loaded in compression is unlikely to be a coincidence. In our experiment, these structures formed when the corners of the cubes - that had buckled - were imaged in an OM.[18] The similarities between the simulated and observed microstructures is striking and strongly suggest we are modeling what is actually occurring. Note that it would be difficult to conceive how such structures could evolve if basal dislocations were the operative mechanism.

This simulation empathizes once again the strong correlation between the presence of large pileups at indenter edges and BR-mediated deformation. At this point it important to note that when twins form under the indenter, such pileups are, for the most part, absent because the latter can accommodate c-axis strain.[28, 41, 42] The same is true when $\langle c+a \rangle$ dislocations are nucleated as in the case of ZnO [38] or Mg.[31]. Said otherwise, the lack of a mechanism to accommodate c-axis strain leads directly to massive pileups near indentation mark edges. This pileup is in turn comprised of KBs and boundaries. In the absence of a micromechanism to

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5 accommodate c-axis strain, the *only* possible mechanism for the material under the indenter to
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7 accommodate the strain is to literally move out of the way as shown in Movie 1 in *Supporting*
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9 *Material* and Fig. 2. At a fundamental level, KBs are nature's solution to the lack of a mechanism
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11 to accommodate strain normal to the 2D planes.
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15 The fidelity by which the simulations – carried out on 8 graphene layers – mimic those
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17 formed at a scale at least 5 *orders* of magnitude larger in scale than in the scale shown in the
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19 inset in Fig. 2c, is important for another reason: It suggests that BRs occur at all scales, from the
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21 atomic to the geologic. This important conclusion cannot be overemphasized.
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25 26 **VI. Summary and Conclusions**

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28 By cyclically nanoindenting (0001) and (10 $\bar{1}$ 1) planes of Ti₃SiC₂ - using 21 and 100 μ m
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30 spherical tips – and analyzing their response, together with a TEM study of the indented volume
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32 we conclude that:
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36 a) The responses of these surfaces were different and consistent with the existence of BRs.
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38 In 3 out of the 4 cases, 3 regimes were observed: linear elastic, pop-in, followed by a
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40 regime where fully and spontaneously reversible stress vs. a/R hysteresis loops were
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42 observed. During the pop-in events, BRs are presumably nucleated and their subsequent
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44 to-and-fro motion with cycling is responsible for both the ϵ_{nl} and W_d .
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48 b) In the last case, the stress was high enough to damage the material irreversibly by the
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50 formation of permanent kink boundaries/bands directly below the indenter. The
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52 formation of the latter, confirmed in the TEM, result in delamination cracks parallel to
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54 the basal planes. These cracks - a signature of BRs - are clear evidence for strain in the c-
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56 direction. Given that basal dislocations cannot result in c-axis strain, they cannot be
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5 implicated, thus mandating the existence of a new micromechanism. The volume under
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7 the indentation was also characterized by massive lattice rotations in some areas,
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9 microcracks and delamination cracks.
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12 c) By plotting W_d vs. a/R for the (0001) and (10 $\bar{1}1$) planes the CRSSs of the BRs were
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14 estimated to be 0.5 GPa and 1.2 GPa, respectively. The difference – at least initially – can
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16 be ascribed to the fact that in the former case the applied load must increase the friction
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18 force, while in the latter, it is more neutral.
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22 d) The results are also consistent with an increase in the amplitude of the BRs with
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24 increased stress. This is particularly salient when the basal planes are loaded edge-on and
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26 explains why delamination in this orientation occurs more readily than if the basal planes
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28 are loaded along [0001].
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32 e) Dark patches/streaks were seen in the TEM. Bragg filtering showed that the atomic
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34 planes within these regions were undulating and thus consistent with our postulated
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36 mechanism. These undulations are directly responsible for the c-axis strain .
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39 f) Lastly the fact that layered materials delaminate readily is nothing more than a
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41 manifestation of the c-strain associated with BRs as their amplitude increases with
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43 increasing stresses. This conjecture partially explains why BRs have not been observed in
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45 more commonly studied layered solids such as mica and graphite. In these cases, simply
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47 thinning the samples for TEM observation results in delaminations and the disappearance
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49 of the BRs. In retrospect it is the strong metallic/covalent bonding in the MAX phases
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51 that, in turn, allowed us to image BRs for the first time. Knowing that they exist also
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53 helped.
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Acknowledgement

We would like to thank Prof. R. Doherty for his usual insightful and helpful comments. This work was partially funded by ARO (W911NF-11-1-0525). ACL and MLT gratefully acknowledge support from the Office of Naval Research under grant number N000141410058. This material is based on work partially supported through GAANN fellowships (Ja. G. and Ju. G). This work was also partially supported by the National Science Foundation under Grant No. DMR-1410970 (GJT).

Appendix A

Referring to Fig. 1b, the total penetration depth of the indenter is h_t , the contact depth, h_c , defined as the distance from the circle of contact to the maximum penetration depth and h_e is the elastic portion of that penetration. By now it is fairly well established that the relationship between them is given by:

$$h_c = h_t \square \frac{h_e}{2} = h_t \square \frac{3P}{4S} \quad (A1)$$

where P is the applied load and S is the stiffness given by dP/dh , which is continually recorded by the continuous stiffness module, CSM. Once h_c is known, assuming the indentation is perfectly spherical, then the contact radius, a , is given by:

$$a = \sqrt{2Rh_c \square h_c^2} \square \sqrt{2Rh_c} \quad (A2)$$

where the right hand side of this equation holds provided $h_c \ll a$. Combining these equations it can be shown that [22]:

$$\square_{NI} = \frac{P}{\square a^2} = \frac{4}{3\square} E_{eff} \left(\frac{a}{R} \right) \quad (A3)$$

where E_{eff} is the effective modulus given by:

$$\frac{1}{E_{eff}} = \frac{1\square\square_s^2}{E_s} + \frac{1\square\square_i^2}{E_i} \quad (A4)$$

where E_s and ν_s are the specimen elastic modulus and Poisson's ratio and E_i and ν_i are the elastic modulus and Poisson's ratio of the diamond indenter assumed to be 1140 GPa and 0.3. The second term on the left in Eq. 3, is the normal Hertzian stress, denoted here as σ_{NI} , which is then plotted against a/R . The slopes of the inclined solid black lines in all σ_{NI} vs. a/R plots are equal to $4E_{eff}/3\pi$, and correspond to an E_s modulus of Ti_3SiC_2 of 325 GPa.[43]

Lastly, it is important to note here that at least *experimentally* relationship Eq. A3 is valid even when the system is in a region far beyond the purely elastic regime. This is clearly seen by examining the slopes of the inclined lines in Figs. 4a and b, for example. These slopes are all equal to each other and to the slope values during the very first loading i.e. before any deformation has occurred. In a previous paper on mica, we showed that this relationship was valid even after some large pop-ins occur. In some cases, even at a/R values of ≈ 0.4 , the correct elastic moduli – i.e. ones parallel to the very initial slopes before pop-ins - were recovered.[12] These results are thus a testament to the robustness of Eqs. A1 and A3 in general, and our approach in particular.

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Figure Captions:

Figure 1: Schematic of, **a)** Idealized NI stress vs. a/R plots typically observed. The total elastic strain at any stress is the sum of a linear, $\Delta a_E/R$, and a nonlinear, $\Delta a_R/R$, component. The energy dissipated per unit volume per cycle, W_d , is given by the area enclosed by the fully reversible stress-strain curves. Inset shows OIM map of sample used. **b)** Spherical NI geometry. The indenter radius, R , contact radius, a , elastic displacement, h_e , total displacement, h_{tot} , and contact depth, h_c , are labeled. Top left inset shows schematic of a surface ripplocation [32]; and top right inset shows schematic of a BR in graphite [33].

Figure 2: Freeze-frames from simulation shown in movie 1 of graphitic basal planes loaded along [0001] with a cylindrical indenter at, **a)** intermediate penetration where two kink bands - comprised of three kink boundaries denoted with short red lines – form on either side of the indenter. Note delaminations. Inset shows initial configuration in which the 10 topmost layers are severed before loading. **b)** Higher penetration and, **c)** after complete unloading. Note permanent delaminations cracks near the bottom of the frame. Right inset in **c)** is an etched OM micrograph of a single Ti_3SiC_2 grain deformed at room temperature when a cube was loaded in compression. The etching imparts the vivid colors seen; the brown background is that of the mounting epoxy.

Figure 3: Typical load vs. displacement curves for indents in locations, **a)** A and B and, **b)** C and D (see Table 1). For indents A and B, $R = 100 \mu m$; for indents C and D, $R = 21 \mu m$. In every case all 50 cycles are shown. The results for location A are shifted by 100 nm to the right for clarity. Note large pop-in that occurs during first cycle and even larger pop-in during third loading cycle for indent D.

Figure 4: Plots of σ_{NI} vs. a/R for indents in locations, **a)** A, B and, **b)** C and D (see Table 1). R for indents A and B was $100 \mu m$; for indents C and D it was $21 \mu m$. In every case all 50 cycles are shown. In **a)**, the (0001) results are shifted to the right by 0.02 for clarity's sake. In **b)**, the $(10\bar{1}0)$ results were shifted to the right by 0.02 for clarity's sake.

Figure 5: a) Nested σ_{NI} vs. a/R loops for indents in locations, a) A and B and, b) C and D. In a, the loops were shifted to the left by 0.0015 for clarity. Dashed inclined lines correspond to an elastic modulus of 325 GPa. σ_c is the *critical* or minimum σ_{NI} needed to open a loop. Referring to panel a, the non-linear reversible value of $\Delta a_r/R$ is equal to the total value of a/R , minus the elastic portion, $\Delta a_e/R$.

Figure 6: Plots of, a) W_d vs. $\Delta a_r/R$; b) same as a, but focusing on W_d values < 0.03 ; c) σ_{NI} vs. $\Delta a_r/R$ and, d) W_d vs. $\sigma_{NI} - \sigma_c$ for indents in locations A (solid blue circles) B (black/white squares) and C (red/white squares).

Figure 7: a) SEM micrograph of location D showing all-important delamination cracks after 50 cycles. Short black lines are 5 μm each. b) SEM micrograph of a location indented with $R = 100 \mu m$, after 50 cycles, for which $a/R = 0.08$. Red horizontal line is 17.5 μm long. c) SEM micrograph of location C after 50 cycles. Red horizontal line is 8.5 μm long. Note hexagonal nature of indent; d) AFM image of indent shown in c. Length of red line is 7 μm .

Figure 8: Collage of cross-sectional TEM micrographs taken beneath indent D, showing multiple cracks, kink bands and boundaries. Approximate location of original surface is shown by dashed red line.

Figure 9: Select higher magnification TEM images taken beneath indent D, viz. Fig. 8. a) and b) Bright field images showing complexity of region below indent, with many multiple regions separated from each other presumably by kink boundaries. The extraordinary extent by which the basal planes have been rotated is noteworthy; c) Magnified images of cracks and, d) Magnified images of kink band/boundaries.

Figure 10: a) Low magnification image of dark streaks in bright field TEM image of region under indent D. The top right inset diffraction pattern shows the orientation of the basal planes; b) two-beam bright field image formed using the g -vector shown in top right and, c) weak-beam

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5 image formed with the g -vector shown in top right. The long lines of contrast parallel to the basal
6 planes are visible regardless of the diffracting condition. There was no $g \perp b$ condition where the
7 contrast of the dark features, shown by red arrows, disappeared.
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12 **Figure 11:** a) Low magnification image of dark streaks, some denoted by white arrows, in bright
13 field TEM image of pristine material, the starred area is a large defect structure present within
14 the sample; b) HRTEM image of an area denoted by a white arrow from a); c) Image in b) - after
15 Bragg filtering - showing clear bending/undulations of basal planes in the dark region and little
16 or no distortion away from the dark regions within the image.
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24 **Figure 12:** a) Collage of cross-sectional TEM micrograph of a lift out from an indentation made
25 using a 21 μm tip into a (0001) surface near a grain boundary; b) Larger magnification dark field
26 image of kink bands formed near the right edge of indent in a.
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34 **Caption for Movie:**

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37 Movie 1: Simulated nanoindentation performed using a cylindrical 20 nm radius indenter moving
38 sinusoidally with a period of 500 ps and an amplitude of 20 nm along the c -direction. Periodic
39 boundary conditions were enforced along the y and z axes. A thin region opposite the indenter on
40 the x -axis was held fixed. The indenter radius is 10 nm radius, the period is 50 ps and the
41 amplitude is 10 nm.
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Figure(s)

Figure 1:

Figure 2:

Figure 3:

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Fig. 9:

Figure 10:

Figure 11

Figure 12:

***Graphical Abstract**

c-axis strain
cannot be due
to basal
dislocations