# Single crystal cleavage of brittle materials

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Abstract. Cleavage of brittle single crystals is reviewed and the historical criteria for the phenomenon are critically examined. Previously proposed criteria, including those based on crystal structure (crystal growth planes, the planes bounding the unit cell, and planar atomic packing) and crystal properties (ionic charge of possible cleavage planes, bond density, elastic modulus, and surface free energy), are found to be applicable only to particular crystals or to isostructural groups, but each lacks universal application. It is concluded that the fracture toughness ( $K_{Ic}$ ) of the crystallographic planes is the most appropriate criterion. Measurements reveal that the 'cleavage toughnesses' of brittle single crystals are usually about 1 MPa m<sup>1/2</sup> or less.

Measurements of the fracture toughnesses of brittle polycrystalline aggregates are then compared to the single crystal cleavage values in those instances where reliable results are available for the same crystal structures. Polycrystalline toughnesses are consistently higher, in part because of the lack of continuity of cleavage cracks through the polycrystalline aggregates. However, the increment of toughness increase is only 1-2 MPa m<sup>1/2</sup>. The role of grain texture or preferred crystal orientation is also addressed. It is concluded that polycrystalline aggregate toughnesses are often highly anisotropic and that the values for intensely oriented microstructures may approach those for single crystal cleavage.

#### 1. Introduction

The cleavage of single crystals is a fascinating phenomenon that instantly arouses the curiosity of every scientist and engineer who considers the fracture process. Practically every mineralogy textbook for rock, mineral, and gemstone collectors has a section on the phenomenon [e.g. 1–9]. The traditional mechanical metallurgy oriented texts [10–13] also discuss cleavage, but rather than a structural approach, the phenomenon is usually discussed in association with an estimation of the theoretical cohesive stress. These texts address the existence of preferred crystallographic cleavage planes such as the (100) for the body-centered cubic (BCC) metals and (0001) for close-packed hexagonal (HCP) structures. They also emphasize the close-packed cubic (CCP) structures which do not show cleavage, but are prone to extensive plastic flow under normal circumstances. The metallurgical texts usually tabulate calculated cleavage stresses to justify fracture on a preferred crystallographic plane.

All the aforementioned texts acknowledge the association of cleavage with brittle fracture. For example, LeMay [11] defines cleavage as the separation of atomic planes in the absence of any plastic flow. However, the physical processes which are involved in cleavage are typically given only cursory treatment, even though it is well known that brittle fracture directly relates to the cleavage process [14]. Because of significant advances in the experimental measurement of the fracture resistance of brittle materials during the past two decades [15], particularly in the structural engineering ceramics field, the consideration of current concepts of single crystal cleavage is both timely and appropriate.

In its purest form, cleavage occurs when a crystalline material preferentially *fractures* along a planar surface which is determined by characteristics of the crystal structure. It is a brittle fracture process that occurs in the traditional tensile or opening mode. Cleavage can occur for a large single crystal or for an individual grain or crystal within a polycrystalline aggregate. Smooth, mirror-like, planar surfaces commonly extend over substantial areas on the cleavage plane of a crystal. These large areas often consist of very sharp and distinctive



*Fig. 1.* The ever-decreasing scale of the geometry of the cleavage of halite (NaCl) on the  $\{100\}$  cubic cleavage planes (a-c). The multiplicity of the cleavage planes in these 3D structures creates a distinctive, repetitive, geometric pattern that can be observed on an increasingly finer scale.

staircase-like patterns on a finer scale when a multiplicity of cleavage planes exists for the particular crystal structure.

Figure 1 illustrates the cleavage surfaces of a halite (NaCl) crystal viewed at increasingly higher levels of magnification. The distinctive crystallographic features of cleavage are easily recognized by the repetitive geometric patterns. It is obvious that fundamental elements of the cubic crystal structure of halite do in fact dominate the fracture process whenever well defined cleavage occurs. It is equally evident from Fig. 1 that as a cleavage crack grows through a crystal at speeds which approach the velocity of sound in the crystal, the local-scale dynamics of the fracture process, including reorientation of the extending crack, must be incredibly complicated. The dynamic analysis of the generation of these multiple, fine-scale, step-like cleavage patterns is beyond the scope of this paper, but their presence serves to illustrate the extremely complex nature of the cleavage process in a crystal.

This brief description of cleavage, along with the definitive illustration shown in Fig. 1 may imply that cleavage is a rather perfect brittle fracture phenomenon, but in fact it varies widely in quality. Although the individual members of isostructural groups of crystals usually exhibit cleavage on the same crystal planes (halite, NaCl,  $\{100\}$ ; sphalerite, ZnS,  $\{110\}$ ; fluorite, CaF<sub>2</sub>,  $\{111\}$ ; BCC metals,  $\{100\}$ ; HCP metals,  $\{0001\}$ ; etc.), the cleavage is not always of uniform quality within a single isostructural group. Quality of cleavage is frequently

categorized in a qualitative sense as *perfect*, *good*, *distinct*, and *indistinct*. The terms *parting* and *quasi-cleavage* are also frequently applied to cases of poorly defined cleavage which may still occur in a crystallographically affected sense. Occasionally, an isostructural group of crystals may exhibit a transition from nearly perfect to indistinct cleavage with a trend of some characteristic of the structural components such as the ionic size, charge or polarizability.

It is appropriate at this point to briefly consider the non-cleavage fracture process. As cleavage is a process dominated by the repetitive geometric character of the crystal structure [e.g. 16, 17], fracture in a non-crystalline or amorphous material such as glass may be expected to exhibit a fracture character which is free of the geometric restraints of crystal structure. In fact, glass fractures in that manner, yielding a characteristic type of fracture surface that is known as *conchoidal* [e.g. 18] for the fracture surface topography has the appearance of a geometric conchoid. Some single crystals that do not possess strongly preferred cleavage planes, such as quartz (SiO<sub>2</sub>), may also exhibit conchoidal fracture under certain conditions. Features of conchoidal fracture surfaces are usually dominated by a combination of the macroscopic externally applied stress state and the crack dynamics, rather than any specific feature of the structure of the material.

It is also appropriate to note that some crystal structures simply do not exhibit distinctive cleavage planes. One such very common crystal structure is that of the garnet group  $(A_3^{2+}B_2^{3+}(SiO_4)_3)$  a cubic crystal structure that finds commercial applications both as an abrasive and as a gemstone. The garnet structure is hard and reportedly tough, but it does not possess a well defined cleavage plane, although garnet is sometimes described as exhibiting  $\{110\}$  parting with uneven fracture that appears somewhat conchoidal in nature [5]. As garnet is an island silicate structure, perhaps that structure does not have a dominant effect on its fracture character.

Metals are considerably less prone to exhibit distinct cleavage than are ionic and covalently bonded crystalline solids. This is because cleavage is an intrinsically brittle phenomenon and even the most brittle of metals commonly exhibit some degree of plastic flow. For example, the close-packed cubic (CCP) metals only rarely exhibit cleavage, because cleavage is an opening-mode type of brittle fracture with very limited crack tip plasticity. The multiplicity of slip planes in the close-packed cubic structure virtually ensures that plastic flow occurs and dominates the cleavage process. The body-centered cubic (BCC) structures such as  $\alpha$ -Fe, W, etc. will occasionally exhibit distinct cleavage on the {100} planes, and the close-packed hexagonal (HCP) structures such as Zn and Mg on the {0001} basal planes and the {10  $\overline{1}$  0} prism planes. However, experimental measurements of the toughnesses on these cleavage planes are lacking, which perhaps lead Broek [17] to suggest that a stress criterion is the appropriate one for the cleavage of metals. As this paper focuses on the cleavage phenomenon, it will not concentrate on metals, but rather will primarily address the ionic and covalently bonded crystal structures which display a more well defined character of cleavage fracture.

In addition to the obvious aesthetic aspects of cleavage, the phenomenon also is one of practical interest. The cleavage of diamond on the  $\{1\ 1\ 1\}$  plane is paramount to its cutting and use as a gemstone [e.g. 19], as are the cleavages of other gemstones for their beauty. In the crushing and comminution of minerals during their beneficiation and extraction from ores, the process of cleavage is every bit as vital as it is to the gemstone industry. Cleavage is also important to the industrial abrasives field, as the performance of many single crystalline commercial abrasives can be related to their cleavage characteristics. Frequently this is because a cleavage type of fracture continually renews the sharp cutting edges of the individual grains

(crystals) during industrial processes. In contrast, the garnet structures, both the pyralspite and ugrandite series, reportedly owe their abrasive qualities to their lack of distinct cleavage planes [5]. Thus, it is evident that one can enthusiastically support and promote the study of cleavage not only for its occurrence, but also for the lack of its occurrence in some crystal structures, or under specific circumstances. This paper attempts to thoroughly address cleavage in brittle crystal structures and establish the appropriate criterion for the phenomenon.

## 2. Criteria for cleavage

#### 2.1. CRITERIA BASED ON CRYSTAL STRUCTURE

For most researchers, observing a single example of cleavage generates the curiosity to question what determines the crystallographic planes on which the cleavage of a single crystal occurs. The answers have not always been very satisfying, but the historically proposed criteria certainly merit review, if for no other reason than to put the entire crystal cleavage process into the proper perspective [20, 21]. As might be imagined, the distinctive geometry of the cleavage process and the *external geometry* of naturally occurring crystals lead to an early association of those two features. However, those crystal planes which dominate during the natural growth of crystals are not consistently the same ones that prominently experience cleavage. This is because the physical processes that control crystal growth are not the same as those that dominate the cleavage phenomenon.

Nevertheless, there are several instances of the correspondence of the cleavage planes and crystal growth planes that are known to most mineralogists and crystallographers. The  $\{100\}$  planes for the halite (NaCl) structure and the  $\{111\}$  planes for the fluorite (CaF<sub>2</sub>) structure are two familiar examples. Halite cubes and fluorite octahedra are abundant in nature. Typical growth crystals are superimposed on the electron micrographs of the cleavage fracture surfaces in Figs. 1, 2 and 3. However, as tempting as this planar association may seem, the critical examination of the growth and cleavage processes quickly reveals that the correspondence of cleavage planes and growth planes is a fortuitous one for those few instances where in fact the two types of planes are coincident.

Once it is appreciated that the common growth planes are not consistently the cleavage planes of crystals, then it is only logical to consider the *planes which bound the unit cell* as a possibility, for they also frequently exhibit the distinctive geometry that is exhibited by cleavage planes. One has only to consider the case of the halite (NaCl) structure to find a familiar example of the correspondence between the unit cell bounding planes and the cleavage planes; i.e. the  $\{100\}$ . However, applying the bounding planes of the unit cell as the criterion for cleavage frequently fails once a wider number of structures are examined. Obviously, the fluorite (CaF<sub>2</sub>) structure, which is cubic, but cleaves on the  $\{111\}$ , and also the sphalerite (ZnS) structure, which is also cubic, but cleaves on the  $\{110\}$ , provide clear contradictions to the criterion of the unit cell bounding planes. That concept must also be rejected as the universally determinant criterion for the cleavage planes of crystals.

Further examining the structural approach to cleavage, it is appropriate to consider the *most closely packed crystal planes* as a possibility. As the slip planes for dislocation motion are usually the closely packed planes and thus have clearly demonstrated their ability to experience the breaking of bonds during plastic flow, there is a natural tendency to suspect that they may also be susceptible to bond breakage during cleavage. Similar to the previous suggestions, the criterion of the most closely packed planes does not yield a general result for



Fig. 2. Cleavage fracture of calcite (CaCO<sub>3</sub>) on the  $\{10 \ \tilde{1} \ 1\}$  rhombohedral cleavage planes at successively higher levels of magnification (a–c). Note that the macroscopic cleavage geometry persists to the micron scale.

all crystal structures. The most frequently quoted example of single crystal cleavage of metals, that of the  $\{100\}$  in BCC structures and  $\alpha$ -Fe refutes that concept because the body-centered cubic structure is not prone to slip on the  $\{100\}$ . The halite (NaCl) structure cubes and the classical cleavage rhombohedra of the calcite (CaCO<sub>3</sub>) structure are also some of the numerous contradictions that could be cited. Other simple structural criteria which have been considered and which are familiar to all those who study crystallography can also be proposed and, in fact, some may appear to apply to cleavage for specific instances. However, continuing pursuit of a universal structural feature that defines the cleavage planes for all crystal structures leads to repeated discouragement that finally leads one to the conclusion that it is the *properties* of the crystal structure which must be examined, rather than the crystal structure itself. Of course the structure and the properties are related, directly in many instances.

# 2.2. CRITERIA BASED ON CRYSTAL PROPERTIES

Once it is realized that consideration of the physical properties of crystals may be a more desirable approach to understanding the cleavage phenomenon, then various crystal properties can be examined as possible criteria. A number have been scrutinized in the past. However, since cleavage involves the breaking of bonds, it naturally follows that any successful cleavage criterion must necessarily physically relate to the bonds and the ions, groups of ions, or the



Fig. 3. Cleavage fracture of fluorite  $(CaF_2)$  on the  $\{1\ 1\ 1\}$  octahedral cleavage planes (a-c). Submicron stair-like cleavage is present.

atoms which constitute those bonds. As simple as it may appear, it is essential to understand that cleavage constitutes the rupture or breaking of the bonds between atoms or ions. Once cleavage occurs, then the two resulting fracture surfaces will consist of matching pairs of ions or atoms across the newly created surfaces.

This paired matching of the fracture surface features is a basic factor which prevents certain crystal planes from experiencing cleavage in the simple ionic structures [e.g. 22]. Ionic crystals will not cleave on those crystal planes which result in all positive charges on one fracture face and all negative charges on the other. From the charge perspective, those crystal planes are known as non-neutral planes. Examples of non-neutral planes in several common ionic structures are the  $\{1\ 1\ 1\}$  in the halite (NaCl) structure, both the  $\{1\ 10\}$  and  $\{1\ 00\}$  in the fluorite (CaF<sub>2</sub>) structure, and the  $\{1\ 00\}$  and  $\{1\ 11\}$  in the sphalerite (ZnS) structure. The converse of this argument is that only neutral planes, in the sense of their ionic charge distribution, can be cleavage planes.

The crystal-plane neutrality condition is easily recognized on the  $\{100\}$  and  $\{110\}$  planes of the halite (NaCl) structure where the configuration of cations and anions is an alternating one, as shown in Fig. 4. It is equally obvious that if those bonds which are perpendicular to the  $\{111\}$  in the halite (NaCl) structure were to cleave, then planes of all cations would separate from planes of all anions, yielding two oppositely charged cleavage surfaces. The ionic neutrality or *charge effect* on crystal planes is not a positive criterion for cleavage; rather,



*Fig.* 4. Charge effect as an exclusionary criterion for cleavage for the example of ionically bonded halite (NaCl). (a) Model of the halite structure showing the unit cell. Small solid ions are sodium, large dotted ones are chlorine. (b)  $\{100\}$  cleavage yielding neutral faces. (c)  $\{110\}$  cleavage which is also neutral. (d)  $\{111\}$  cleavage which would yield non-neutral faces. Cleavage occurs on the  $\{100\}$  and  $\{110\}$ , but not on the  $\{111\}$ .

it is an exclusionary one. It specifies that non-neutral planes can not experience cleavage in any highly ionic crystal structures.

Having focused on the bonds within a crystal structure, it is appropriate to address several of the various cleavage criteria that have been suggested on the basis of the bonds. These criteria all suffer from the rather imprecise nature of bonds, their varying strengths, a balance of ionicity versus covalency, and the anisotropy which they impart to the various crystal structures. Nonetheless, this approach does provide some additional structural insight and certainly merits serious review and consideration.

The popular *bond density concept* simply proposes that the minimum number of bonds per unit area determines the cleavage planes. Lower bond densities are associated with the more weakly bonded crystal planes, and it is those planes that are more readily cleaved. Differences in directional bonding strengths are quite obvious for graphite and for talc, where one set of bonds is van der Waals in character and the others are covalent. Few other crystal structures are so distinct. The bond density approach is not very satisfactory, nor has it been very successful, for it cannot easily incorporate the different bond strengths and the anisotropy of those bond strengths into the criterion.

Another bond character approach to cleavage plane prediction has been advanced by Whittaker [22]. In an attempt to circumvent the difficulties in specific bond strengths or a calculated bond density into the criterion for the cleavage of ionic crystals, Whittaker has incorporated the concepts of Madelung energy and Evjen cells to define tetrahedral building blocks within a crystal structure. The common or shared faces of those blocks represent potential cleavage planes. This approach does have intuitive appeal, but it lacks in universal application to all crystals. As noted by Whittaker, an obvious exception to this approach is halite (NaCl).

Of course, the natural extension of applying the bond density concept is to consider that physical property which is directly related to the strength of the bonds, the *elastic modulus*. Stronger bonds should result in a higher Young's modulus perpendicular to the crystal plane. In contrast, weaker bonds should be associated with lower elastic moduli and thus identify the cleavage planes as those with the minimum Young's modulus. As attractive as this approach

appears, the elastic modulus criterion does not consistently apply even to the most simple structures. For example, sylvite (KCl) and galena (PbS), which both have the halite (NaCl) structure and exhibit  $\{1\,00\}$  cleavage planes, also have their Young's moduli maxima in the (100). The diamond cubic structure, which has the Young's modulus maximum in the (111), also readily cleaves on the  $\{1\,1\,1\}$ . Cleavage in these crystals is not in agreement with that which is expected from the application of the minimum elastic modulus criterion. It is evident that the elastic modulus is not, by itself, capable of consistently predicting the cleavage planes of crystal structures.

The same type of summary statement can also be applied to a criterion based on the *surface free energy* of the crystal planes. It can be argued that an energy criterion, in which the cleavage plane is the plane of the minimum surface energy, should apply. However, similar to the previously discussed criteria, Gilman [20] applies the minimum surface energy concept and notes that it has exceptions, most notably the potassium halides. The minimum surface energy concept is not a sufficient one to consistently predict the preferred cleavage planes of crystals. It may be more applicable to crystal growth planes.

In an effort to arrive at a suitable criterion for cleavage, investigators have attempted to theoretically calculate the cleavage strength of various single crystals on low indice crystal planes [23, 24]. The approach invariably necessitates an estimate of the surface energies of crystal planes and reveals the need for the application of dynamic, rather than static, elastic moduli. In a related approach that was based on an equilibrium calculation of Coulomb and Born-Mayer repulsive-interaction potentials of spinel (MgAl<sub>2</sub>O<sub>4</sub>). Mishra and Thomas [25] suggest that the  $\{1 \ 1 \ 1\}$  planes of spinel should have the lowest surface energy and should be the cleavage plane, whereas the actually observed cleavage plane for spinel is the  $\{100\}$ . Often, values of the parameters which are utilized in the calculations based on potential functions are not known with certainty, yet these types of theoretical approaches to cleavage do illustrate several important points. When dynamic conditions are incorporated into the calculations, the cleavage strengths are different than for static or quasi-static equilibrium conditions; usually greater strengths are predicted. Some success results from using the dynamic theories, similar to the previous criteria. However, the results do not appear to be sufficiently refined because the surface energy magnitudes and cleavage strength predictions are less than satisfactory. At the present, theoretical approaches to cleavage plane prediction, although not without merit, cannot be considered very successful. Their primary contribution appears to be that of heralding the importance of the dynamics of the cleavage phenomenon.

In summarizing the various cleavage criteria which are based on the structure of a crystal or its properties, it may be concluded that each of the aforementioned characteristics will correctly predict the cleavage plane for certain crystal structures. However, every one of those criteria fails when applied in a universal sense. In retrospect, this should not be surprising because cleavage is a dynamic fracture process, and none of the aforementioned structural attributes or physical properties is actually a dynamic one; rather, they are all static, or quasistatic in nature. If any cleavage criterion is to be universally applicable, then an appropriate dynamic *fracture criterion* must be applied.

### 3. Fracture toughness as the criterion for cleavage

Because cleavage occurs rapidly and catastrophically, application of the critical crack growth resistance parameters for the opening mode, either the fracture toughness  $K_{Ic}$  or the strain energy release rate  $G_{Ic}$  [26, 27], is appropriate to consider as the criterion for cleavage fracture.

Crystal	Plane	$K_{Ic}(MPa m^{1/2})$	Reference
LiF (griceite)	{100}*	0.50	[29]
	{110}	0.70	[29]
	$\{111\}$	1.50	[29]
GaP	{100}	0.73	[30]
	{110}*	0.65	[30]
	{111}	0.81	[30]
Si (silicon)	{100}	0.95	[31]
	{110}	0.90	[31]
	{111}*	0.82	[31]
MgAl <sub>2</sub> O <sub>4</sub> (spinel)	{100}*	1.18	[32]
	{110}	1.54	[32]
	{111}	1.90	[32]

Table 1. Experimental cleavage toughnesses for several single crystals

\*Indicates the commonly observed cleavage plane.

As the focus of this paper is primarily on brittle single crystals and because the stress intensity concept is currently being used extensively in the design, evaluation, and testing of brittle ceramics, it is desirable to consider the fracture toughness  $K_{Ic}$  as the single crystal cleavage criterion.

The fracture toughness of a material  $K_{Ic}$  is a measure of the resistance of the material to crack growth [28]. To consider the fracture toughness  $(K_{Ic})$  as a cleavage criterion, it is appropriate to directly refer to several independent experimental studies where different researchers have actually made experimental measurements of crack growth resistance on several crystallographic planes of different crystal structures. The fracture toughness for cleavage planes in individual crystals will be referred to as the 'cleavage toughness.' Usually these fracture toughness measurements are made by some form of indentation pre-cracking, or by utilizing guide notches to force the incipient crack to initiate on the crystallographic plane of interest (see review in [15]). Of course, after extending only a very short distance, every propagating crack in the single crystal will be redirected by the crystal structure onto the preferred cleavage plane, as a number of the authors have illustrated in their publications.

In Table 1, experimental cleavage toughnesses ( $K_{Ic}$  values) are listed for several low indice crystal planes each for single crystals of griceite (LiF), gallium phosphide (GaP), silicon (Si), and spinel (MgAl<sub>2</sub>O<sub>4</sub>). For each of these four crystal structures, the well established cleavage plane has the *lowest* experimentally measured fracture toughness value. It must be concluded that the experimental  $K_{Ic}$  value, the fracture toughness, is the appropriate criterion for the cleavage of ionic and covalently bonded crystal structures. Interestingly, for the primarily ionic halite structure of griceite (LiF), where charge effects are expected to be highly dominant, the cleavage toughness differences between the three low indice crystal planes are much more pronounced than for the primarily covalently bonded gallium phosphide (GaP) and silicon (Si) and the mixed character bonds of the spinel (MgAl<sub>2</sub>O<sub>4</sub>) structure. This point will be further addressed during the consideration of other structures.

As the literature is not always specific, nor even very clear as to the technique by which

the fracture toughness is experimentally measured or calculated, the original references are included in the following summaries for the reader to consult for the specific experimental details. For those cases from the literature where some form of a surface energy value has been presented or perhaps determined from a  $K_{1c}$  value, the cleavage toughnesses have been calculated for the various tables included in the paper by applying the following formula

$$K_{\rm lc} = (2E\gamma)^{1/2},\tag{1}$$

where  $\gamma$  is the fracture surface energy and E is the single crystal Young's modulus perpendicular to the cleavage plane ([28], p. 42). Values of the cleavage fracture toughness are expressed in the units of megapascals (10<sup>6</sup> Pa) meter to the one-half power (MPa m<sup>1/2</sup>). Equation (1) does not include the  $(1 - \nu^2)$  term in the denominator of the square root term for the plane strain condition, which is assumed in many instances [27]. As most brittle single crystals have a Poisson's ratio  $\nu$  equal to only about 0.2, that term is 0.96, or a difference of only 1.02 once the square root is considered. That minor amount (2%) is not a significant difference in terms of the concepts which are advanced in this paper. As a reader will appreciate, neither is the fact that some of the measured toughnesses which are referenced in the summaries may not fully meet some of the specimen size restrictions which are imposed by standards for obtaining valid measurements of  $K_{\rm Ic}$  [33].

# 4. Cleavage toughnesses of ionic and covalent crystals

It is convenient, pedagogically sound, and necessary to address the *cleavage toughnesses* of brittle materials in terms of some form of classification related to their crystal structure. The cleavage of various brittle ionic and covalently bonded crystal structures can be considered by systematically applying the mineralogically based structural approach which is presented by Sorrell [1]. Figure 5 illustrates a modification of that approach to cleavage which is based on the geometric aspects of the directionality and dimensionality of the cleavage of the crystal structure. The structural categories begin with the traditional mineralogical layer structures, including mica and graphite, two materials which are well known for their ease of cleavage. Sorrell's classification then proceeds with two-directional geometries that are familiar to all crystallographers.

However, not all brittle materials of interest, nor those for which fracture toughnesses have been measured, can be conveniently classified into the structural groups presented in Fig. 5, namely those with multiple cubic, rhombohedral, or octahedral cleavage planes. Consequently, several crystal structures must be discussed on individual bases which extend beyond the initial structural classification by Sorrell [1]. It should be noted that other systematic approaches are possible, including the crystal symmetry classification [34]. However, the Sorrell structural scheme appears to be quite adequate for cleavage classification and discussion.

# 4.1. LAYER STRUCTURES

Cleavage in the layer structures, such as the different mica structures and graphite, may be expected to be similar for all other layer structures, such as the many clays and also molybdenite ( $MoS_2$ ). Unfortunately, only a few of these materials have been the subject of extensive single crystal cleavage measurements. Nevertheless, the experimental results for those layer structures do provide a reliable baseline for the discussion of all other single



*Fig. 5.* A structural geometric classification of cleavage, after Sorrell [1]. Cleavage planes denoted by 'c'; other planes (dark shading in a-c) are non-cleavage fracture surfaces. (a) One-directional layer-structure cleavage, as in micas and graphite. (b) Two-directional cleavage at nearly right angles, as in the single-chain structures or pyroxenes. (c) Two-directional cleavage, not at right angles, as in the double-chain structures or amphiboles. (d) Three-directional cubic cleavage at right angles, as in halite. (e) Three-directional cleavage, not at right angles, as occurs in fluorite and diamond.

Material	Plane	$K_{Ic}$ (MPa m <sup>1/2</sup> )	Reference
graphite	{0001}	0.03	[20]
pyrolytic carbon	{0001}	0.53	[35]
muscovite mica	{0001}	0.19	[20]
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>x</sub>	{001}	1.10	[36]
ice		0.11	[37]

Table 2. Cleavage toughnesses of several layer structures

crystal cleavage toughness measurements. Layer structures also provide a convenient basis to understand just how easy the single crystal cleavage process may be under nearly ideal conditions of brittle fracture.

Table 2 summarizes the cleavage toughness values for several layer structures. The first toughness listed, that of graphite, is estimated from the theoretical surface energy and elastic modulus in Gilman's [20] classical review paper. It seems to be extraordinarily low. However, the following explanation can be offered which suggests that actual experimental results may be preferable to those types of theoretical estimates. For example, if the graphite toughness calculated from theory ( $K_{1c} = 0.035$  MPa m<sup>1/2</sup>) is compared with the experimental results which Sakai et al. [35] have measured for a highly oriented pyrolytic carbon ( $K_{1c} = 0.53$  MPa m<sup>1/2</sup>), then it is evident that about an order of magnitude difference exists. Theoretical approaches to the calculation of surface energies are based on static or quasi-static equilibrium models, in contrast to the actual fracture process which leads to the formation of cleavage surfaces and which is a highly dynamic, non-equilibrium process. It should not be surprising that differences are observed. In retrospect, it would be remarkable if static equilibrium theory and irreversible dynamic experiment yielded the same cleavage toughnesses. It must be concluded that the difference illustrated in Table 2 for the two graphite cleavage toughnesses is not at all unreasonable. However, the most important message revealed by this summary of layer



Fig. 6. Relationship of cleavage planes to the silica tetrahedra linkages in the chain silicates. Chains are depicted on-end, showing approximate trapezoidal cross sections. (a) Single chain cleavage, as observed in pyroxenes. (b) Double chain cleavage, as observed in the amphiboles. Note the angles as they appear in a macroscopic situation.

structure cleavage toughnesses is that they are consistently less than 1 MPa  $m^{1/2}$ . Cleavage of layer structures is a relatively easy process as most materials scientists are well aware.

Also listed in Table 2 is the reported cleavage toughness for the ceramic superconductor,  $YBa_2Cu_3O_x$  [36]. Similar to the other layer structures, its toughness is also low, although the toughness appears to be somewhat higher than the values for graphite and the mica. It might be argued that the measurement (1.10 MPa m<sup>1/2</sup>) is perhaps too high. However, the cleavage toughness of this structure is not too different than the other layer structures and is still relatively low in comparison with the toughnesses of many other materials [27]. The  $YBa_2Cu_3O_x$  result supports the conclusion that the cleavage toughnesses of layer structures are not very high. Most cleavage toughnesses of layer structures appear to be less than 1 MPa m<sup>1/2</sup>.

Recently, Wan et al. [38] have been studying the cleavage of muscovite mica. They have observed that moisture has a significant effect on the crack growth resistance as first noted by Obriemoff [39], often by as much as a factor of five. That finding and its relationship to charging effects on the mica fracture surfaces is highly significant from a fundamental perspective. However, even a factor of five times the reported fracture toughness value given in Table 2 for mica  $(0.19 \text{ MPa m}^{1/2})$  does not alter the conclusion that the cleavage toughnesses of layer structures are rather low.

#### 4.2. CHAIN STRUCTURES

The cleavage of single crystal chain structures is typically parallel to the structural chains in those crystals. In the literature it is often referred to as prismatic, after the prism-like geometric forms that result. Cleavage toughness values for single or double chain silicate structures as specified in the classification by Sorrell [1] do not appear to have been measured, as none have been reported in the literature. Nevertheless, a number of facts have been established regarding the cleavage of these interesting structures. The cleavage planes are always parallel to the chain lengths as the chains consist of the strongest bonds in the structures. Crystals having the *single chain structure* are typified by the pyroxene group of rock forming minerals, including enstatite ( $Mg_2Si_2O_6$ ), diopside (CaMgSi\_2O\_6), wollastonite (CaSiO\_3), hedenbergite (CaFeSi\_2O\_6), ferrosilite (FeSiO\_3), hypersthene ((Mg,Fe)SiO\_3), and jadeite (NaAlSi\_2O\_6). Cleavage in these single chain silicate structures is two-directional and yields intersecting surfaces that appear to be at right angles, as shown in Fig. 6. Although cleaved pyroxenes appear to exhibit right angles, they actually cleave at angles of  $87^{\circ}$  and  $93^{\circ}$ .

Crystal	Plane	$K_{Ic}(MPa m^{1/2})$	Reference
KBr	{100}	0.12	[42]
KCl (sylvite)	{100}	0.15	[42]
NaCl (halite)	{100}	0.17	[42]
LiF (griceite)	{100}	0.31	[43]
	{100}	0.50	[29]
MgO (magnesia)	{100}	0.81	[20]
PbS (galena)	{100}	0.18	[44]
	{100}	0.32	[20]
FeS <sub>2</sub> (pyrite)	{100}	0.96	[44]
MgAl <sub>2</sub> O <sub>4</sub> (spinel)	{100}	1.18	[32]

Table 3. Cleavage toughnesses for some cubic structures

Crystals having the *double chain structure* are typified by the amphibole group of silicate minerals, including tremolite  $(Ca_2Mg_5(Si_8O_{22})(OH, F)_2)$ , actinolite  $(CaFe_5Si_8O_{22})(OH, F)_2)$ , hornblende ((Ca, Na, K)<sub>2-3</sub>(Mg, Fe, Al)<sub>5</sub>(Si, Al)<sub>8</sub>O<sub>22</sub>(OH, F)<sub>2</sub>), and glaucophane (Na<sub>2</sub>Mg<sub>3</sub> Al<sub>2</sub>Si<sub>8</sub>O<sub>22</sub>(OH, F)<sub>2</sub>). Cleavage in these double chain crystals is also two-directional, but results in angles which are different from 90° (Fig. 6). It is well established that these chain silicates cleave in a manner to yield surfaces which intersect at characteristic angles of nearly 60° and 120° (actually 56° and 124°). Cleavage toughnesses of the single and double chain silicate structures are likely to be less than 1 MPa m<sup>1/2</sup> once they are measured and reported.

Cleavages of other chain structures, such as the sulfides stibnite  $(Sb_2S_3)$  and bismuthenite  $(Bi_2S_3)$ , are also of interest. These may also be expected to follow the same principles as for the cleavage of the silicate chain structures. These sulfide structures contain zigzag chains in the form of ribbons in which S and Sb or Bi alternate 'parallel' to the (001) of the orthorhombic crystals [40]. The chains are not broken during perfect cleavage on the  $\{0\ 1\ 0\}$ , planes which are parallel to the chain lengths. Cleavage toughnesses of these sulfide chain structures have not been measured either. Similarly, the toughnesses of borate chain structures whose cleavage is usually described as perfect [41] have not been measured either. Both the sulfide and the borate chain structures are expected to have cleavage toughnesses less than 1 MPa m<sup>1/2</sup>.

#### 4.3. CUBIC STRUCTURES

Continuing from the cleavage of the chain structures, Sorrell [1] describes the three-directional (dimensional) cleavage situations. The simplest of these geometrically aesthetic cleavages is the *cubic* variety as commonly observed for the halite (NaCl) structure, a cubic crystal structure which also yields a cubic cleavage geometry on the  $\{100\}$ . Figure 1 illustrates the virtually perfect 90° cubic cleavage of halite (NaCl). Structures other than the halite (NaCl) structure also exhibit cleavage that displays a cubic geometry. Table 3 lists a number of materials for which cubic cleavage is observed and for which the cleavage toughnesses have been measured and are reported in the refereed literature. Similar to the previous layer structure cleavages, these cleavage toughnesses are not very large either. In fact, with the exception of the spinel (MgAl<sub>2</sub>O<sub>4</sub>), all are less than 1 MPa m<sup>1/2</sup>.

The fracture toughness values in Table 3 suggest the presence of an ionic size effect on

Crystal	Plane	$K_{\rm Ic}({\rm MPa}~{ m m}^{1/2})$	Reference
GaP	{110}	0.65	[30]
ZnS (sphalerite)	{110}	0.23	[20]
InS	{110}	0.21	[20]

Table 4. Cleavage toughnesses for the dodecahedral cleavage geometry

the cleavage toughness. That effect is apparent when the toughnesses of griceite (LiF) and magnesia (MgO) are compared with those of potassium bromide (KBr) and galena (PbS). The former two crystals consist of higher elastic modulus structures with much smaller ions, whereas the latter two consist of larger, more highly polarizable ions, but all four have the NaCl structure. The cleavage toughnesses of the former (LiF and MgO) are about three times those of the latter (KBr and PbS). The more tightly bonded, higher elastic modulus ionic crystal structures exhibit substantially larger cleavage toughnesses.

Pyrite (FeS<sub>2</sub>) and spinel (MgAl<sub>2</sub>O<sub>4</sub>) single crystals do not have the simple halite (NaCl) structure, but they do exhibit cubic cleavage on the {100} planes. It is of interest that these two crystal structures both exhibit much higher cleavage toughnesses, about 1 MPa m<sup>1/2</sup>. Pyrite (FeS<sub>2</sub>) is a metallic-like crystal, where in the case of the spinel (MgAl<sub>2</sub>O<sub>4</sub>) the increased toughness may arise from the stronger bonds with the trivalent (Al<sup>3+</sup>) cations. This is partially speculative, but the sequence of increasing cleavage fracture toughness in the series LiF: MgO: MgAl<sub>2</sub>O<sub>4</sub> may be related to the ionic charge contributions. These subtleties notwithstanding, the cleavage toughnesses for the cubic cleavage geometry, i.e. the {100} of cubic crystal structures, are similar in magnitude to those of the layer structures, although perhaps slightly larger. Some of the cubic cleavages appear to exhibit cleavage toughnesses of about 1 MPa m<sup>1/2</sup>, but in general, the crystals which exhibit cubic cleavages are not very tough.

#### 4.4. RHOMBOHEDRAL, OCTAHEDRAL, AND DODECAHEDRAL CLEAVAGES

Following the cubic cleavage geometry, Sorrell [1] lists the *rhombohedral* and *octahedral* geometric cleavage forms. However, there are several published results of cleavage toughnesses for the sphalerite (ZnS) structure, a cubic crystal structure which cleaves on the  $\{110\}$ . If the Sorrell structural classification were extended, then this would be a form of *dodecahedral* cleavage, which is a three-dimensional type of cleavage with some of the angles between intersecting planes being orthogonal and some not. Several dodecahedral cleavage toughnesses are listed in Table 4.

The cleavage toughnesses of the *dodecahedral* geometry which are summarized in Table 4 are all less than 1 MPa m<sup>1/2</sup>, similar to the previous cleavage toughness values. This level of toughness is not very impressive, yet having previously summarized and considered other cleavage toughnesses, it is perhaps the magnitude of cleavage toughness which should be expected. From the values in Table 4, one can imagine a Coulomb-like charge effect as GaP( $3 \times 5$ ) slightly exceeds ZnS( $2 \times 6$ ) and thus might be expected to be slightly tougher (15/12). Of course, additional experimental measurements of related structures are needed

to substantiate that hypothesis. It does, however, ascribe to the trend of the ionic charge contributions as previously suggested for cubic cleavage of the halite (NaCl) structure.

*Rhombohedral* cleavage as exhibited by the calcite (CaCO<sub>3</sub>) structure on the {1011} is Sorrell's [1] next category. That geometry is depicted on several different scales on the micrographs in Fig. 2. It is quite familiar to every mineralogist and mineral collector as the large cleavage rhombohedra of optical quality calcite ( $CaCO_3$ ) which are often displayed for their doubly refracting characteristics. The entire structural series from calcite (CaCO<sub>3</sub>) to magnesite (MgCO<sub>3</sub>), including rhodochrosite (MnCO<sub>3</sub>), siderite (FeCO<sub>3</sub>), and smithsonite (ZnCO<sub>3</sub>), exhibit virtually perfect  $\{10\overline{1}1\}$  rhombohedral cleavage, as does dolomite, the double carbonate of calcium and magnesium  $(CaMg(CO_3)_2)$ . However, calcite  $(CaCO_3)$  is the only one which has had its cleavage toughness measured and reported. Three different authors report nearly identical experimental results for calcite, including Gilman [20]  $(0.18 \text{ MPa m}^{1/2})$ , Santhanam and Gupta [45]  $(0.22 \text{ MPa m}^{1/2})$ , and Atkinson and Avdis [44]  $(0.19 \text{ MPa m}^{1/2})$ . Obviously, calcite (CaCO<sub>3</sub>) has a quite low cleavage toughness as it cleaves very easily. No doubt that is why virtually perfect cleavage rhombohedra abound in nature and the crystallographic dominance of the cleavage persists to the submicron levels which are illustrated in Fig. 2. As calcite (CaCO<sub>3</sub>) has the lowest elastic modulus of the isostructural series (CaCO<sub>3</sub>,..., MgCO<sub>3</sub>), simply on the basis of (1) it might be surmised that the other crystals of that isostructural group will all be tougher. However, they are probably only marginally so, for all exhibit distinctive rhombohedral cleavage.

The *octahedral* cleavage displayed by fluorite (CaF<sub>2</sub>) on its  $\{1 \ 1 \ 1\}$  is the last element of the structural classification for cleavage presented by Sorrell [1]. Figure 3 illustrates fluorite cleavage. Several other crystals which are known to cleave with that geometry have had their toughnesses measured and published. Table 5 summarizes those cleavage toughness results. The three alkaline earth fluorides have toughnesses of the magnitudes typical for cleavage, less than 1 MPa  $m^{1/2}$ . The toughness values decrease from Ca through Ba as do the elastic moduli. It should be noted that the covalent bonding which is dominant in both silicon (Si) and diamond (C) yields significantly higher cleavage toughnesses. This effect may be expected from some of the previous discussions on charge and bond effects. The diamond (C) cleavage toughnesses which are in the 3–5 MPa  $m^{1/2}$  range are some of the highest reliable single crystal cleavage toughness values which have ever been reported. As the high hardness of diamond is well known, it is evident that coupling this high cleavage toughness value with the extraordinarily high hardness value makes diamond almost ideal for the industrial abrasive applications for which it is well known to excel. It might be expected that Borazon, the synthetic cubic structure of BN, will exhibit a similar cleavage toughness to that of diamond, 3-5 MPa m<sup>1/2</sup>, once large crystals are grown and the cleavage toughness is measured.

A related crystal structure which might also be expected to exhibit the octahedral cleavage geometry is that of stabilized cubic zirconia (ZrO<sub>2</sub>), which has a defect fluorite structure. Guillou et al. [49] have measured calcia (CaO) stabilized cubic zirconia and Pajares et al. [50] have considered the yttria (Y<sub>2</sub>O<sub>3</sub>) stabilized form. The measured cleavage toughnesses of those single crystals varied from about 0.9 to 1.9 MPa m<sup>1/2</sup>. In another study [51] the toughness was reported to be 1.5 MPa m<sup>1/2</sup>. Interestingly, none of those crystals cleaved on the {111}, the established cleavage plane for the fluorite (CaF<sub>2</sub>) structure. It may be suggested that the introduction of the numerous anion vacancies into the stabilized defect fluorite structure of cubic zirconia has a profound effect on the role which the crystal structure assumes in defining the cleavage plane. That effect is not understood, but for it to create a non-{111} cleavage tendency in the fluorite (CaF<sub>2</sub>) structure, the effect must be a highly

Crystal	Plane	$K_{1c}$ (MPa m <sup>1/2</sup> )	Reference
CaF <sub>2</sub> (fluorite)	{111}	0.45	[20]
	{111}	0.33	[46]
$SrF_2$	{111}	0.27	[46]
BaF <sub>2</sub> (frankdicksonite)	{111}	0.22	[46]
Si (silicon)	{111}	0.82	[31]
C (diamond)	{111}	3.60	[47]
	{111}	2.90	[20]
	{111}	4.10	[47]
	{111}	5	[48]

Table 5. Octahedral cleavage toughnesses

significant one.

#### 4.5. OTHER CRYSTAL STRUCTURES

There are, of course, numerous other crystal structures which exhibit well defined cleavage that cannot be readily categorized within the aforementioned structural classification scheme. Large single crystals of quartz (SiO<sub>2</sub>) occur naturally at many locations throughout the world. It also is synthetically produced on a commercial scale by hydrothermal techniques for use in piezoelectric devices. The fracture of single crystal quartz often assumes the appearance of a totally conchoidal surface. However, Bloss and Gibbs [52] have suggested that those apparent conchoidal fractures are really a submicroscopic combination of cleavage planes similar to those which are depicted in Fig. 1 for halite (NaCl), Fig. 2 for calcite (CaCO<sub>3</sub>), and Fig. 3 for fluorite (CaF<sub>2</sub>). Table 6 summarizes some of the published cleavage toughness measurements for the fracture of quartz on specific planes at room temperature. Atkinson and Meredith [33] list another dozen toughness values for quartz, but some of those appear to have been measured by questionable techniques and are not included in Table 6.

The summary of cleavage toughness values in Table 6 is an excellent point from which to address the occurrence of macroscopic conchoidal fracture as compared with distinct planar cleavage on a microscale for single crystal quartz. From the cleavage perspective, Brace and Walsh [56], Bloss and Gibbs [52], and Martin and Durham [57] all observed and reported distinct rhombohedral cleavage on the  $\{10\overline{1}1\}$ . A zig-zag form of crack growth on these planes prior to macroscopic crack bifurcation [19] has also been noted by Ball and Payne [58]. However, equally or more significant is the additional observation by Ball and Payne that for single crystals oriented to fracture on the  $\{11\overline{2}0\}$ , a completely smooth planar fracture surface results and no macroscopic crack bifurcation occurs. They have reported that the  $\{11\overline{2}0\}$  fracture surfaces of single crystal quartz are very much like those of glass. For natural quartz, the results in Table 6 just barely support the  $\{11\overline{2}0\}$  as the preferred cleavage plane over the  $\{01\ \overline{1}\ 1\}$ , although the toughness differences between a number of different crystal planes of quartz are not very great. It must be concluded that it is the near equality of the cleavage fracture toughnesses of quartz on a number of different crystal planes that causes the conchoidal appearance of macroscopic fractures, but yet may result in a distinct cleavage character for some specific conditions.

Plane	$K_{\rm Ic}({\rm MPa}~{ m m}^{1/2})$	Reference
{0001}	1.15	[53]
{01 Ĩ 0}	0.97	[53]
{01 Ī 1}	0.86	[53]
$\{11\bar{2}0\}$	0.85	[53]
$\{11\bar{2}1\}$	0.94	[53]
{0001}	1.17	[53]
{1120}	0.96	[53]
{0001}	1.24	[53]
{1120}	0.95	[53]
{01 Ī 1}	0.85	[54]
{0Ī11}	1.00	[54]
{0 Ĩ 11}	1.01	[55]
	Plane $\{0001\}$ $\{01\bar{1}0\}$ $\{01\bar{1}1\}$ $\{11\bar{2}0\}$ $\{0001\}$ $\{11\bar{2}0\}$ $\{0001\}$ $\{11\bar{2}0\}$ $\{0001\}$ $\{01\bar{1}1\}$ $\{0\bar{1}11\}$	Plane $K_{Ic}(MPa m^{1/2})$ $\{0001\}$ 1.15 $\{01\bar{1}0\}$ 0.97 $\{01\bar{1}1\}$ 0.86 $\{11\bar{2}0\}$ 0.85 $\{11\bar{2}1\}$ 0.94 $\{0001\}$ 1.17 $\{11\bar{2}0\}$ 0.96 $\{0001\}$ 1.24 $\{11\bar{2}0\}$ 0.95 $\{0\bar{1}1\}$ 0.85 $\{0\bar{1}11\}$ 1.00 $\{0\bar{1}11\}$ 1.01

Table 6. Measured cleavage toughnesses of single crystal quartz

The cleavage of single crystal corundum or sapphire  $(Al_2O_3)$  has been addressed from several different perspectives by Iwasa and Bradt [59] in their extensive review of its fracture characteristics. All viewpoints agree, however, that the rhombohedral plane  $\{10\bar{1}2\}$  has the lowest fracture toughness and is the cleavage plane at room temperature, while the basal plane, the  $\{0001\}$ , is considerably tougher. The r-plane has a cleavage toughness of only about 2.38 MPa m<sup>1/2</sup> while the c-plane is reported to be 4.54 MPa m<sup>1/2</sup>. The m-plane and the *a*-plane are intermediate at 3.14 MPa  $m^{1/2}$  and 2.43 MPa  $m^{1/2}$ , respectively. The cleavage toughnesses for sapphire are significantly higher than any of the previously reported single crystal values in this paper, except for those values reported for the cleavage of diamond (C) on the  $\{111\}$ . The reason for this is undoubtedly related to the strength of the bonding in sapphire, which leads to high Young's modulus values for that crystal structure. Another interesting aspect of the cleavage of sapphire is the effect of temperature on the preferred cleavage plane. As Bradt and Scott [60] point out in their review, between about 800°C and 1500°C, the basal or c-plane  $\{0001\}$  becomes the lowest toughness plane and then it exhibits distinct cleavage. Very likely at different temperatures, or pressures, some of the previously discussed crystal structures may also be expected to exhibit cleavage plane transitions.

#### 4.6. SUMMARY OF SINGLE CRYSTAL CLEAVAGE TOUGHNESSES

Having considered the cleavage toughnesses for a number of crystal structures, it is appropriate to reach some general conclusions. In some respects, it is not an easy task; however, one very obvious point is that most of the fracture toughnesses for the cleavage of brittle single crystals are less than 1 MPa m<sup>1/2</sup>. Cleavage planes of brittle crystals are simply not very tough by any measure or standard. This is why distinctive, geometric cleavage patterns are easily created by the fracture process and why they are so prevalent in nature.

There exists a general tendency for the more complex crystal structures, those containing multiple ions and a greater degree of covalent bonding to exhibit higher cleavage toughnesses than the simple ionic crystal structures. As not every crystal structure has been measured,

and in fact only relatively few have, it is not possible to assign an absolute upper bound to the cleavage toughnesses of all brittle single crystals. However, on the basis of the results for diamond (C) and for sapphire (Al<sub>2</sub>O<sub>3</sub>), an argument for a conservative upper limit estimate of about 5 MPa m<sup>1/2</sup> could be advocated with substantial supporting evidence. This is not a very large toughness.

#### 5. Fracture toughnesses of polycrystalline aggregates

The fracture of polycrystalline materials or crystal aggregates is also often described as cleavage whenever failure occurs in an opening mode and in a brittle fashion. Metallurgists often refer to all forms of transgranular fracture as cleavage. While these authors do not advocate the general utilization of that terminology, it does exist. A number of reliable fracture toughness measurements have been reported in the literature for polycrystalline specimens of the same materials which have just been addressed from the single crystal cleavage point of view. It is only natural to also consider those polycrystalline fracture toughness values for no other reason than to compare them with the single crystal cleavage toughness values for the identical crystal structures. The following comparisons are interesting, although they are not all inclusive of the fracture toughness measurements of brittle polycrystalline materials. Unfortunately, it is not possible to address all of the effects of the polycrystalline microstructure of brittle materials on their fracture toughnesses in a very extensive manner, for it has not been the subject of very many systematic studies to date.

A good starting point is with the layer structures and a comparison of the fracture toughnesses of polycrystalline graphites with the cleavage toughness of single crystal graphite in Table 2. Wood et al. [61] have measured the fracture toughnesses of a number of commercial graphites and summarized other researchers' published values, too. There is a strong textural dependence relative to the molding and extrusion directions, such that the toughness parallel to it. This dependence arises because fracture parallel to the orientation direction tends to follow the cleavage planes of the individual graphite flakes or crystals which have been aligned by the manufacturing process. However, even for the toughest situations, the fracture toughnesses of polycrystalline graphites are only about 1.4-1.5 MPa m<sup>1/2</sup>. This is an increase over the cleavage toughness on the graphite basal plane of only about 1 MPa m<sup>1/2</sup>. Polycrystalline graphite is not a very tough material.

Approximately following the structural classification of Sorrell, there have been a number of reports of the fracture toughness of polycrystalline spinel (MgAl<sub>2</sub>O<sub>4</sub>) [62–64]. At room temperature the fracture toughness of polycrystalline MgAl<sub>2</sub>O<sub>4</sub> appears to be between about 1.8 and 2.0 MPa m<sup>1/2</sup>, a value which is essentially independent of the grain (crystal) size of that cubic crystal structure. Again, similar to the results for graphite, this is not a very significant increase beyond the cleavage toughness of single crystal spinel, as previously noted by Stewart et al. [65]. In fact, the polycrystalline to single crystal toughness ratio for graphite seems to be somewhat greater than that for spinel. Perhaps this is because of the multiplicity of {100} cleavage planes and their various orientations for the cubic cleavage geometry of spinel, as opposed to only the single dimension of the layer plane cleavage for graphite. That is, a macroscopic crack in a polycrystalline aggregate of spinel does not need to undergo significant reorientation in order to 'locate' a cleavage plane when entering a new grain or crystal. Additional measurements for other crystal structures are needed to more critically examine this hypothesis. In their article on the cleavage of the alkaline earth fluorides, Becher and Freiman [46] also report several fracture toughness values for dense, transparent polycrystalline fluorite (CaF<sub>2</sub>). Values from 1.6 to 3.6 MPa m<sup>1/2</sup> were reported. These toughnesses are significantly greater than the 0.33 to 0.45 MPa m<sup>1/2</sup> values obtained for the single crystal cleavage of fluorite (CaF<sub>2</sub>) on its {111}. As the octahedral cleavage geometry of CaF<sub>2</sub> has an even greater multiplicity of cleavage planes than does the cubic cleavage of the spinel, this polycrystalline to single crystal ratio of toughnesses appears to be inordinately large. Perhaps a crack which follows a tortuous path in polycrystalline spinel (MgAl<sub>2</sub>O<sub>4</sub>) can also readily orient itself to cleave on the {110} and {111} planes in the spinel structure, albeit in a slightly more difficult fashion. In fluorite (CaF<sub>2</sub>), however, the {100} and {110} are both non-neutral planes and simply cannot cleave, thus any advancing cracks must experience a much more severe reorientation process in polycrystalline fluorite than in a polycrystalline spinel structure to propagate catastrophically. This explanation may account in part for the higher reported polycrystalline fluorite (CaF<sub>2</sub>) toughnesses, relative to those of the polycrystalline spinel (MgAl<sub>2</sub>O<sub>4</sub>).

Fracture of naturally occurring polycrystalline quartz has been the subject of research by a number of geologists. The fracture toughness of Arkansas novaculite [66–68] has been reported to range from 1.1 to 1.8 MPa m<sup>1/2</sup>, while a Mojave quartzite [69] has been measured at 2.10 MPa m<sup>1/2</sup>. These measurements compare favorably with those of a cryptocrystalline jasper, ~2 MPa m<sup>1/2</sup> [70]. The approximate two to one toughness ratio for polycrystalline quartz fracture versus the single crystal cleavage of quartz lends additional insight to the effect of microstructure on the crack propagation resistance characteristics of this material. As the cleavage of single crystal quartz is practically isotropic and about 1 MPa m<sup>1/2</sup>, and the fracture toughnesses of the polycrystalline quartz samples which have been measured are only about twice that of the single crystal cleavages, it may be reasonable to assume that most polycrystalline microstructures should be capable of doubling the cleavage toughness of single crystals, or at the very least increasing the fracture toughness about another 1 MPa m<sup>1/2</sup>. Neither level of increase is a very remarkable toughening effect.

Many and varied measurements of the fracture toughness have been made for polycrystalline corundum (Al<sub>2</sub>O<sub>3</sub>). Those measurements have been reviewed by Bradt and Scott [60]. Reliable toughness measurements for dense polycrystalline corundum samples appear to vary from about 3 to 5 MPa m<sup>1/2</sup>. This is not the level of increase beyond the single crystal cleavage toughnesses that one might expect. In fact, it is only about a factor of two tougher than sapphire cleavage on the *r*-plane and it is similar to the level of toughness increment observed for quartz (SiO<sub>2</sub>). It must be concluded that the microstructural features which have been studied or developed at the present do not yield very significant toughness increases for the polycrystalline forms of brittle crystal structures which readily experience cleavage fracture in single crystal form. On the other hand, another interpretation may relate the polycrystalline toughness levels to the minimum cleavage toughness for different crystal planes. However, when all published results are considered in total, it suggests that toughness increments for polycrystalline aggregates above the minimum cleavage toughness values for their single crystal counterparts are only a couple of MPa m<sup>1/2</sup> at best.

Beall [71] has reported fracture toughnesses for several polycrystalline ceramics consisting of chain silicates produced from glass. The toughnesses are 4.0 MPa m<sup>1/2</sup> for enstatite (MgSiO<sub>3</sub>), a pyroxene; 3.2 MPa m<sup>1/2</sup> for potassium fluorrichterite (KNaCaMg<sub>5</sub>Si<sub>8</sub>O<sub>22</sub>F<sub>2</sub>), an amphibole; and 5.0 MPa m<sup>1/2</sup> for canasite (Ca<sub>5</sub>Na<sub>4</sub>K<sub>2</sub>Si<sub>12</sub>O<sub>30</sub>F<sub>4</sub>), a rare quadruple chain silicate. These rather large toughness values are due in part to the extremely complex composite-

like fibrous microstructures that are believed to inhibit crack extension in these glass ceramic materials. Constrained transgranular fracture and crack branching are also thought to contribute to the large toughnesses reported for jadeite, 7–8 MPa  $m^{1/2}$  [72].

There are not a large number of well documented studies of textural effects on the fracture toughnesses of brittle materials, although Atkinson and Meredith [33] do summarize a few in their commpilation and the earlier comments on commercial graphites are certainly applicable. Several measurements are meritorious for comparison with single crystal cleavage toughnesses. Coal has been measured to have fracture toughnesses of 0.063 and 0.047 MPa m<sup>1/2</sup>, normal and parallel to the bedding plane, respectively. A marble has been reported to have fracture toughnesses of 0.7 and 1.4 MPa m<sup>1/2</sup> and a shale exhibits fracture toughnesses which vary from 1.1 to 1.9 MPa m<sup>1/2</sup>. These are all orientation-dependent values of fracture toughness that clearly demonstrate an anisotropic textural effect. They also confirm the low polycrystalline toughnesses compared with the cleavage toughnesses which have been discussed for single crystals.

Atkinson and Meredith [33] also list fracture toughness values for a natural halite (NaCl) normal and parallel to layering, after Rummel and Müller [73]. The fracture toughness normal to the layering is 0.57 MPa m<sup>1/2</sup>, while parallel values of 0.23 and 0.40 MPa m<sup>1/2</sup> are reported. These are only modestly greater than the values of 0.17 MPa m<sup>1/2</sup> for the single crystal cleavage toughness of NaCl on its {100}. These values further confirm that microstructural effects in polycrystalline aggregates are capable of only modest increases in the fracture toughnesses above the single crystal cleavage toughness values for brittle materials.

Salem et al. [74] have addressed the effect of texture of an extruded alumina ( $Al_2O_3$ , corundum) on the crack-growth resistance, or *R*-curve, character of the material [17], and also measured the fracture toughnesses for the same textured material. For orthogonal directions, they report fracture toughnesses of 3.6, 3.9, and 4.9 MPa m<sup>1/2</sup>. These values compare favorably with the cleavage toughnesses previously discussed for single crystal sapphire (2.4–4.5 MPa m<sup>1/2</sup>). The largest polycrystalline toughness exceeds the basal plane cleavage toughness of corundum, which is not surprising as both grain size and textural effects may be expected to provide a modest degree of toughening.

#### 6. Conclusions

The fracture toughnesses of brittle single crystal structures for specific crystallographic planes provide an excellent criterion for cleavage fracture. It is the only consistently reliable criterion. Addressing cleavage from the structural classification that has been advanced by Sorrell [1] for minerals is a useful geometric description for the phenomenon. It is evident that the fracture toughnesses for cleavage are not very large for most simple brittle crystal structures. Values of  $K_{\rm Ic}$  for brittle single crystals are usually less than 1 MPa m<sup>1/2</sup>. Even the most strongly bonded covalent structures such as diamond and sapphire have cleavage toughnesses which are only about 4–5 MPa m<sup>1/2</sup>. Single crystals of brittle materials simply are not very resistant to crack extension on their cleavage planes. This is precisely why those materials readily experience cleavage under natural conditions and in utilitarian applications.

When the fracture toughnesses of polycrystalline aggregates are compared with single crystal cleavage toughnesses, it is evident that microstructural factors have only a modest toughening effect. That effect can be considered to be a two-fold one. The first aspect is simply a geometric one of the microstructure, perhaps related to the point that an extending crack in a polycrystalline aggregate of grains or crystals does not lie fully on the individual

cleavage plane of a single grain or crystal. This crack deflection or toughening mechanism has only a slight effect of increasing the toughness, perhaps doubling the value or increasing its level by 1 or 2 MPa m<sup>1/2</sup>. A directly related effect is that of the preferred crystallographic orientation or texture of the grains or crystals. This microstructural anisotropy appears to provide an additional increment of toughening for the non-cleavage plane orientations. It also may be expected to reduce the toughness level for fracture parallel to the oriented cleavage planes. Texture creates a significant toughness anisotropy which can reach levels of several MPa m<sup>1/2</sup>, but the toughness enhancement in one orientation is usually accompanied by a complementary reduction.

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