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Chiral indices of crystalline surfaces as a measure of enantioselective potential

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9 Abstract

Chiral crystal surfaces lack mirror or glide plane symmetry. Nevertheless, some chiral surfaces deviate more significantly from an achiral 10 configuration, and thus possess greater enantioselective potential, than others. We describe a procedure to calculate chiral indices, I_C (in Å), 11 of any two-dimensional (2D) periodic atomic surface based on atomic displacements from ideal mirror or glide plane symmetry. We define a 12 2D unit cell parallel to the surface, identify coordinates of atoms associated with that surface unit cell, and employ minimization procedures 13 to determine the positions and orientations of best-fit pseudo-mirror and pseudo-glide plane operators perpendicular to that surface. Achiral 14 surfaces invariably have $I_{\rm C} = 0$, but we find that surfaces of intrinsically chiral crystals [e.g., quartz (101)] may also display $I_{\rm C} = 0$, 15 depending on the surface atoms selected. Of 14 surfaces modeled, I_C is greatest for chiral faces of achiral crystals: the (214) scalenohedral 16 faces of calcite ($I_c = 2.60$ Å), the (110) faces of diopside ($I_c = 1.54$ Å), and the (643) faces of FCC metals such as copper and platinum 17 18 $(I_{\rm C} = 1.29 \,\text{\AA}).$

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20 Keywords: Chiral indices; Crystalline surfaces; Enantioselective potential

21 1. Introduction

The ability of some chiral crystalline surfaces to adsorb 22 chiral molecules and to promote heterogeneous enantiose-23 lective catalysis has received considerable recent attention 24 from researchers in science and industry [1-9]. Prebiotic 25 enantioselective adsorption of amino acids onto mineral sur-26 faces has been proposed as a viable mechanism to account 27 for the exclusive incorporation of left-handed amino acids 28 in biological organisms [10,11]. Enantiomeric selection on 29 crystalline surfaces, furthermore, presents a promising av-30 enue for efficient chiral purification of pharmaceuticals and 31 in other industrial applications [7]. 32

In a strict crystallographic sense any periodic two-dimensional (2D) surface is either chiral or achiral, depending on whether mirrors or glide planes (both improper symmetry operators) exist perpendicular to that surface [12]. Nevertheless, some chiral arrangements of surface atoms deviate only

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slightly from their enantiomer, whereas other enantiomeric 38 pairs of surfaces differ significantly from each other. In other 39 words, some surfaces are "more chiral" than others, and thus 40 have a greater intrinsic enantioselective potential [13]. The 41 extent of chiral discrimination achieved for a given combi-42 nation of crystal surface and chiral molecule will, of course, 43 depend on structural details. But, lacking a detailed structural 44 model of surface interactions, crystal surfaces with greater 45 intrinsic enantioselectivity warrant special consideration. 46

No single number can characterize uniquely the "degree of 47 chirality" of an exposed crystalline surface. Indeed, several 48 factors, including positions of terminal atoms, their effec-49 tive charge, and their bonding environments, can contribute 50 to deviations of a crystal surface from ideal mirror or glide 51 plane symmetry. Nevertheless, the extent to which atomic 52 positions of a periodic 2D surface structure deviate from 53 strict mirror or glide plane symmetry can provide the basis 54 for a conceptually useful and mathematically well-defined 55 "chiral index"-a measure of the enantioselective poten-56 tial of that surface. This idea of a chiral index builds on a 57 long tradition of crystal-chemical distortion indices, which 58 have proven exceptionally useful in describing deviations of 59

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groups of atoms from an ideal symmetry. Thus, for example, 60 a variety of distortion indices have been devised to charac-61 terize cation coordination polyhedra, such as SiO₄ tetrahe-62 dra and MgO₆ octahedra in ionic compounds [14–16]. Sim-63 ilarly, a distortion index described by Thompson and Downs 64 [17] quantifies the deviation of a periodic three-dimensional 65 66 oxygen array in a quasi-close-packed mineral from an ideal close-packed array. These and other distortion indices quan-67 tify the misfit of an observed atomic structure superimposed 68 onto an idealized structure, for example, through a mini-69 mized sum of the squares of distances between observed and 70 idealized atom positions. 71

This minimization strategy suggests a potentially useful 72 approach to defining chiral indices in terms of the deviation 73 of the observed positions of surface atoms from those of an 74 idealized surface with mirror or glide plane symmetry. Such 75 chiral indices define the intrinsic chirality of a surface as 76 the extent to which that surface is non-superimposable on 77 its enantiomer. Thus, for example, a slight distortion of an 78 achiral surface may lead to a chiral surface with low chi-79 ral index, because the two enantiomers almost superimpose. 80 81 By contrast, enantiomeric surfaces of left- and right-handed quartz (SiO₄), with opposite-handed helices of corner-linked 82 SiO₄ tetrahedra, might be predicted to have relatively large 83 chiral indices because they are not obviously superimpos-84 able [13]. The usefulness of such a chiral index is that one 85 can assess a priori the potential of a given surface structure 86 for chiral selectivity. Greater misfit of enantiomeric surfaces 87 (i.e., deviation of observed atomic coordinates from ideal-88 ized mirror or glide plane symmetry) should correlate with 89 a greater probability for an energy difference in the adsorp-90 tion of molecular enantiomers, and thus a greater potential 91 92 for enantioselectivity.

93 2. Calculation of chiral indices

94 2.1. Computational strategy

Two steps are necessary to calculate a chiral index. First, 95 we specify a 2D periodic surface structure in terms of a sur-96 face unit cell (defined by two vectors, **a** and **b**, with lengths 97 a and b, and an angle, γ , between them) and a set of coor-98 dinates for all atoms associated with that surface unit cell 99 (x, y, z), where x and y are fractional coordinates in terms 100 of **a** and **b**, and z is height relative to the surface. Note that 101 the third dimensional coordinate z is required because many 102 103 common crystal surfaces have atoms at varying heights.

Once a surface unit cell has been defined, then we gener-104 ate a comprehensive range of fictive mirror and glide plane 105 symmetry operators perpendicular to the surface, compute 106 fictive atom coordinates based on those operators, and cal-107 culate deviations of observed atom positions from the fic-108 tive atom positions. We propose two complementary chiral 109 indices based on these deviations. The "average displace-110 ment index" (I_{CA}) is based on the mirror or glide plane for 111

which the average deviation of atomic positions from ideal 112 positions (in Å) is minimized. 113

Alternatively, we report a "maximum displacement index" 114 $(I_{\rm CM})$, which is derived by determining the largest deviation 115 of an observed atom position (also in Å) from its ideal position for each possible fictive mirror or glide plane. The $I_{\rm CM}$ 117 is the smallest of all possible maximum displacements. 118

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2.2. Determination of the 2D unit cell

A surface (2D) unit cell is a parallelogram defined by 120 vectors, \boldsymbol{a} and \boldsymbol{b} , with lengths a and b, and an angle, γ , 121 between them. The surface unit cell can be translated by 122 integral steps of \boldsymbol{a} and \boldsymbol{b} to generate the entire surface. The 123 symmetry of the periodic surface must conform to one of 124 the 17 plane groups, as listed in the *International Tables of* 125 *Crystallography*. 126

The choice of surface atoms and their coordinates is not 127 unique. In this study we define the 2D structure of a sur-128 face (hkl) as an idealized slice of the crystal that contains 129 all terminal atoms in the surface [13]. Note, however, that 130 the surface of real oxide and silicate crystals feature atoms 131 whose positions are usually relaxed from those of the 3D 132 crystal structure [18-21]. Similarly, real surfaces of FCC 133 metals are known to undergo considerable fluctuations in lo-134 cal structure due to thermal diffusion [22,23]. For this paper, 135 however, we employ idealized atomic coordinates from the 136 bulk crystal, as determined from 3D diffraction experiments 137 (e.g., for calcite [24], diopside [25], orthoclase [26], quartz 138 [27], and FCC copper with unit-cell edge a = 3.60 Å). Most 139 surface structures have some associated depth; therefore, we 140 define a z-coordinate that provides a measure of the height 141 of the atom in angstroms for each atom. The basis vector as-142 sociated with this depth is perpendicular to the surface. The 143 slice of atoms is generated with the interactive visualization 144 software, XtalDraw [28]. 145

By definition, a direct space vector, $[\boldsymbol{v}]_{D} = [x \ y \ z]^{t}$, is per-146 pendicular to a reciprocal lattice vector, $[\mathbf{h}]_{D*} = [h k l]^t (h,$ 147 k, and l are integers), only if hx + ky + lz = 0 (nomenclature 148 after Boisen and Gibbs [29]: bold \boldsymbol{v} denotes the name of the 149 vector, $[\cdot]$ denotes the triple associated with the vector \boldsymbol{v} with 150 respect to the basis indicated by the subscript D, and the su-151 perscript t designates the transpose of the triple). A surface 152 lattice must exist in the plane parallel to a crystal face, be-153 cause the equation has solutions for integer values of x, y, 154 and z. We generate this surface lattice by finding atoms and 155 their translational equivalents, where the translation vector 156 is made of integers. In general, we choose the shortest vec-157 tor from the set of all such translations, and define it to be 158 one of the axes of the surface lattice. We find another rea-159 sonably short vector that defines a primitive surface lattice 160 and that is as close as possible to being perpendicular to the 161 first axis. The interaxial angle, γ , is found from the inner 162 product of these lattice vectors, **a** and **b**. The coordinates of 163 the atoms in the surface are then transformed from the 3D 164 crystallographic basis to the new 2D surface basis. 165

The basis vectors of the 2D unit cells of 14 surfaces examined in this study are recorded in Table 1 with the coordinates of all atoms in the cell with respect to the surface basis.
Several features of these 2D unit cells should be noted.

- 170 1. The dimensions of a surface unit cell may be significantly
- larger than those of the 3D unit cell. This situation often arises in surfaces with relatively high-Miller-indices,
 such as those of FCC metals, because of the oblique intersection of the surface with the 3D unit cell.
- 2. The number of atoms in the 2D asymmetric unit com-175 monly differs from that of the 3D asymmetric unit. In 176 the case of high-Miller-indices, the 2D number of atoms 177 may greatly exceed that of the 3D structure. For exam-178 ple, a single atom forms the 3D asymmetric unit of FCC 179 metals, but FCC surfaces that incorporate kink sites re-180 quire a minimum of five atoms. By contrast, a low Miller 181 index surface such as (001) of many layer minerals may 182 have only one atom in the 2D asymmetric unit, whereas 183 3D structures can require more than a dozen atoms. 184
- 1853. A 2D lattice with $a \neq b$ and $\gamma \neq 90^{\circ}$ lacks mirror or186glide plane symmetry and thus is inherently chiral; the187surface structure will have plane group symmetry P1 or188P2 (see also [12]). Orthogonal 2D lattices or lattices with

Table 1 Surface (2D) unit cells (*a*, *b*, and γ) and atom coordinates (*x*, *y*, *z*)

a = b may also be chiral if at least two atoms form the asymmetric unit and at least one of those atoms is in a 190 2D general position (*xy*).

2.3. Determination of chiral indices 192

We computed two separate chiral indices, I_{CA} and I_{CM} , 193 for each crystal surface. The index, I_{CA} , is a measure of the 194 average deviation of surface atoms from a best-fit mirror or 195 glide plane image. Alternatively, the index, ICM, is the min-196 imum of the family of maximum deviations of individual 197 atoms from their mirror or glide images. The chiral indices 198 were computed using a FORTRAN code specifically devel-199 oped for this purpose. The general principle involves (1) the 200 creation of a mirror or glide plane image of a surface; (2) 201 the association of each atom in the surface with its closest 202 image in the mirror or glide plane image; and (3) computa-203 tion of the distances separating the pairs of mirror- or glide 204 plane-related atoms. 205

The values of chiral indices associated with mirror or glide 206 plane operations depend on both the orientation and the lo-207 cation of the mirror or glide plane. In the special case of lat-208 tices that contain mirror or glide plane symmetry (e.g., any 209 orthogonal lattice or lattice with a = b), an integer vector in

Compound	Surface $(h \ k \ l)$	a (Å)	b (Å)	γ (°)	Atom	x	у	z
Calcite ^a	(1 0 4) no Ca	4.9900	8.0959	90	01	0.1289	0.9876	0.000
					02	0.8711	0.4876	0.000
	(1 0 4) with Ca	4.9900	8.0959	90	Ca1	0.5000	0.1397	0.000
					Ca2	0.5000	0.6397	0.000
					O1	0.2578	0.3897	0.000
					O2	0.7422	0.8897	0.000
					O3	0.1289	0.9876	0.783
					O4	0.8711	0.4876	0.783
	(2 1 4)	13.2023	6.3753	107.208	Ca	0.0959	0.1714	0.000
					O1	0.5103	0.9431	0.346
					O2	0.7574	0.9461	0.393
					O3	0.9218	0.4679	0.739
					O4	0.9266	0.9708	0.787
					05	0.3381	0.4956	1.180
Diopside ^b	(1 1 0)-a	5.2510	6.5984	101.476	Ca	0.5847	0.3386	0.564
					01	0.1734	0.1436	0.000
					O2	0.8551	0.7006	0.134
					O3	0.3468	0.6674	0.362
	(1 1 0)-c	5.2510	6.5984	101.476	Mg	0.4915	0.9662	0.410
					O1	0.3988	0.2575	0.000
					02	0.5550	0.6701	0.535
	(1 1 0)-e	5.2510	6.5984	101.476	Mg	0.4915	0.9662	0.410
					O1	0.3988	0.2575	0.000
					O2	0.5550	0.6701	0.535
					O3	0.8574	0.0922	1.127
Orthoclase	(1 1 0)	7.2099	7.7680	104.020	01	0.2278	0.2409	0.000
					O2	0.8528	0.2142	0.186
					O3	0.3750	0.8274	0.563
					O4	0.0001	0.8007	0.749

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$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Table 1 (Contin	uued)							
Quartz (1 0 1) 4.9137 7.3045 109.655 0.1 0.1071 0.8946 0.000 (0 1 1) 4.9137 7.3045 109.655 01 0.1366 0.9337 0.009 (1 0 0) 4.9137 7.3045 109.655 01 0.1366 0.9357 0.009 (1 0 0) 4.9137 5.4047 90 01 0.2246 0.32381 0.355 Copper (5 3 1) 4.4091 4.4091 99.594 0.1 0.3857 0.7143 0.009 (6 4 3) 8.0498 6.7350 111.012 0.1 0.4508 0.8361 0.009 (2 2 0.557 0.2387 0.7143 0.609 0.2313 0.461 (4 4 3) 8.0498 6.7350 111.012 0.1 0.4088 0.8361 0.000 (2 2 0.577 0.5350 1.132 0.6439 0.2370 0.5502 (2 4 0.3700 0.5002 0.9272 1.333 0.616 0.600	Compound	Surface (h k l)	a (Å)	b (Å)	γ (°)	Atom	x	у	z
(0 1 1) 4.9137 7,345 109.655 01 0.136 0.933 (1 0 0) 4.9137 5,4047 90 01 0.2397 0.4351 0.9353 (1 0 0) 4.9137 5,4047 90 01 0.2397 0.7452 0.9161 (5 3 1) 4.4091 4.4091 99.594 0.1 0.2397 0.7143 0.000 (6 4 3) 8.0498 6.7350 111.012 0.1 0.4597 0.430 0.2001 1.217 (6 4 3) 8.0498 6.7350 111.012 0.1 0.4598 0.8361 0.000 (6 4 7) 0.909 0.231 0.6439 0.2311 0.646 0.010 (6 4 7) 8.0498 9.1783 95.032 0.11 0.4598 0.8277 1.133 (2 0 0.3693 0.2131 0.466 0.213 0.469 0.233 0.497 0.592 0.232 (2 0 4 0.379 0.5932 0.673 0.133 0.434 1	Quartz	(1 0 1)	4.9137	7.3045	109.655	01	0.1071	0.8946	0.000
(0 1 1) 4.9137 7.3045 109.655 01 0.1364 0.9537 0.000 (1 0 0) 4.9137 5.4047 90 01 0.2797 0.785 0.000 Copper (5 3 1) 4.4091 4.4091 99.594 0.1 0.2797 0.4521 0.515 Copper (5 3 1) 4.4091 4.4091 99.594 0.1 0.4571 0.409 0.4571 0.0699 (6 4 3) 8.0498 6.7350 111.012 0.11 0.4508 0.8631 0.000 (6 4 3) 8.0498 6.7350 111.012 0.11 0.4508 0.8631 0.000 (2 2 0.5771 0.5906 0.2311 0.461 0.222 0.573 0.2102 0.202 0.263 0.2080 0.213 0.208 0.8371 0.209 0.222 0.63 0.2376 0.232 0.276 0.313 0.343 0.344 0.130 0.343 0.344 0.131 0.365 0.213 0.365 0.213						O2	0.8749	0.4304	0.932
Corport Corport <t< td=""><td rowspan="3"></td><td>$(0 \ 1 \ 1)$</td><td>4 9137</td><td>7.3045</td><td>109 655</td><td>01</td><td>0.1366</td><td>0.9537</td><td>0.000</td></t<>		$(0 \ 1 \ 1)$	4 9137	7.3045	109 655	01	0.1366	0.9537	0.000
(1 0 0) 4.9137 5.4047 90 01 0.2370 0.458 Copper (5 3 1) 4.4091 4.4091 99.594 Cu1 0.4371 0.000 Cu2 0.7437 0.000 0.2370 0.4511 0.409 Cu2 0.7439 0.4511 0.000 0.2000 0.2000 0.2000 1.217 Cu4 0.6571 0.9499 1.826 0.23 0.6487 0.246 0.231 0.464 0.703 0.214 0.246 0.233 0.2141 0.464 0.703 0.2141 0.464 0.2797 0.8361 0.000 Cu2 0.5574 0.5246 0.233 0.2141 0.461 0.216 0.9376 0.318 0.461 0.709 0.9161 0.9161 0.9161 0.9171 1.52 Cu6 0.9902 0.922 Cu6 0.9903 0.038 0.000 Cu2 0.2239 0.9903 0.000 0.021 0.223 0.2924 0.138 0.449 0.135 0.213 <td< td=""><td>(0 1 1)</td><td>,</td><td>10010</td><td>1071000</td><td>02</td><td>0.6619</td><td>0.2026</td><td>0.099</td></td<>		(0 1 1)	,	10010	1071000	02	0.6619	0.2026	0.099
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(6 1 4) (1 4) (1 4) (1 4) (1 4) (2 0, 6597) (0, 422) (0, 513) Copper (5 3 1) 4,4091 4,4091 99,594 Cul (2, 257) (0, 143) (0, 000) Cui 0,2000 0,2000 0,2000 0,2000 1,133 0,0000 Cui 0,6571 0,04329 1,826 0,033 0,2468 0,8841 0,000 Cui 0,6571 0,04329 1,826 0,233 0,0498 0,236 0,233 0,0492 0,226 0,233 0,0492 0,222 0,2571 0,338 0,0498 0,238 0,2787 1,152 Cui 0,9836 0,2787 1,152 Cui 0,9933 0,000 Cui 0,4098 2,0787 1,152 Cui 0,2933 0,0003 0,000 Cui 0,4098 0,1328 2,074 Cui 0,0338 0,0433 0,544 0,1429 0,333 0,544 0,1429 0,233 0,0903 0,000 0,000		$(1 \ 0 \ 0)$	4.9137	5.4047	90	01	0.2797	0.7855	0.000
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$ \left(\begin{array}{cccccccccccccccccccccccccccccccccccc$	Copper	(5 3 1)	4.4091	4.4091	99.594	Cu1	0.2857	0.7143	0.000
Cu3 0.0000 0.2000 1.826 Cu5 0.1143 0.6857 2.434 (6 4 3) 8.0498 6.7350 111.012 Cu1 0.4038 0.8361 0.000 Cu3 0.6639 0.2131 0.461 0.452 0.9016 0.6491 Cu3 0.8639 0.2131 0.461 0.705 0.9016 0.6491 Cu5 0.9877 0.9902 0.9672 1.833 0.285 0.6393 0.2131 0.441 Cu1 0.5144 0.7025 0.8577 1.613 0.2033 0.3443 1.844 Cu10 0.9167 1.833 0.203 0.4998 0.2328 2.074 Cu12 0.2033 0.3443 1.844 0.2403 0.2393 0.2493 0.2035 Cu12 0.2033 0.4903 0.0303 0.414 0.2305 0.8294 0.159 Cu12 0.2033 0.4903 0.3034 0.410 0.3034 0.410 0.4574 1.55 <td></td> <td>· · ·</td> <td></td> <td></td> <td></td> <td>Cu2</td> <td>0.7429</td> <td>0.4571</td> <td>0.609</td>		· · ·				Cu2	0.7429	0.4571	0.609
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Cus 0.1143 0.6857 2.434 (6 4 3) 8.0498 6.7350 111.012 Cu1 0.4598 0.8361 0.000 Cu3 0.6639 0.2131 0.461 0.7075 0.9016 0.691 Cu4 0.7705 0.9016 0.691 0.536 0.2787 1.52 Cu5 0.8770 0.5902 0.922 Cu3 0.9033 0.3443 1.844 Cu7 0.0902 0.9672 1.333 1.844 Cu10 0.4098 2.074 Cu8 0.1967 0.4333 1.844 Cu10 0.4098 2.204 Cu11 0.5164 0.7213 2.305 Cu12 0.6230 0.4098 2.535 Cu12 0.6230 0.4098 9.1783 95.032 Cu1 0.2023 0.3868 0.634 Cu10 0.5175 0.4575 0.5039 0.0388 0.634 Cu2 0.2829 0.2929 0.2924 0.416 0.516 0.317						Cu4	0.6571	0.9429	1.826
(6 4 3) 8.0498 6.7350 111.012 Cu1 0.4598 0.8361 0.000 Cu2 0.5574 0.5246 0.230 0.6639 0.21131 0.6163 Cu4 0.7705 0.8907 0.5902 0.9222 Cu6 0.9836 0.2787 1.152 Cu6 0.9833 0.3413 1.844 Cu10 0.4098 0.0328 2.074 Cu11 0.5164 0.7213 2.305 Cu12 0.6230 0.4098 2.355 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0003 0.000 Cu2 0.4309 0.33024 0.4776 0.5752 0.119 Cu3 0.366 0.5658 0.317 Cu3 0.3566 0.5573 0.159 Cu3 0.366 0.5658 0.317 Cu4 0.4302 0.3024 0.476 0.5753 0.7752 0.793 Cu3 0.3504 0.476 0.5775 0.7752 0.793 Cu1 0.9979 0.7984 0.9844 1.285 Cu1 <t< td=""><td></td><td></td><td></td><td></td><td></td><td>Cu5</td><td>0.1143</td><td>0.6857</td><td>2.434</td></t<>						Cu5	0.1143	0.6857	2.434
Cu2 0.5574 0.5246 0.230 Cu3 0.6639 0.2131 0.461 Cu4 0.7705 0.9016 0.681 Cu5 0.8770 0.5902 0.922 Cu6 0.9836 0.2737 1.152 Cu7 0.9092 0.9672 1.383 Cu1 0.4098 0.0328 2.074 Cu10 0.4098 0.0328 2.074 Cu11 0.4164 0.7213 2.305 Cu12 0.6230 0.4098 0.324 Cu2 0.333 0.3438 0.448 Cu12 0.2829 0.8294 0.189 Cu2 0.3838 0.544 0.476 Cu2 0.3775 0.7752 0.793 Cu3 <t< td=""><td></td><td>(6 4 3)</td><td>8.0498</td><td>6.7350</td><td>111.012</td><td>Cu1</td><td>0.4508</td><td>0.8361</td><td>0.000</td></t<>		(6 4 3)	8.0498	6.7350	111.012	Cu1	0.4508	0.8361	0.000
(8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 0.0003 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 0.0003 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 0.000 (11 0.3575 0.775 0.775 0.775 0.775 0.775 0.775 0.775 (11 0.9477 0.9571 0.1377 0.4574 0.4544 0.466 2.219 (11 0.0476 0.0400 0.0000						Cu2	0.5574	0.5246	0.230
(8 7 4) 8.0498 9.1783 95.032 Cu1 0.0901 0.0902 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2033 0.3443 1.844 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 2.074 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.04098 0.213 2.305 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0000 Cu2 0.2293 0.8294 0.159 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0308 0.6314 (2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0						Cu3	0.6639	0.2131	0.461
(8 7 4) 8.0498 9.1783 95.032 Cui 0.0936 0.02787 1.152 (8 7 4) 8.0498 9.1783 95.032 Cui 0.0902 0.0932 2.043 (8 7 4) 8.0498 9.1783 95.032 Cui 0.2993 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cui 0.2993 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cui 0.2993 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cui 0.2993 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cui 0.2993 0.0903 0.000 (8 7 4) 8.0498 9.1782 10.0 0.3566 0.568 0.317 Cui 0.3566 0.5618 0.5775 0.7752 0.773 0.7752 0.793 Cui 0.0910 0.010 Cui 0.4377 0.4574 1.585 Cui 0.0130 0.9322 1.902 Cui 0.9484 1.266						Cu4	0.7705	0.9016	0.691
(8 7 4) 8.0498 9.1783 95.032 Cu1 0.0902 0.0672 1.383 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0090 2.535 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0090 2.032 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0090 2.032 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0090 2.032 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2023 0.3024 0.159 (2 4 0.4302 0.3024 0.159 Cu2 0.3024 0.476 (2 4 0.4302 0.3024 0.159 Cu3 0.3566 0.367 (2 4 0.4302 0.3024 0.159 Cu3 0.5775 0.7752 0.738 (2 10 0.913 0.9303 0.9302 1.160 Cu1 0.9430 0.9032 2.199 (2 11 0.9457 0.4574 1.585 Cu12 0.1310 0.1396 2.378 <tr< td=""><td></td><td></td><td></td><td></td><td>Cu5</td><td>0.8770</td><td>0.5902</td><td>0.922</td></tr<>						Cu5	0.8770	0.5902	0.922
$ \begin{pmatrix} \mathrm{Cu}^7 & 0.0902 & 0.9672 & 1.383 \\ \mathrm{Cu}^8 & 0.1967 & 0.6557 & 1.613 \\ \mathrm{Cu}^9 & 0.3033 & 0.3443 & 1.844 \\ \mathrm{Cu}10 & 0.4098 & 0.0328 & 2.074 \\ \mathrm{Cu}11 & 0.5164 & 0.7213 & 2.305 \\ \mathrm{Cu}12 & 0.6230 & 0.4098 & 2.535 \\ \mathrm{Cu}12 & 0.6230 & 0.4098 & 2.535 \\ \mathrm{Cu}2 & 0.2829 & 0.8294 & 0.159 \\ \mathrm{Cu}2 & 0.2829 & 0.8294 & 0.159 \\ \mathrm{Cu}2 & 0.3024 & 0.476 \\ \mathrm{Cu}3 & 0.3024 & 0.476 \\ \mathrm{Cu}4 & 0.4302 & 0.3024 & 0.476 \\ \mathrm{Cu}5 & 0.5075 & 0.7752 & 0.793 \\ \mathrm{Cu}7 & 0.6512 & 0.5116 & 0.951 \\ \mathrm{Cu}7 & 0.6512 & 0.5116 & 0.951 \\ \mathrm{Cu}9 & 0.7984 & 0.2480 & 1.110 \\ \mathrm{Cu}9 & 0.7984 & 0.9844 & 1.268 \\ \mathrm{Cu}10 & 0.8771 & 0.7210 & 1.427 \\ \mathrm{Cu}11 & 0.4677 & 0.4574 & 1.585 \\ \mathrm{Cu}12 & 0.0194 & 0.1938 & 1.744 \\ \mathrm{Cu}3 & 0.0930 & 0.9302 & 1.902 \\ \mathrm{Cu}14 & 0.1667 & 0.6666 & 2.061 \\ \mathrm{Cu}15 & 0.3403 & 0.4032 & 2.219 \\ \mathrm{Cu}16 & 0.3140 & 0.1396 & 2.378 \\ \mathrm{Cu}17 & 0.3876 & 0.8760 & 2.536 \\ \mathrm{Cu}2 & 0.4810 & 0.0000 & 0.000 \\ \mathrm{Cu}2 & 0.4810 & 0.1762 & 0.176 \\ \mathrm{Cu}3 & 0.6169 & 0.2858 & 0.527 \\ \mathrm{Cu}4 & 0.6429 & 0.2858 & 0.527 \\ \mathrm{Cu}5 & 0.7238 & 0.0476 & 0.7632 \\ \mathrm{Cu}6 & 0.8048 & 0.8096 & 0.879 \\ \mathrm{Cu}7 & 0.8857 & 0.5714 & 1.054 \\ \mathrm{Cu}3 & 0.619 & 0.5288 & 0.527 \\ \mathrm{Cu}4 & 0.6429 & 0.2858 & 0.527 \\ \mathrm{Cu}5 & 0.7238 & 0.0476 & 0.7032 \\ \mathrm{Cu}6 & 0.8048 & 0.8096 & 0.879 \\ \mathrm{Cu}7 & 0.8857 & 0.5714 & 1.054 \\ \mathrm{Cu}10 & 0.1286 & 0.8572 & 1.406 \\ \mathrm{Cu}10 & 0.1286 & 0.8572 & 1.581 \\ \mathrm{Cu}11 & 0.2095 & 0.6109 & 1.757 \\ \mathrm{Cu}2 & 0.738 & 0.357 & 0.5714 & 1.054 \\ \mathrm{Cu}10 & 0.1286 & 0.8572 & 1.581 \\ \mathrm{Cu}12 & 0.2905 & 0.6109 & 1.757 \\ \mathrm{Cu}3 & 0.714 & 0.1498 & 2.108 \\ \mathrm$						Cu6	0.9836	0.2787	1.152
(8 7 4) 8.0498 9.1783 95.032 Cu1 0.2033 0.3443 1.844 Cu1 0.5164 0.7213 2.305 Cu2 0.6230 0.4098 2.535 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2033 0.0903 0.0003 Cu3 0.3566 0.5658 0.317 Cu3 0.3566 0.5658 0.317 Cu4 0.4302 0.3204 0.476 0.577 0.7752 0.773 Cu4 0.4302 0.3204 0.476 0.5775 0.7752 0.793 Cu4 0.4302 0.3204 0.476 0.5715 0.7752 0.793 Cu5 0.5039 0.0388 0.634 1.100 Cu5 0.2480 1.110 Cu4 0.7248 0.2480 1.110 Cu1 0.9930 0.9302 1.902 Cu10 0.8721 0.7210 1.427 Cu11 0.9437 0.4574 1.585 Cu12 0.01						Cu7	0.0902	0.9672	1.383
(8 7 4) 8.0498 9.1783 95.032 Cu1 0.2033 0.3443 1.844 Cu10 0.4098 0.0328 2.074 Cu11 0.5164 0.7213 2.305 Cu12 0.6230 0.4098 2.535 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2023 0.8294 0.159 Cu2 0.2829 0.8294 0.159 Cu3 0.3566 0.5658 0.317 Cu4 0.4302 0.3024 0.443 0.2440 1.100 Cu5 0.5039 0.0388 0.634 Cu6 0.5775 0.7752 0.793 Cu6 0.5775 0.7724 0.2480 1.110 Cu9 0.7984 0.2480 1.110 Cu11 0.9457 0.4577 0.4574 1.585 Cu12 0.0194 0.1398 1.744 Cu13 0.0303 0.9302 1.909 Cu14 0.1667 0.6666 2.061 Cu14 0.1667						Cu8	0.1967	0.6557	1.613
(8 7 4) 8.0498 9.1783 95.032 Cu1 0.2033 0.0903 0.000 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2033 0.0903 0.000 (u1 0.3566 0.5658 0.317 Cu2 0.2829 0.3024 0.476 Cu3 0.3566 0.5658 0.317 Cu4 0.4302 0.3024 0.476 Cu5 0.5039 0.0388 0.634 Cu6 0.5775 0.7752 0.775 Cu7 0.6512 0.5116 0.951 Cu8 0.7984 0.9844 1.100 Cu9 0.7984 0.9484 1.268 Cu10 0.8721 0.7210 1.427 Cu11 0.9457 0.4574 1.585 Cu12 0.0194 0.1398 1.784 Cu13 0.0930 0.9302 1.902 Cu14 0.1667 0.2403 0.4032 2.219 Cu16 0.3140 0.1396 2.378 Cu16 0.3140 0.7620						Cu9	0.3033	0.3443	1.844
(8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0903 0.000 Cu2 0.2829 0.8294 0.159 Cu3 0.3566 0.5658 0.317 Cu4 0.4302 0.3024 0.476 Cu5 0.5039 0.0388 0.634 Cu6 0.5775 0.7752 0.7752 Cu7 0.6512 0.5116 0.951 Cu7 0.6512 0.1142 0.2480 1.110 Cu9 0.7984 0.9844 1.268 Cu10 0.8721 0.7120 1.427 Cu11 0.9457 0.4574 1.585 Cu10 0.8721 0.03930 0.9302 1.902 Cu11 0.9457 0.4574 1.585 Cu12 0.0194 0.1336 1.744 Cu13 0.0930 0.0302 2.219 Cu14 0.1667 0.6666 2.061 Cu14 0.1667 0.6666 2.061 Cu15 0.2433 0.4032 2.219 Cu16 <						Cu10	0.4098	0.0328	2.074
Cu12 0.6230 0.4098 2.535 (8 7 4) 8.0498 9.1783 95.032 Cu1 0.2093 0.0003 0.000 Cu2 0.2829 0.8294 0.159 Cu3 0.3566 0.5658 0.317 Cu4 0.4302 0.3024 0.479 0.634 Cu5 0.5039 0.0388 0.634 Cu5 0.5075 0.7752 0.7752 0.793 Cu7 0.6512 0.5116 0.951 Cu6 0.5775 0.7754 0.7884 0.2480 1.110 Cu9 0.7984 0.9844 1.268 Cu10 0.8721 0.7210 1.427 Cu11 0.9457 0.4574 1.585 Cu12 0.0194 0.1938 1.744 Cu12 0.0194 0.1938 1.744 Cu13 0.09302 2.219 Cu14 0.1667 0.66666 2.061 Cu16 0.3140 0.1396 2.378 Cu12 0.2403 0.4392 0.2538 <						Cu11	0.5164	0.7213	2.305
$ (8\ 7\ 4) \\ 8.0498 \\ 9.1783 \\ 95.032 \\ Cu1 \\ Cu2 \\ 0.2829 \\ Cu3 \\ 0.3566 \\ 0.568 \\ 0.3566 \\ 0.568 \\ 0.3160 \\ Cu4 \\ 0.4302 \\ 0.3024 \\ 0.4302 \\ 0.3024 \\ 0.4302 \\ 0.3028 \\ 0.3038 \\ 0.634 \\ Cu6 \\ 0.5775 \\ 0.751 \\ 0.752 \\ 0.751 \\ 0.751 \\ 0.752 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.752 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.752 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.751 \\ 0.752 \\ 0.751 \\ 0.$						Cu12	0.6230	0.4098	2.535
$ \begin{pmatrix} Cu2 & 0.2829 & 0.8294 & 0.159 \\ Cu3 & 0.3566 & 0.5658 & 0.317 \\ Cu4 & 0.4302 & 0.3024 & 0.476 \\ Cu5 & 0.5039 & 0.0388 & 0.634 \\ Cu6 & 0.5775 & 0.7752 & 0.793 \\ Cu7 & 0.6512 & 0.5116 & 0.951 \\ Cu8 & 0.7248 & 0.2480 & 1.110 \\ Cu9 & 0.7948 & 0.9844 & 1.268 \\ Cu10 & 0.8721 & 0.7210 & 1.427 \\ Cu10 & 0.8721 & 0.7210 & 1.427 \\ Cu11 & 0.9457 & 0.4574 & 1.585 \\ Cu12 & 0.0194 & 0.1938 & 1.744 \\ Cu13 & 0.0930 & 0.9302 & 1.900 \\ Cu14 & 0.1667 & 0.6666 & 2.061 \\ Cu15 & 0.2403 & 0.4302 & 2.219 \\ Cu16 & 0.3140 & 0.1396 & 2.378 \\ Cu17 & 0.3876 & 0.3760 & 2.536 \\ Cu17 & 0.3876 & 0.3760 & 0.3528 & 0.527 \\ Cu3 & 0.5619 & 0.5238 & 0.527 \\ Cu3 & 0.5619 & 0.2538 & 0.527 \\ Cu4 & 0.6429 & 0.2858 & 0.527 \\ Cu4 & 0.6429 & 0.2858 & 0.527 \\ Cu5 & 0.7238 & 0.0476 & 0.795 \\ Cu6 & 0.8048 & 0.8066 & 0.879 \\ Cu7 & 0.8857 & 0.5714 & 1.054 \\ Cu8 & 0.9667 & 0.3334 & 1.230 \\ Cu9 & 0.0476 & 0.9952 & 1.406 \\ Cu10 & 0.1286 & 0.8572 & 1.581 \\ Cu11 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2095 & 0.6190 & 1.757 \\ Cu13 & 0.3714 & 0.128 & 2.108 \\ Cu3 & 0.5619 & 0.3724 & 1.931 \\ Cu13 & 0.3714 & 0.128 & 2.108 \\ Cu3 & 0.5619 & 0.3734 & 2.108 \\ Cu4 & 0.6429 & 0.3734 & 1.230 \\ Cu4 & 0.6429 & 0.3334 & 1.230 \\ Cu3 & 0.5619 & 0.3334 & 1.230 \\ Cu3 & 0.5619 & 0.3334 & 1.230 \\ Cu4 & 0.6429 & 0.3334 & 1.230 \\ Cu14 & 0.1286 & 0.8572 & 1.581 \\ Cu15 & 0.3748 & 0.9667 & 0.3334 & 1.230 \\ Cu4 & 0.6429 & 0.3314 & 0.230 \\ Cu4 & 0.6429 & 0.3314 &$		(8 7 4)	8.0498	9.1783	95.032	Cu1	0.2093	0.0903	0.000
$ \begin{pmatrix} Cu3 & 0.3566 & 0.5658 & 0.317 \\ Cu4 & 0.4302 & 0.3024 & 0.476 \\ Cu5 & 0.5039 & 0.0388 & 0.634 \\ Cu6 & 0.5775 & 0.7752 & 0.793 \\ Cu7 & 0.6512 & 0.5116 & 0.951 \\ Cu8 & 0.7248 & 0.2480 & 1.110 \\ Cu9 & 0.7984 & 0.9844 & 1.268 \\ Cu10 & 0.8721 & 0.7210 & 1.427 \\ Cu11 & 0.9457 & 0.4574 & 1.585 \\ Cu12 & 0.0194 & 0.1398 & 1.744 \\ Cu13 & 0.0930 & 0.9302 & 1.902 \\ Cu14 & 0.1667 & 0.6666 & 2.061 \\ Cu15 & 0.2403 & 0.4032 & 2.219 \\ Cu16 & 0.3140 & 0.1396 & 2.378 \\ Cu17 & 0.3876 & 0.8760 & 2.536 \\ Cu2 & 0.4810 & 0.7620 & 0.070 \\ Cu2 & 0.4810 & 0.7620 & 0.070 \\ Cu4 & 0.6429 & 0.2858 & 0.527 \\ Cu5 & 0.7238 & 0.0476 & 0.703 \\ Cu4 & 0.6429 & 0.2858 & 0.527 \\ Cu5 & 0.7238 & 0.0476 & 0.703 \\ Cu6 & 0.8048 & 0.8096 & 0.879 \\ Cu7 & 0.8857 & 0.5714 & 1.054 \\ Cu8 & 0.9667 & 0.3334 & 1.230 \\ Cu9 & 0.0476 & 0.0952 & 1.406 \\ Cu10 & 0.1286 & 0.8572 & 1.581 \\ Cu11 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2905 & 0.3810 & 1.933 \\ Cu11 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2905 & 0.3810 & 1.933 \\ Cu13 & 0.7514 & 0.1428 & 2.108 \\ Cu14 & 0.1628 & 0.8572 & 1.581 \\ Cu11 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2905 & 0.3810 & 1.933 \\ Cu13 & 0.7514 & 0.1428 & 2.108 \\ Cu14 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2905 & 0.3810 & 1.933 \\ Cu13 & 0.7514 & 0.1428 & 2.108 \\ Cu14 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2905 & 0.3810 & 1.933 \\ Cu13 & 0.7514 & 0.1428 & 2.108 \\ Cu3 & 0.7514 & 0.1428 & 2.108 \\ C$						Cu2	0.2829	0.8294	0.159
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu3	0.3566	0.5658	0.317
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu4	0.4302	0.3024	0.476
$ \begin{array}{c cccc} Cu6 & 0.5775 & 0.7752 & 0.793 \\ Cu7 & 0.6512 & 0.5116 & 0.951 \\ Cu8 & 0.7248 & 0.2480 & 1.110 \\ Cu9 & 0.7984 & 0.9844 & 1.268 \\ Cu10 & 0.8721 & 0.7210 & 1.427 \\ Cu11 & 0.9457 & 0.4574 & 1.585 \\ Cu12 & 0.0194 & 0.1938 & 1.744 \\ Cu13 & 0.0930 & 0.9302 & 1.902 \\ Cu14 & 0.1667 & 0.6666 & 2.061 \\ Cu15 & 0.2403 & 0.4032 & 2.219 \\ Cu16 & 0.3140 & 0.1396 & 2.338 \\ Cu17 & 0.3876 & 0.8760 & 2.536 \\ Cu17 & 0.3876 & 0.8760 & 2.536 \\ Cu12 & 0.4810 & 0.7620 & 0.176 \\ Cu3 & 0.5619 & 0.5238 & 0.352 \\ Cu4 & 0.6429 & 0.28588 & 0.527 \\ Cu5 & 0.7238 & 0.0476 & 0.703 \\ Cu6 & 0.8048 & 0.8096 & 0.879 \\ Cu6 & 0.8048 & 0.8096 & 0.879 \\ Cu7 & 0.8857 & 0.5714 & 1.054 \\ Cu8 & 0.9667 & 0.3334 & 1.230 \\ Cu9 & 0.0476 & 0.0952 & 1.406 \\ Cu9 & 0.0476 & 0.0952 & 1.406 \\ Cu10 & 0.1286 & 0.8572 & 1.581 \\ Cu11 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2905 & 0.3810 & 1.737 \\ Cu13 & 0.3714 & 0.1428 & 2.108 \\ \end{array} $						Cu5	0.5039	0.0388	0.634
$ \begin{pmatrix} Cu7 & 0.6512 & 0.5116 & 0.951 \\ Cu8 & 0.7248 & 0.2480 & 1.110 \\ Cu9 & 0.7984 & 0.9844 & 1.268 \\ Cu10 & 0.8721 & 0.7210 & 1.427 \\ Cu11 & 0.9457 & 0.4574 & 1.585 \\ Cu12 & 0.0194 & 0.1938 & 1.744 \\ Cu13 & 0.0930 & 0.9302 & 1.902 \\ Cu14 & 0.1667 & 0.6666 & 2.061 \\ Cu15 & 0.2403 & 0.4032 & 2.219 \\ Cu16 & 0.3140 & 0.1396 & 2.378 \\ Cu17 & 0.3876 & 0.8760 & 2.536 \\ Cu17 & 0.3876 & 0.8760 & 2.538 \\ Cu17 & 0.3876 & 0.8760 & 2.538 \\ Cu17 & 0.3876 & 0.8760 & 2.538 \\ Cu17 & 0.3876 & 0.8760 & 0.000 \\ Cu2 & 0.4810 & 0.7620 & 0.176 \\ Cu3 & 0.5619 & 0.5238 & 0.527 \\ Cu5 & 0.7238 & 0.0476 & 0.703 \\ Cu4 & 0.6429 & 0.2858 & 0.527 \\ Cu5 & 0.7238 & 0.0476 & 0.703 \\ Cu6 & 0.8048 & 0.8096 & 0.879 \\ Cu7 & 0.8857 & 0.5714 & 1.054 \\ Cu8 & 0.9667 & 0.0952 & 1.406 \\ Cu10 & 0.1286 & 0.8572 & 1.581 \\ Cu11 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2905 & 0.6190 & 1.757 \\ Cu12 &$						Cu6	0.5775	0.7752	0.793
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu7	0.6512	0.5116	0.951
$ \begin{pmatrix} Cu^9 & 0.7984 & 0.9844 & 1.268 \\ Cu^{10} & 0.8721 & 0.7210 & 1.427 \\ Cu^{11} & 0.9457 & 0.4574 & 1.585 \\ Cu^{12} & 0.0194 & 0.1938 & 1.744 \\ Cu^{13} & 0.0930 & 0.9302 & 1.902 \\ Cu^{14} & 0.1667 & 0.6666 & 2.061 \\ Cu^{15} & 0.2403 & 0.4032 & 2.219 \\ Cu^{16} & 0.3140 & 0.1396 & 2.378 \\ Cu^{17} & 0.3876 & 0.8760 & 2.536 \\ Cu^{17} & 0.3876 & 0.8760 & 2.536 \\ Cu^{2} & 0.4810 & 0.7620 & 0.176 \\ Cu^{3} & 0.5619 & 0.5238 & 0.352 \\ Cu^{4} & 0.6429 & 0.2858 & 0.527 \\ Cu^{5} & 0.7238 & 0.0476 & 0.703 \\ Cu^{6} & 0.8048 & 0.8096 & 0.879 \\ Cu^{7} & 0.8857 & 0.5714 & 1.054 \\ Cu^{8} & 0.9667 & 0.3334 & 1.230 \\ Cu^{9} & 0.0476 & 0.0952 & 1.406 \\ Cu^{10} & 0.1286 & 0.8572 & 1.581 \\ Cu^{11} & 0.2095 & 0.6190 & 1.757 \\ Cu^{12} & 0.2905 & 0.3100 & 1.757 \\ Cu^{12} & 0.2905 & 0.3100 & 1.757 \\ Cu^{13} & 0.3714 & 0.1428 & 2108 \\ Cu^{14} & 0.428 & 0.4880 & 0.879 \\ Cu^{14} & 0.2995 & 0.6190 & 1.757 \\ Cu^{13} & 0.3714 & 0.1428 & 2108 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.295 & 0.3810 & 0.257 \\ Cu^{14} & 0.295 & 0.3810 & 0.757 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.2995 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.295 & 0.3810 & 0.757 \\ Cu^{14} & 0.295 & 0.3810 & 0.757 \\ Cu^{14} & 0.295 & 0.3810 & 0.757 \\ Cu^{14} & 0.1428 & 2108 \\ Cu^{14} & 0.2905 & 0.3810 & 0.757 \\ Cu^{$						Cu8	0.7248	0.2480	1.110
$ \begin{pmatrix} Cu10 & 0.8721 & 0.7210 & 1.427 \\ Cu11 & 0.9457 & 0.4574 & 1.585 \\ Cu12 & 0.0194 & 0.1938 & 1.744 \\ Cu13 & 0.0930 & 0.9302 & 1.902 \\ Cu14 & 0.1667 & 0.6666 & 2.061 \\ Cu15 & 0.2403 & 0.4032 & 2.219 \\ Cu16 & 0.3140 & 0.1396 & 2.378 \\ Cu17 & 0.3876 & 0.8760 & 2.536 \\ Cu17 & 0.3876 & 0.8760 & 2.536 \\ Cu2 & 0.4810 & 0.7620 & 0.176 \\ Cu3 & 0.5619 & 0.5238 & 0.352 \\ Cu4 & 0.6429 & 0.2858 & 0.527 \\ Cu5 & 0.7238 & 0.0476 & 0.703 \\ Cu6 & 0.8048 & 0.8096 & 0.879 \\ Cu7 & 0.8857 & 0.5714 & 1.054 \\ Cu8 & 0.9667 & 0.3334 & 1.230 \\ Cu9 & 0.0476 & 0.0952 & 1.406 \\ Cu10 & 0.1286 & 0.8572 & 1.581 \\ Cu11 & 0.2095 & 0.6190 & 1.757 \\ Cu13 & 0.3714 & 0.1428 & 2.108 \\ \end{pmatrix} $						Cu9	0.7984	0.9844	1.268
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu10	0.8721	0.7210	1.427
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cull	0.9457	0.4574	1.585
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu12	0.0194	0.1938	1.744
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu13	0.0930	0.9302	1.902
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu14	0.1007	0.0000	2.001
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu15	0.2405	0.4052	2.219
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu10 Cu17	0.3140	0.1390	2.578
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		(0.5.4)	0.0400	0.1700	116010	Cul,	0.3070	0.0700	2.550
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		(8 5 4)	8.0498	9.1782	116.010	Cul	0.4000	0.0000	0.000
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						Cu2	0.4810	0.7620	0.176
$\begin{array}{c ccccc} Cu4 & 0.6429 & 0.2858 & 0.527 \\ Cu5 & 0.7238 & 0.0476 & 0.703 \\ Cu6 & 0.8048 & 0.8096 & 0.879 \\ Cu7 & 0.8857 & 0.5714 & 1.054 \\ Cu8 & 0.9667 & 0.3334 & 1.230 \\ Cu9 & 0.0476 & 0.0952 & 1.406 \\ Cu10 & 0.1286 & 0.8572 & 1.581 \\ Cu11 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2905 & 0.3810 & 1.933 \\ Cu13 & 0.3714 & 0.1428 & 2.108 \end{array}$						Cu3	0.5619	0.5238	0.352
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						Cu4	0.6429	0.2858	0.527
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						Cus	0.7238	0.04/6	0.703
$\begin{array}{c cccc} Cu7 & 0.8857 & 0.5714 & 1.054 \\ Cu8 & 0.9667 & 0.3334 & 1.230 \\ Cu9 & 0.0476 & 0.0952 & 1.406 \\ Cu10 & 0.1286 & 0.8572 & 1.581 \\ Cu11 & 0.2095 & 0.6190 & 1.757 \\ Cu12 & 0.2905 & 0.3810 & 1.933 \\ Cu13 & 0.3714 & 0.1428 & 2.108 \end{array}$							0.8048	0.8096	0.8/9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$							0.0001	0.3714	1.034
Cu3 0.0470 0.0522 1.400 Cu10 0.1286 0.8572 1.581 Cu11 0.2095 0.6190 1.757 Cu12 0.2905 0.3810 1.933 Cu13 0.3714 0.1428 2.108						Cuo	0.9007	0.0057	1.230
Cu10 0.1260 0.87/2 1.381 Cu11 0.2095 0.6190 1.757 Cu12 0.2905 0.3810 1.933 Cu13 0.3714 0.1428 2.108						Cu ³	0.0470	0.0952	1.400
Cu11 0.2095 0.0190 1.757 Cu12 0.2905 0.3810 1.933 Cu13 0.3714 0.1428 2.108						Cu10	0.1200	0.6572	1.301
Cu12 0.2505 0.3810 1.555 Cu12 0.2705 0.3810 1.555 Cu13 0.3714 0.1428 2.108 0.3810 1.555 Cu13 0.3810 Cu13 0.3810 1.555 Cu13 C						Cu12	0.2095	0.0190	1.737
						Cu12	0.3714	0.1428	2.108

^a Calcite Miller indices are based on the hexagonal structural unit cell, as opposed to the morphological unit cell [13].

^b Diopside (1 1 0) features at least three alternative surface terminations. The terminations (1 1 0)-a, -c, and -e correspond to structures described and illustrated by Hazen [13] in Fig. 8a, c and e, respectively.

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either direct or reciprocal space can be used to describe the 210 orientation of the symmetry plane. However, the orientation 211 of a symmetry plane is not so straightforward to define when 212 the lattice, itself, does not possess mirror or glide plane sym-213 metry. On the one hand, if a mirror is defined perpendicu-214 lar to an integral reciprocal lattice vector, then there is no 215 216 guarantee that the separation between a given atom and its mirror image will be the same for any translation-equivalent 217 pair because the image of lattice points may not be super-218 imposed. Consequently, a direct space vector must be used 219 to define the orientation of a mirror plane. In this case, we 220 define the mirror by [uv]m, where [uv] is a integral direct 221 space vector perpendicular to the mirror plane. The coordi-222 nates, (u, v), are defined with respect to the surface bases 223 listed in Table 1. On the other hand, a necessary condition 224 for a glide plane is that the composition of a glide operation 225 with itself must produce a lattice translation (i.e., defined 226 by integers) that is perpendicular to the plane normal. This 227 condition can be guaranteed only if the orientation of the 228 glide plane is defined by integers in reciprocal space (again, 229 because hx + ky + lz = 0). In this case, we define the glide 230 by ${}^{(h\,k)}g$, where $(h\,k)$ designate the integral coordinates of 231 a reciprocal space vector that is perpendicular to the glide 232 plane. In our algorithm, the orientations of the planes were 233 defined by examining every mirror or glide plane with in-234 dices h and k between -10 and 10 [a total of (128) possible 235 nonequivalent (hk) in the appropriate direct or reciprocal 236 space, respectively. 237

We examined the effect of the location of a given symmetry plane by computing chiral indices with the plane displaced systematically from the origin of the surface unit cell. Our algorithm translated the symmetry plane across one surface unit cell, from one corner to another, displacing the plane in (100) equally spaced steps and computing the chiral indices at each step.

We computed chiral indices at each of (128) orientations 245 and each of (100) displacements for mirror and for glide 246 symmetry planes with the following algorithm. First, we 247 generated the coordinates of all atoms in a 3×3 array of 248 surface unit cells. A new Cartesian basis, designated the 249 250 plane basis, was computed with its x-axis perpendicular to the symmetry plane, z-axis parallel to the surface z-axis, 251 and y-axis perpendicular to x and z, and consequently par-252 253 allel to the plane. Note that the y-axis defines the direction of translation resulting from the composition of a glide 254 with itself. The 3×3 array of surface atomic coordinates 255 were transformed to the plane basis. We varied the origin of 256 257 the plane basis for each of the (100) plane displacements, so that the plane always passed through the origin of the 258 plane basis. Simply changing the sign of the x-coordinate 259 then generates the mirror image. The glide image was 260 computed from the mirror image by adding the translation 261 vector determined from the composition of the glide with 262 itself. 263

Each atom in the plane basis was paired with its closest atom in the mirror or glide plane image and the sep-

Table	2
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Chiral indices of best-fit mirrors or glide planes computed for 14 crystal surfaces

Compound	Surface $(h \ k \ l)$	$I_{\rm CA}$ (Å)	$I_{\rm CM}$ (Å)	Orientation
Calcite	(1 0 4) no Ca	0	0	[0 1]
	(1 0 4) with Ca	0	0	(1 0)
	(2 1 4)	1.73	2.60	[2 1]
Diopside	(1 1 0)-a	0.65	1.16	[1 0], [1 4]
	(1 1 0)-c	0.53	0.85	[0 1], (1 0)
	(1 1 0)-e	0.72	1.54	[0 1], (0 1)
Orthoclase	(1 1 0)	0.52	1.01	[1 0]
Quartz	(1 0 1)	0	0	[1 0]
	(0 1 1)	0.36	0.46	[1 2]
	(1 0 0)	0.54	0.59	[10 9], [1 0]
Copper	(5 3 1)	0.77	0.96	[-1 1]
	(6 4 3)	0.80	0.96	[0 1]
	(8 7 4)	0.85	1.22	[2 5], [0 1]
	(8 5 4)	0.84	1.29	[1 1], [0 1]

The name of the mineral and its surface indices are given in the first two columns. The average displacement index, I_{CA} , and maximum displacement index, I_{CM} , are given in units of angstroms. The orientation of the symmetry plane is given in the last column with respect to the surface basis (see Table 1). When only one orientation is given then the symmetry planes for I_{CA} and I_{CM} coincide, and when two orientations are given, then the first is with respect to I_{CA} . Orientations given with square brackets represent mirrors, [xy]m, and those with round brackets represent glides, $(hk)_g$.

arations between them were determined. We computed an 266 average index, $I_{\rm A}$, for each orientation and displacement by 267 summing each of the atomic-pair separations, and dividing 268 by the number of atoms; I_{CA} is the minimum of these in-269 dices. A maximum displacement index, $I_{\rm M}$, was computed 270 by finding the maximum atomic-pair displacement at each 271 orientation and displacement; ICM is the minimum of these 272 indices. The computed values of ICA and ICM along with the 273 orientation of the best-fit mirror or glide symmetry plane 274 for each of 14 different crystalline surfaces are given in 275 Table 2. 276

An illustration of the effect of displacing a mirror across 277 a surface unit cell is provided in Fig. 1 for the (011) sur-278 face of quartz. Fig. 1a is a plot of the average index, I_A , 279 versus the displacement of the mirror, [12]m, as it is dis-280 placed in (100) steps across the surface cell from (00) to 281 (01). Note that the surface unit cell has four local minima, 282 each occurring where the pseudo mirror intersects an atom, 283 and the global minimum occurs where the pseudo mirror 284 is halfway between a pair of atoms and is perpendicular to 285 the surface projection of the interatomic vector. To illus-286 trate these pseudo mirrors, Fig. 1b displays a 3×3 array 287 of surface unit cell contents along with fictive mirrors that 288 pass through the local and global minima in I_A . In general, 289 local minima in the chiral index can be found when a mir-290 ror intersects an atom or when the mirror is halfway be-291 tween a pair of atoms and is perpendicular to the interatomic 292 vector. 293

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Fig. 1. Displacing a mirror across a surface unit cell has a significant effect on the chiral index, as illustrated for the $(0\ 1\ 1)$ surface of quartz. The pseudo mirror associated with I_{CA} is perpendicular to the direct space vector [12]. (a) Average chiral index, I_A , plotted against the displacement of the mirror, $^{[12]}m$, as it is displaced in $(1\ 0\ 0)$ steps across the surface cell from $(0\ 0)$ to $(0\ 1)$. Note that there are four local minima and one global minimum, I_{CA} . The local minima occur for pseudo-mirrors that pass through the atomic locations. In this example, the global minimum occurs where the pseudo mirror is placed half way between pairs of atoms. (b) A 3×3 array of surface unit cell contents with a bold line that indicates the pseudo mirror associated with I_{CA} , and four thin lines that indicate the location of the pseudo mirrors associated with the local minima in (a). The pseudo mirror associated with I_{CA} looks like a true mirror from this projection of the atoms; however, the mirror image pairs of atoms are at different heights.

294 3. Results

Calculated chiral indices, I_{CA} and I_{CM} , for 14 different crystalline surfaces (Table 2) reveal a number of significant, and in some instances unanticipated, features. In the following sections we summarize our analyses of 10 common mineral surfaces described and illustrated by Hazen [13], including those of calcite (CaCO₃), diopside (CaMgSi₂O₆), orthoclase (KAlSi₃O₈), and quartz (SiO₂), as well as four different kinked surfaces of FCC copper. The face-centered 302 cubic (FCC) unit cell edge of Cu is 3.60 Å, yielding a radius 303 for Cu of ≈ 1.27 Å, which is similar to the radius of O. Thus, 304 the chiral indices of Cu and minerals are comparably scaled. 305

Calcite dramatically illustrates the potential for an achiral crystal to exhibit strongly chiral surfaces. The common 308

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Fig. 2. Calcite (2 1 4) is a strongly chiral surface. The best-fit mirror (solid line) for both I_{CA} and I_{CM} is parallel to the cell edge. Smaller and larger spheres represent Ca and O, respectively.

(214) scalenohedral face of calcite (CaCO₃), which is a chi-309 ral surface that adsorbs D- and L-aspartic acid differentially 310 [11], displays by far the largest calculated chiral indices 311 among the 14 surfaces modeled in this study. The greatest of 312 these indices ($I_{CM} = 2.60 \text{ Å}$) is comparable in magnitude to 313 nearest neighbor anion-anion distances in many oxides and 314 silicates and thus may represent a near-maximum possible 315 value for $I_{\rm CM}$ of typical rock-forming minerals. This face 316 also exhibits the largest calculated I_{CA} (1.73 Å). 317

The reason for these relatively large chiral indices is 318 evident from the terminal atomic structure (Fig. 2). The 319 distribution of oxygen atoms at the calcite (214) surface 320 shows little hint of mirror or glide plane symmetry. This 321 atomic surface is characterized by the oblique intersection 322 of alternating planes of Ca and CO3 groups-an arrange-323 324 ment that produces a strongly contoured, chiral surface [13]. The large chiral indices thus reflect the irregular structure, 325 326 and point to the strong enantioselective potential of this surface. 327

By contrast, we find that the achiral calcite (104) cleavage surface has $I_{CA} = I_{CM} = 0$ Å for symmetry planes perpendicular to the [10] surface basis vector (Fig. 3), as required by symmetry constraints.

3.2. Diopside

Chiral (110) cleavage surfaces of the common rock-333 forming silicate diopside (CaMgSi₂O₆) illustrate the strong 334 dependence of chiral indices on details of surface structure. 335 This surface can be modeled with at least three distinct 336 arrangements of oxygen, magnesium and calcium atoms 337 [13], depending on the presumed oxygen coordination of 338 terminal divalent cations (Fig. 4). While details of these 339 surface structures differ, all three feature complex distribu-340 tions of O, Mg and Ca that deviate from mirror or glide 341 plane symmetry. All of these arrangements thus possess 342 relatively large chiral indices (maximum $I_{CA} = 0.72$ Å and 343 $I_{\rm CM} = 1.54$ Å), and none of these arrangements displays an 344 obvious pseudo-mirror or pseudo-glide plane. The diopside 345 (110) cleavage thus represents another promising surface 346 for enantioselectivity. 347

3.3. Orthoclase

Feldspar, the commonest rock-forming mineral in Earth's 349 crust, often features the chiral (110) growth face. We mod-350 eled (110) of a monoclinic potassium end-member feldspar, 351 orthoclase (KAlSi₃O₈). As in the case of diopside, the struc-352 tural complexity of the terminal oxygen atoms, coupled with 353 near-surface tetrahedrally coordinated Al and Si cations, re-354 sults in a strongly chiral surface structure (Fig. 5). This face, 355 consequently, possesses significant chiral indices (I_{CA} = 356 $0.52 \text{ Å} \text{ and } I_{\text{CM}} = 1.01 \text{ Å}).$ 357

Quartz (SiO₂) is the only common chiral rock-forming 359 mineral. Its structure features helices of corner-linked SiO₄ 360 tetrahedra that can adopt either left- or right-handed con-361 figurations. One might predict, therefore, that quartz should 362 display among the largest chiral indices. Indeed, many pre-363 vious researchers employed powdered left- and right-handed 364 quartz in studies of enantioselectivity based on this assump-365 tion [3,30,31]. 366

Surprisingly, we find that the commonest quartz crystal 367 growth surfaces, including (100), (101) and (110), possess 368 relatively small chiral indices. Indeed, the calculated chiral 369 indices for (101) are zero, because the idealized terminal 370 oxygen atom positions yield strict mirror symmetry. In this 371 case near-surface Si atoms, which are not included in our 372 idealized surface structure, will break the mirror symmetry, 373 because surface relaxation of terminal oxygen positions will 374 lead to shifts in surface atom positions [19]. Thus the actual 375 (101) surface is probably somewhat chiral. Nevertheless, 376 this quartz surface is not well suited to chiral discrimination 377 of adsorbed molecules. 378

The (100) prismatic and (011) rhombohedral surfaces 379 of quartz are more promising, with maximum chiral indices 380 of $I_{CA} = 0.54$ Å and $I_{CM} = 0.59$ Å (Table 2). Nevertheless, 381 unlike the chiral surfaces described above for calcite, diop-382

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Fig. 3. The achiral $(1 \ 0 \ 4)$ surface of calcite possesses mirror symmetry and thus has chiral indices = 0.

side and orthoclase, pseudo-mirrors are clearly discernable
on (100) and (011) quartz surfaces Figs. 6 and 1b, respectively).

The relatively low (or zero) chiral indices of quartz are a 386 consequence of the constraint that every silicon atom, even 387 those near the crystal termination, remains four-coordinated. 388 Only oxygen atoms appear at the idealized surface, therefore, 389 and these atoms possess a quasi-regular spacing—a topology 390 that leads to pseudo-mirror and glide plane symmetry. The 391 enantioselective potential of quartz thus appears, at best, to 392 be weak compared to other common rock-forming minerals. 393

394 3.5. Copper

Copper, gold, platinum and silver possess the achiral 395 face-centered cubic structure. Intuitively, it might seem 396 that these high-symmetry metallic elements are unlikely 397 to provide surfaces of interest in studies of chiral selec-398 tion. However, a number of recent studies demonstrate 399 that high-Miller-index planes of these metals may be cut, 400 polished and annealed to yield chiral faces that feature 401 periodically stepped surfaces with "kink sites" that act 402 as chiral centers [1,2,4,32,33]. We modeled four of these 403 planes—(531), (643), (874), and (854)—and find that all 404 four possess relatively large chiral indices (0.77 \leq $I_{CA} \leq$ 405 $0.85 \text{ Å} \text{ and } 0.96 \le I_{\text{CM}} \le 1.29 \text{ Å}).$ 406

One unanticipated result is that the FCC (531) surface
displays the lowest chiral indices among the four terminations examined, even though the (531) surface has the greatest density of kink sites (and thus a greater density of chiral

centers). This result arises because our chiral indices mea-
sure not only the short-range effects of chiral centers, but
also the long-range distribution of these centers about fictive411mirrors or glide planes.414

4. Discussion 415

4.1. General considerations

Data in Tables 1 and 2 lead to a number of general observations regarding chiral indices, I_{CA} and I_{CM} . 418

- 1. For all mirrors and glide planes $I_{CA} \leq I_{CM}$, because 419 the maximum atom displacement must be greater than or 420 equal to the average atom displacement. In several cases, 421 however, the best-fit symmetry planes for I_{CA} and I_{CM} 422 differ in orientation with respect to the surface unit cell. 423
- 2. Mirrors and glide planes often yield different chiral in-424 dices. For quartz (100), diopside (110)-e, copper (874) 425 and copper (854) mirrors provide the smallest indices, 426 whereas for orthoclase (110) and calcite (104) with Ca 427 glide planes provide the minimum indices. For diopside 428 (110)-e and copper (643) mirrors yield smaller I_{CA} , 429 but mirrors and glide planes are equal for $I_{\rm CM}$. For the 430 remaining five samples, mirrors and glide planes yield 431 identical results. 432
- The orientations of best-fit mirrors and glide planes usually bear simple relationships to the surface unit cell, 434 even though we do not constrain these orientations. For 435 orthogonal surface unit cells, best-fit mirrors and glide 436

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planes are invariably parallel to one of the two unit-cell
axes. For non-orthogonal surface unit cells, best-fit mir-

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rors and glide planes are usually parallel or perpendicular

to one of the unit-cell axes or to the unit-cell diagonal.

4.2. Alternative chiral indices

Our calculations of I_{CA} and I_{CM} for 14 surfaces demonstrate that chiral indices can provide a useful relative mea-



(b)



Fig. 4. Three different atomic terminations of the diopside $(1 \ 1 \ 0)$ surface (see Table 1) result in different chiral indices and best-fit symmetry planes. Smaller and larger spheres represent cations and anions, respectively. (a) The $(1 \ 1 \ 0)$ -a surface has different best-fit mirrors for I_{CA} (thicker line) and I_{CM} (thinner line), oriented parallel to [1 0] and [1 4], respectively. (b) The diopside $(1 \ 1 \ 0)$ -c surface has a best-fit mirror parallel to [0 1] for I_{CA} and a best-fit glide plane parallel to [1 0] for I_{CM} . (c) The $(1 \ 1 \ 0)$ -e surface has a best-fit mirror parallel to [0 1] for I_{CA} (solid line), and a best-fit glide plane parallel to [0 1] for I_{CM} (dashed line).

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Fig. 4. (Continued).



Fig. 5. The (1 1 0) face of the orthoclase. Minimum chiral indices ($I_{CA} = 0.52$ Å and $I_{CM} = 1.01$ Å) result from a mirror plane oriented perpendicular to [1 0].

443

sure of the intrinsic potential of crystalline surfaces to discriminate between chiral molecules. Surfaces with relatively
large chiral indices have an inherently greater enantioselectve potential than those with indices near zero, and are

447 perhaps worthy of special consideration in developing enantioselective chemical systems. However, no single chiral index is sufficient to characterize all interactions between a crystalline surface and a chiral molecule. Our two proposed 451

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Fig. 6. The (1 0 0) surface of quartz has the largest chiral indices of the three common quartz crystal faces examined ($I_{CA} = 0.54$ Å and $I_{CM} = 0.59$ Å). Nevertheless, pseudo-mirror symmetry is evident for mirror planes oriented perpendicular to [1 0] and [10 9].

indices I_{CA} and I_{CM} , for example, focus specifically on the deviations of a 3×3 array of surface unit cells from ideal mirror or glide plane symmetry. As such, these indices provide a measure of intermediate-range features, typically 15–45 Å in length, but they may not adequately characterize interactions between these surfaces and chiral molecules at significantly larger or smaller scales.

In some instances, the scale of the calculation is not important. For example, if a 2D unit cell is orthogonal or if a = b, then the best-fit symmetry plane must be oriented parallel to a cell edge or a cell diagonal. In such a case I_{CA} and I_{CM} are independent of the number of surface unit cells considered.

In the case of a non-orthogonal unit cell, however, 465 chiral indices may be a function of the number of unit 466 cells included in the calculation. Consider, for example, 467 a pseudo-orthogonal cell ($a = 3 \text{ Å}, b = 5 \text{ Å}, \gamma = 85^{\circ}$) 468 with one atom at the origin, as illustrated in Fig. 7. In 469 this case, the best-fit mirror is always oriented close to the 470 471 pseudo-orthogonal cell edge, but the exact orientation of that mirror varies with the number of 2D unit cells under 472 consideration, and the average and maximum deviations of 473 474 atomic positions from that mirror increase as more unit cells are considered. Thus, in some cases I_{CA} and I_{CM} may vary 475 depending on the scale of the calculation. Note that surfaces 476 of this type may be more likely to interact selectively with 477 large chiral molecules than small ones. 478

By contrast, a "kink site" on an FCC metal surface 479 provides an effective chiral center at the scale of a few 480 angstroms, even though much of the metal surface area 481 may be intrinsically achiral. The local kinks, rather than 482 the entire surface, provide chiral sites for enantioselectivity. 483 Given these effects of scale, at least two alternative types 484 of useful chiral indices could be devised with strategies 485 similar to those outlined above. 486

4.2.1. Three-point interactions

Chiral selection of molecules requires three non-colinear 488 points of interaction [34]. One could, therefore, define a 489 chiral index based on the maximum enantiomeric mismatch 490 of triangles formed by nearest-neighbor atoms. Such a chiral 491 index thus probes short-range effects of chiral centers over a 492 few Angstroms, rather than long-range effects over several 493 unit cells. 494

The first step in calculating such a three-point chiral in-495 dex is to identify all symmetrically distinct triangles formed 496 by three non-colinear, nearest-neighbor surface atoms. Each 497 atom in the surface unit cell will be incorporated into such 498 triangles. For a surface unit cell with only one atom there 499 exists only two different triangles, but this number increases 500 significantly with additional atoms in the unit cell, espe-501 cially if two or more different atomic species are present. 502 For a surface to display a high degree of enantioselectivity 503 two criteria must be met. 504

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Fig. 7. A pseudo-orthogonal 2D surface unit cell (with mirror pseudo-symmetry) will have chiral indices, I_{CA} and I_{CM} , that increase as more unit cells are included in the calculation. A 3 × 3 array of unit cells (a) has smaller chiral indices and a slightly different best-fit mirror orientation than a 13 × 9 array (b).

505	1. At least one triangular, three-atom configuration must
506	deviate significantly from an isosceles triangle (which
507	possesses mirror symmetry and thus is inherently achi-
508	ral). Greater enantioselective potential will be associated
509	with three-point configurations that deviate more from
510	an isosceles triangle.

2. In addition, at least one of these non-isosceles, three-atom
triangles must differ significantly from the mirror images
of itself and of all other triangles. This restriction arises
because a surface will be achiral if every non-isosceles

triangle is present in both enantiomeric forms.

A three-point chiral index, therefore, will be based on the maximum misfit between a three-atom surface triangle and mirror images of itself and of all other surface triangles.

519 4.2.2. Molecule-specific interactions

520 Many studies of chiral selection are concerned with the efficient separation of specific molecular enantiomers. An 521 alternative chiral index strategy, therefore, is to model the 522 relative fit (or lack thereof) of a target chiral molecule on 523 various crystalline surfaces versus that of its enantiomer. One 524 could devise a misfit index that evaluates the conformity of 525 any desired molecule (and that of its enantiomer) adsorbed 526 onto various surfaces, based on likely three-point bonding 527 configurations of the molecule and surface. The optimum 528

surface for chiral resolution will have significantly different 529 misfit parameters (one close to zero and the other large) 530 for the two molecular enantiomers. This approach, which 531 requires realistic atomic models of both the crystal surface 532 and the chiral molecules, would facilitate the identification 533 and engineering of surfaces for optimal selectivity. 534

5. Conclusions

Calculations of the chiral indices, I_{CA} and I_{CM} , of various 536 crystalline surfaces reveal several trends. 537

- Achiral crystals often display strongly chiral surfaces. 538 The (2 1 4) surface of calcite, the (1 1 0) surface of diopside, and various high-index planes of FCC metals, for example, possess surfaces with no obvious mirror or glide plane symmetries, as indicated by their relatively large chiral indices. These surfaces thus are important targets for further study.
- By contrast, the intrinsically chiral surfaces of quartz 545 display relatively low chiral indices. Indeed, the ideal 546 distribution of surface oxygen atoms on the (101) face 547 is achiral. 548
- In oxides and silicates, larger chiral indices are often associated with the presence of both terminal cations and anions. Thus, diopside (110) faces have significantly greater chiral indices than quartz, which has only terminal oxygen atoms.
- 4. Relatively large chiral indices are often associated with stepped and kinked surfaces. This effect is demonstrated both by the high-index faces of FCC metals and by the (2 1 4) surfaces of calcite. 557

No one parameter can define the "degree of chirality" 558 of a surface. Nevertheless, chiral indices provide a direct 559 measure of the deviation of a surface from mirror or glide 560 plane symmetries, and thus can prove useful in identifying 561 promising surfaces for further study. 562

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