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Near-degenerate stereomorphs of the doubly-chiral *hcp*-{21$\bar{3}$1} surface

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ABSTRACT

The surfaces of *hcp* crystals can show a variety of structural features and classes of symmetry that differ markedly from those of simpler *fcc* or *bcc* crystals. The *hcp*-{21$\bar{3}$1} surface, for example, can occur in four distinct stereomorphs, interconverted by a combination of mirror operations (linking degenerate enantiomorphically related surfaces) and/or the removal of the outermost atomic layer (linking non-degenerate diamorphically related surfaces). The strict pattern of degeneracy amongst these stereomorphs is analogous to that found for molecules with two chiral centres, and hence it is possible to view this system as doubly-chiral. Simple nearest-neighbour bond-counting arguments, however, suggest that for {21$\bar{3}$1} even the diamorphically related cases should be near-degenerate, despite the fact that they differ in having either a notably short or notably long interlayer spacing between the outermost layers (ideal spacing ratio 1:5). In the present work, this counterintuitive result is confirmed at the level of density functional theory, both for the ideal and relaxed {21$\bar{3}$1} surfaces of Co, Ru and Re.

1. Introduction: the symmetry and structure of *hcp* surfaces

The high-index surfaces of hexagonal close-packed (*hcp*) materials have barely been explored to date, which is unfortunate because they offer intriguing structure and symmetry possibilities not present in the surfaces of either face-centred cubic (*fcc*) or body-centred cubic (*bcc*) crystals. A recently developed technique of *symmetry-structure surface stereography* (4S) allows us to enumerate and explore these possibilities systematically [1]. The stereographic representations presented in Fig. 1 usefully summarise many of the main findings.

From a structural viewpoint, the surfaces of *fcc* and *bcc* materials can be classified as being *kinked*, *stepped* or *flat*, according to whether respectively zero, one, or more-than-one direction within the surface plane corresponds to a close-packed linear chain of atoms [1,2]. This situation is highlighted in the stereographic representation by the presence of zero, one, or more-than-one "primary structural zone" passing through the pole of the surface normal (see Fig. 1). For *fcc* crystals, the {100} and {111} surfaces are *flat* within this definition; the surfaces lying between {100} and {111}, or between {111} and {110}, are *stepped* (including {110} itself); and all other surfaces are *kinked* [1,2]. For *bcc*, in contrast, only the {110} surfaces are *flat*; the surfaces lying between {110} and {211} are *stepped* (including {211} itself); and all others are *kinked* [1,2].

In the case of *hcp* materials, however, these same three surface structural types are supplemented by three additional categories of surface, namely the *geminal*, *meandering row* and *interrupted-flat* surface types, whose structures are distinguished by the possession of close-packed pairs of atoms lying within the surface plane (and on the stereogram by the presence of at least one "interrupted" primary structural zone passing through the pole of the surface normal). Now those surfaces lying on a primary *and* at least one interrupted primary structural zone are of the *interrupted flat* type; those lying on two interrupted primary structural zones are of *meandering row* type; and those lying on nothing but a single interrupted primary structural zone are of *geminal* type [1].

Regarding their symmetry properties, the surfaces of *fcc* and *bcc* materials can be classified as being *chiral*, *reflexive* or *multiply-reflexive*, according to whether respectively zero, one, or more-than-one mirror plane exists perpendicular to the surface plane (the latter category being sub-divided into *doubly*-, *triply*- and *quadruply-reflexive* cases on a fairly obvious basis) [1,2]. Again these categories may be identified easily by inspection of the stereogram, where each "mirror zone" passing through the pole of the surface normal indicates the presence of a distinct mirror plane lying perpendicular to the surface (see Fig. 1). For both *fcc* and *bcc* crystals, therefore, the {100} surface is *quadruply-reflexive*; the {111} surface is *triply-reflexive*; and the {110} surface is *doubly-reflexive*; all other surfaces with either two repeated Miller indices or one zero Miller index are simply *reflexive*; and all other surfaces are *chiral*.

For *hcp* materials, however, nine distinct symmetry classes are identified, namely: *doubly-chiral*, *pure one-chiral*, *racemic two-chiral*, *glissadic*, *reflexive*, *uniterminated-reflexive*, *doubly-reflexive*, *reflexive-glissadic* and *bayonet*. The additional classes stem from the existence of "glide zones" on the stereogram, relating to surfaces for which a glide plane of the bulk structure lies perpendicular to the surface

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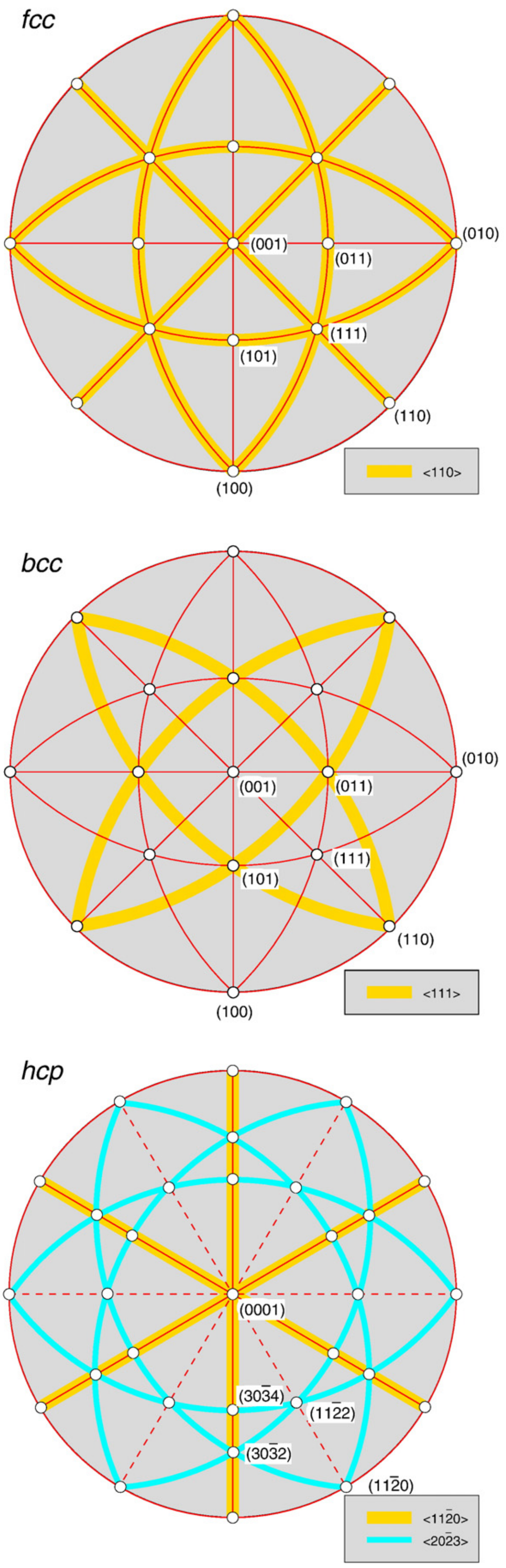

Fig. 1. Stereograms for *fcc*, *bcc* and *hcp* surfaces, showing mirror zones in solid red, glide zones in dashed red, primary structural zones in yellow and interrupted primary structural zones in cyan.

plane. A complete description of these extra classes and their relationship to the glide symmetry would be excessive within the present short paper, but the interested reader is referred to our earlier exhaustive account for details [1]. Selected examples are depicted in Fig. 2 for illustrative purposes.

In essence, the important points to note are that chirality can arise at *hcp* surfaces in two independent ways (*one-chirality* and *two-chirality* in the 4S terminology) and that achirality can arise due to the presence of either mirror planes (the *reflexive* property) or of glide planes (the *glissadic* property). Furthermore, whilst most *hcp* surfaces can have two possible ideal terminations, interchanged by removal of the uppermost atomic layer, a subset have only one (the *untermination* property, arising from a certain kind of truncation symmetry). It may also be shown that *bayonet*, *reflexive-glissadic*, *unterminated-reflexive* and *glissadic* surfaces each exist in only a single stereomorphic manifestation, whilst *doubly-reflexive*, *reflexive*, *racemic two-chiral* and *pure one-chiral* surfaces each exist in two such stereomorphs, and *doubly-chiral* surfaces exist in four. We define a set of "stereomorphic surfaces" to be a number of physically-distinct surface structures with surface normals related by operations within the bulk crystallographic point group. Stereomorphically distinct surfaces may be degenerate and related to one another by mirror symmetry ("enantiomorphic surfaces") or non-degenerate and unrelated by mirror symmetry ("diamorphic surfaces") [1].

With six distinct structural categories and nine distinct symmetry categories, one might anticipate a total of fifty-four different types of *hcp* surface, once all possible combinations are considered. In fact, it may be shown that only fourteen of these combinations can actually occur for the surfaces of the *hcp* crystal structure [1]. Thus the *stepped hcp* surfaces, for instance, can exhibit either *reflexive*, *unterminated-reflexive* or *doubly-reflexive* symmetry, but can never fall into any of the other six symmetry categories. *Doubly-chiral hcp* surfaces, to choose another example, can only ever fall into the *kinked* structural category.

Of the three highest-symmetry *hcp* surfaces (i.e. those most often studied in the literature to date) the {0001} surface has *flat* structure and *bayonet* symmetry; the {10$\bar{1}$0} surface has *stepped* structure and *doubly-reflexive* symmetry; and the {11$\bar{2}$0} surface has *meandering row* structure and *reflexive-glissadic* symmetry. Owing to the importance of Co and Ru in heterogeneous catalysis, these relatively simple *hcp* surfaces have indeed been rather heavily studied, but less symmetric cases have not. One notable exception, however, is the case of Re{21$\bar{3}$1}, a *kinked* surface in the *doubly-chiral* symmetry category, which has been investigated recently by the Madey group [4–7].

In fact, the {21$\bar{3}$1} surface may be demonstrated to have the smallest primitive surface unit cell of all *doubly-chiral hcp* surfaces [1]. The four stereomorphic versions of this surface are given the *composite symmetry symbols* DD_{τ}, LL_{τ}, $\mathrm{DL}_{\bar{\tau}}$ and $\mathrm{LD}_{\bar{\tau}}$ within the 4S scheme, of which the DD_{τ} and LL_{τ} stereomorphs for this particular surface feature a long outermost interlayer spacing (a situation symbolically labelled by the descriptor λ), while the $\mathrm{DL}_{\bar{\tau}}$ and $\mathrm{LD}_{\bar{\tau}}$ stereomorphs feature a short outermost interlayer spacing (labelled by the descriptor σ). Within the composite symmetry symbol, the first letter (D or L) indicates the *one-chirality* of the stereomorph (arising due to truncation of the Bravais lattice) while the second letter (also D or L) indicates the *two-chirality* of the stereomorph (arising due to the relationship between the structural basis vector and the surface-truncated lattice); the subscript (τ or $\bar{\tau}$) indicates that the stereomorph is one of a pair of non-degenerate structurally complementary terminations that can be interconverted by removal of the uppermost atomic layer (implying that two stereomorphs sharing the same subscript are necessarily identical to within a possible mirror operation, while two stereomorphs