MINIMAL SURFACE DESCRIPTION OF CRYSTAL STRUCTURES

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Since the birth of crystallography, solid state crystalline forms have been analysed in terms of aggregates of plane-faced Euclidean polyhedra. Crystals have been viewed as translationally symmetric collections of "unit cells" - the basic building block of a crystal - with atoms located in special positions within the polyhedral array which describes the crystal. This approach has been vindicated largely empirically, with surprisingly recent attempts to place it on firm theoretical ground [1].

Thus, the symmetry of the macroscopic crystal reflects the symmetry of the unit cell, giving rise to the characteristic prismatic morphologies of crystal faces. The archetypal "classical" solid-state crystal is completely specified by its unit cell, with translation periodicity and symmetry dictated by the unit cell geometry. In the jargon of a crystallographer, the classical crystal has complete "long-range order".

In contrast, another atomic arrangement exists in the solid state. This is conventionally described as a random network, with short-range order with respect to each skeletal atom (eg. silicon in silicate glasses) but lacking long-range order [2]. These short-range ordered structures have been described as random packings of various polyhedra [3].

For decades solid-state materials were conveniently classified as crystals or glasses - complete order or statistical chaos. However, over the past ten - fifteen years, cracks have appeared in this scheme. So-called "modulated structures" have been found where the crystal consists of a classical component, as well as a modulated structural component which does not conform to the translational symmetry requirements of the backbone classical component. In fact, in some cases the translational periodicity of the modulated component has been found to be an irrational multiple of the translational periodicity of the backbone structure - so called incommensurate structures [4]. Recently, a body blow was dealt to the corpus of classical crystallography with the announcement of an aluminium:manganese alloy containing atomic arrangements with long-range icosahedral point symmetry [5] - a forbidden crystal symmetry since a tesselation of R^3 by translationally symmetric icosahedra is impossible. (The structure is remarkably similar in cross-section to the Penrose tiling pattern of R^2 which requires 2 unique building blocks.). It is widely conjectured that this alloy is the first example of a whole class of "quasi-crystals" - with long range orientational order, but short range translational order.

Thus the conventional crystallographic solid classification of long-range order (crystals) or disorder (glasses) has grown to a virtual continuum of glasses, "quasi-crystals", incommensurate structures and crystals.

In order to accommodate these newcomers, solid state crystallography has adopted tesselations of R^4 [6] for incommensurate structures and R^6 for quasicrystals [7]. While this approach seems reasonable as a descriptive technique, it has some serious physical inconsistencies. All models are unable to account for structural transitions between the various structure types. For example, a single sample of the aluminium:manganese alloy contains regions straddling the spectrum of solid phases; from glass to ordered crystal in addition to the quasicrystalline phase [8]. Also incommensurate crystal phases are frequency associated with crystal phase transitions.

It would be more satisfying if all solid state phases could be interpreted within a single covering space - preferably R^3. Here we describe a special class of 2 manifolds - periodic minimal surfaces - and their applications to 'classical crystallography' - and speculate as to the usefulness of a 2-manifold description of solids in their totality.

About 3 years ago, one of us (S.A.) realised that complicated crystal structures, which have units cells containing many atoms, consisting of 2 interpenetrating networks of simpler structures with little bonding between component structures, may be more simply described using triply periodic minimal surfaces in R^3. The minimal surface separates each structural component, with the 2 structures occupying the labyrinth on either side of the surface. In most cases, the structures can be understood solely with reference to the minimal surface, with atoms occupying special positons off the surface.

This description has subsequently been applied to simple crystal structures, where the minimal surface appear to fit (calculated) electrostatic equipotentials, with charged atoms in either labyrinth [9]. For example, Schwarz' P-surface (figure 1) describes the equipotential surface of CsCl, with Cs^+ ions on one side of the surface and Cl^- ions on the other. There is also an empirical correlation between electrostatic field and Gaussian curvature, suggesting powerful links between differential geometry and solid-state physics [10].

In some cases the atoms are situated at special positions on the periodic minimal surface, where the surface consists of all field lines between atoms. Any point, $\underline{r}$, on the surface satisfies

$$\frac{\delta \underline{E}}{\delta \hat{n}} (\underline{r}) = 0$$

(where $\underline{E}$ is the electrostatic field, $\hat{n}$ is the surface normal vector at $\underline{r}$) and we call the surface the 'critical field surface' [11] (c.f. the conjugate nature of field and equipotential lines in 2-D electrostatics) [12]. Chemical bonds between structures are described by geodesic arcs on these surfaces, which need not be straight lines.

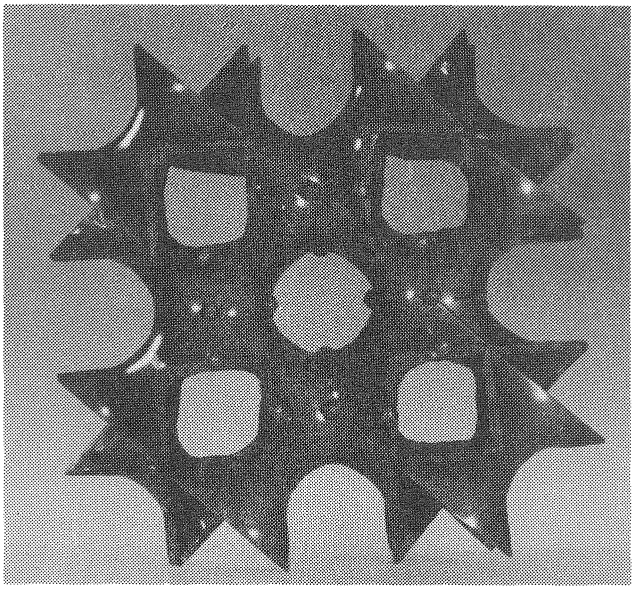

Fig 1: Schwarz' P-surface. This surface describes an electrostatic equipotential of the CsCl structure, with Cs^+ cations in the centre of the picture, and Cl^- anions in the four spaces around the central hole on the other side of the surface (and equivalent positions). The P-surface also represents the critical field surface for the network silicate, sodalite. The small spheres on the surface represent silicon atom positions in the sodalite structure, where they occupy all saddle points of the surface.

The (vector) electric field on the critical field surface may be described using singularities located at atoms (sources, sinks), midway along (like) atom-atom bonds (2-fold saddles), and inside atomic rings (multi-fold saddles). Thus topological characteristics of solid structures may be determined using Hopf's theorem relating genus to singularity index [13]. So far we have found both orientable and non-orientable surfaces to be applicable to crystal structures.

Structural Transitions

The advantage of a minimal surface description of crystal structures is clear when considering phase transitions. For example, the flat points of Schwarz' F-surface describe the face-centred cubic atomic lattice, while the flat points of the gyroid describe body centred cubic packing - corresponding to the structures of the austenite and martensite phases of iron. (The martensitic phase transition is crucial to the formation of useful steels.) Austenitic iron transforms from the fcc to the bcc (martensite) phase. This is conventionally described by the Bain mechanism, with the fcc unit cell distorted into the bcc unit cell - a purely phenomenological model [14].

In fact, the minimal manifolds describing martensite (gyroid) and austenite (F-surface) are isometric surfaces, related by the Bonnet transformation. If we Bonnet transform the F-surface (suitably scaled to the austenite unit cell dimension) to the gyroid, we find the new unit cell dimensions (which are fixed by the isometry) correspond closely to those found in Nature. Thus the structures are related through an isometric family of minimal manifolds. The inherent relative orientations forced upon the structures by the Bonnet transformation are also consistent with those seen in Nature (where bulk shears of the material occur, so that the straight line scratches on the surface of austenite are rotated in the martensite) [15] (figure 2).

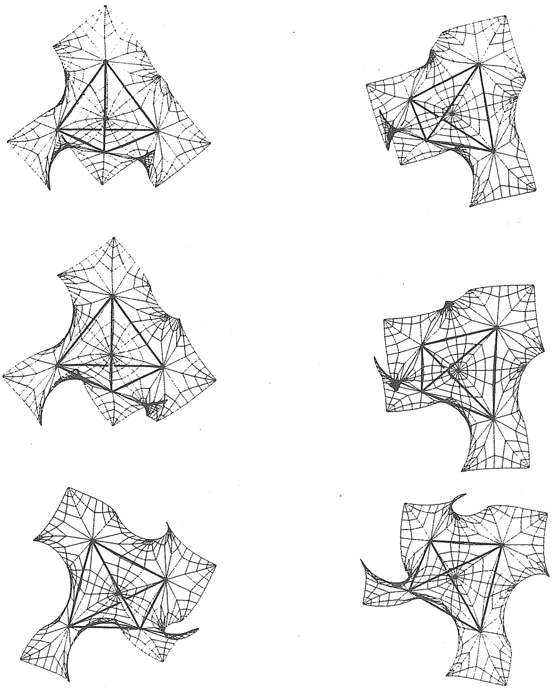

Fig 2: The Bonnet transformation from the F-surface to the gyroid. If the association parameter for the F-surface is 0°, the gyroid is formed for $\Theta = \pm 38.015^\circ$. The figure shows, from top to bottom, surface portions for $\Theta = \pm 10^\circ$, $\pm 20^\circ$ and $\pm 38.015^\circ$ (left and right images). Atoms are located at the vertices of the tetrahedra (flat points of the surface), and transform from face-centred cubic symmetry (F-surface), to body-centred cubic (the gyroid). The relative orientations of the $\pm\Theta$ surfaces show the mirror related intermediate structures.

The Bonnet transformation is of further potential interest in describing incommensurate structures. The surfaces intermediate to periodic minimal surfaces appear to be non-periodic in the sense of incommensurate structures - a natural explanation to the frequent existence of incommensurate structures during phase transitions.

A point on an associate surface to a linear periodic minimal surface is related to the known surface and adjoint surface to the known surface via:

$$(1) \qquad \underline{r}_i = \underline{r}_i\,(S) \cos\theta + \underline{r}_i\,(S^*).\ \sin\theta$$

where θ is the association parameter of the Bonnet transformation. Equation (1) is consistent with an understanding of incommensurate structures as the resolution of two independent structures, modulated 90° out of phase [16]. Efforts to directly compare incommensurate structures with aperiodic isometric relatives of simpler periodic minimal surfaces are severely hampered at the moment by lack of suitable polynomials to paramatrise isometric families of minimal surfaces via the Weierstrass equations. Nevertheless, we are confident that the incommensurate structures arise naturally within the context of minimal surfaces - in contrast to their uneasy alliance with "classical crystallography".

This manifold description of solid state structures suggests tantalising concepts for understanding other structures. Since second order phase transformations involve continuous changes in atomic position [17] we expect all such transformations to be describable in terms of homeomorphisms of 2-manifolds. Thus, the orientability of structures in terms of their manifold must be preserved during the transformation. Minimal surface preserving homeomorphisms would be expected to be most favourable, limiting possible homeomorphisms to be conformal surface transformations [18], placing useful restrictions on structural candidates for phase transformations.

Since the quasi-crystal aluminium:manganese alloy has been found to have coexisting phases of glass, crystal and quasi-crystal, we expect the structure of the quasi-crystal to be related via a surface transformation to the manifold description of the crystalline phase. If we consider the representation of the discrete group [3,5] in the sphere (the symmetry group of the icosahedron) as the Gaussian image of a minimal surface [19], we may generate an infinite family of minimal surfaces with icosahedral point symmetry. Work is underway to determine whether these surfaces adequately account for the atomic structure in the quasi-crystal. Again, the concept of a quasi-crystal seems to accommodate a 2-manifold description more naturally than more complex higher dimensional theories, and the success of such a description extends to a natural understanding of the coexistence (and hence transformation) of the phases; all phases are related by a homeomorphism (at least). Finally it should be noted that 2-manifolds other than minimal surfaces are likely to be useful. "Stationary" surfaces in the sense of Nitsche are also likely to be of use in modelling the solid state [20].

Conclusion

Periodic minimal surfaces in R^3 have been found to describe crystal structures and structural transitions. The proposal that a 2-manifold description of solid structures permits a physically accessible understanding of other less ordered solid forms, with natural explanations of the increasingly observed phase transitions between these forms, in terms of 2-manifold homeomorphisms.

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