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# "Generalised Crystallography"[1]

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"Nulla cogente natura, sed concursu quodam fortuito atomorum"
Cicero[2] (106-43 BC) De Natura Deorum 1:24
*[Not by teleology, but by the chance association of atoms]*

**X-ray crystal structure analysis can now be seen as a special kind of microscopy which is being extended to the recognition and examination of many kinds of ordered structure more general than crystals and which leads to their synthesis or construction by various methods. Electron microscopy and many other techniques now combine to give a coherent science of structure at the scale range of Ångstroms to microns, atoms to assemblies visible to the eye, which should continue to be called "crystallography" although it overlaps with nanotechnology, molecular biology and solid state physics. Most generally, "a crystal is a structure the description of which is much smaller than the structure itself" and this view leads to the consideration of structures as carriers of information and on to wider concerns with growth, form, morphogenesis and life itself.**

Democritos of Abdera (ca. 400 BC) first formulated the idea that the properties of all matter, including life and mind, might be understood in terms of an underlying fine structure. This approach was, however, actively suppressed by the propagators of the view that things are determined from above[3] (rather than from below), in a hierarchy of scales. The text of Lucretius' Latin poem, expanding on Dremocritos, laying out a complete vision of how the macro-world might be explained as a consequence of the micro-world, was first printed in Brescia in 1473, although it must have been written about 60 BC. The confusion between the real world and the noumenal world, propagated by Plato[4] and numerous religious and philosophical leaders, is still with us, made more acute by information, dysinformation, ideology and post-modernism[5].

The aim of **generalised crystallography** is to understand the properties of matter, inert and living, at our human scale, in terms of the arrangement and operation of atoms at a level which, until X-ray crystal analysis, remained unobservable. The techniques for the observation of atoms are now so numerous that the term '**crystallography**' is perhaps no longer suitable and might now be replaced by **'structural chemistry'[6]**. The manipulation in space of structures at the level of atoms and molecules is now the science of '**nanotechnology**', but it was only in 1874 that Van't Hoff[7] began to draw the consequences of the spatial arrangement of atoms in with the postulation of the tetrahedral carbon atom, although Archibald Scott Cooper (1831-1892) had discussed tetrahedral carbon atoms in 1858 and Pasteur had made the crucial discovery of molecular cheirality in 1848[8]. René-Just Haüy had noted the left- and right-handed forms of quartz crystals and was responsible for the hypothesis that macroscopic crystals were made up of identical unit cells which were below the level of direct observation, thus giving a special case of the connection between the microscopic and macroscopic worlds. In 1934 J. D. Bernal and Dorothy Crowfoot (Hodgkin) showed that a protein actually had a structure, with each atom in its proper place, and today an immense project of "proteomics", to find the structure of all proteins involved in human life, is under way. The relation of DNA to protein, the dialectical relation between description and referent, was the key discovery of the last century and has meant that crystallography is also now concerned with information, informational structures, growth and form and morphogenesis generally, involving dynamic as well as static structures in space. Classical crystallography has given access to what atoms do. Crystallographers, for example A. D. Booth at Birkbeck College, were foremost in the development of the electronic computer and had a sharp appreciation of the problems of information handling.

## The reality of spatial structure

Isaac Newton (1642-1727)[9], being occupied with alchemy, suspected that the chemical properties of matter depended on atoms interacting in space, like the planets, but he had no access to this level.

> "I suspect that they may all depend upon certain forces by which the particles of the bodies, by some causes hitherto unknown, are either mutually impelled towards one another, and cohere in regular figures, or are repelled and recede from one another. These forces being unknown, philosophers have hitherto attempted the search of Nature in vain;" (Preface to the Principia..)

These forces are now well understood and their use in computing the properties of real crystals and molecules verifies their accuracy, and gives every confidence in predictions for hypothetical systems, although the prediction of the topology of complex crystal structures from composition alone is still elusive.

The empirical model-making tradition of William Barlow[10] and W. J. Pope, W. H. and W. L. Bragg, Kelvin (William Thomson (1824-1907))[11], Bernal, Crick and Watson and many others, can be traced to the Enlightenment and the escape, started by Galileo, through experimental testing of theories, from the religious world outlook, through the Reformation and Dissent to modern humanism[12]. Model-making has recently been enormously enhanced by the use of the computer.

Computer graphics can do almost everything, but our tactile senses are coupled to our vision and our mental manipulation of space, so that physical models still help the understanding. Stereolithography is a rapidly developing technique which fabricates three-dimensional models from plastic providing effectively a general 3-D computer printer[13]. It can present the results of 3-D image processing from microscopy as solid models for the committee table. Model-making remains essential in thinking about the microcosmos[14], strange as quantum mechanics has now revealed it to be.

The particular British tradition in crystallography has been characteristically empirical, model-making and engineering, flowing from the Industrial Revolution. In contrast, only recently, a Franco-German physicist and academic, confirmed the characteristics of the rather different continental tradition: "... in the case of conflict between theory and practice, the Gallo-Germans tend to choose theory"[15]. But, however, the quantum world is not like the world at the human scale and only very sophisticated experiments can elucidate it. The electronic devices of nanotechnology are now so small that quantum effects cannot be neglected[16]. Theory and experiment now intimately interact and, for example, it has been confirmed that carbon-60 molecules are diffracted in the same way as electrons and that the traditional billiard ball models of molecules are now not enough. The problems of reductionism are answered immediately from the consideration of the wave equation for two electrons where there is a cross-term so that two electrons together are more than the "sum" of the parts.

Immense progress has been made in understanding our human perception of spatial structures developed in the course of our evolution although "It is because nothing required us to apprehend atomic structure during our evolutionary development that we are incapable of understanding what it is that quantum physics describes."[17] (David Mermin). But now we have to use physical models in more subtle ways to exploit what we can do well as animals in order to understand the counter-intuitive.

The Industrial Revolution in Britain required the mastery of reality[18] and people such as Boris Mikhailovich Hessen (1883-1938)[19] showed, in 1931, that even Newton was greatly affected by the technological problems and needs of the day. Today the connection between science and technology is much closer, being recognised in the 1960s as the scientific and technological revolution which now provides economic, military and political power.

## Generalised microscopy

It is somewhat of an accident that the X-ray diffraction analysis was the first technique to give direct access to structure at the scale of atoms[20]. W. H. Bragg first added sine waves together linearly by photography to give a picture of the positions of the atoms in diopside. The phases in which the waves were added came from the comparison of the observed and calculated structure factors. However, a real crystal is the non-linear superposition of waves, the connections between the phases contain the chemistry and the non-linearity is expressed as the Karle-Hauptman determinant. Later, W. L. Bragg, and separately Martin Buerger at MIT, came close to the invention of the hologram which was achieved by Denis Gabor at Imperial College as a result of considering the electron microscope. In attempts to implement the techniques of X-ray structure analysis B. K. Vainshtein greatly deepened the understanding of electron microscopy which now complements X-ray techniques[21]

The emphasis on infinite periodicity, which is what a Bragg diffraction spot provides, has somewhat distorted the development of crystallography. It led to the use of the 14 Bravais lattices and the 230 crystallographic space groups which presume infinite crystals. Development could have taken another emphasis, namely the ways in which space-filling polyhedra pack together. This approach, pioneered by B. N. Delone[22], started with 24 space-filling polyhedra and asked about local order, developing a theory which asked "out to what range are identical points required to have identical surroundings to generate crystallinity?" rather than, given an infinite repeating structure, asking "under what operations is this whole object invariant?" Delone's approach is more suitable for a unified theory of crystals, quasi-crystals, hierarchic and amorphous or statistically ordered materials.

Of course the development of other instruments, especially the atomic force microscope and its many variants, the synchrotron and the neutron generator, has enormously extended the experimental examination of crystals and other materials and has made many kinds of observation and experiment possible in combination with microscopy. Solid (and indeed liquid and gas) state physics has been greatly developed and merged with crystallography.

## **Generalised geometric algebra** (Clifford Algebra)

It is clear, particularly with the entry of considerations of six-dimensional geometry into analysis of the structure of quasi-crystals, that Clifford[23] algebra is the appropriate language for generalising crystallography[24]. However, although present practices are adequate, the notation needs popularising and it would be desirable to recast the formalism of classical crystallography in Clifford form, although nothing new would emerge and the results would be valuable chiefly for extension to N-dimensions.

Barycentric coordinates, developed by Möbius, where the coordinates of a point are given as the weighted sum of the coordinates of four other points is also a useful way of describing structures free of arbitrary axial systems but the mathematical description of structure, independent of arbitrary axes, is still not perfected. It would be desirable, as Lazare Carnot perceived, to be able to describe spatial structures entirely in terms of chemically significant structure invariants (bond lengths = distance geometry; bond angles and torsion angles), but there is still some way to go.

Altogether, the development of computer systems, most obviously "Mathematica", has greatly extended our mathematical capabilities at all levels.

## **The description of structure**

With the discovery of the genetic code and the problems of the transmission and encryption of data, the whole topic of information has become connected with that of structure. DNA describes a protein, if we know the language, but both descriptor and referent are made of atoms which have to follow the laws of chemistry. We can now ask how much information a structure contains, what is its complexity and, very significantly, following G. Chaitin, what is the length of the smallest computer programme necessary to generate or describe it. For example, the number of operations necessary to sort a sequence of N numbers into a specified order is about $N \log_2 N$. The analogy with natural language thus enters crystal chemistry. We might note that Charles Babbage invented a "Mechanical Notation", an abstract general descriptive language, which he used a great deal, and that this would bear investigation, since the complex machines which he designed with its aid have proved successful. The descriptions of inorganic crystal structures are still rather rudimentary and without great predictive value. Enormous databases are being compiled and await exploitation in unexpected directions. Questions of the mathematical description of shape and form[25] lead to questions as to whether corresponding natural laws operate. There is still much to gain from a dialogue between mathematics and crystallography.

The computer has made possible the exploration of spatial structures of various kinds, especially enabling the construction and use of huge databases. For example, certain categories of networks related to those involved in zeolites can be exhaustively enumerated[26] and periodic minimal surfaces have entered the vocabulary of the description of the surfaces which separate networks. In the crystallographic domain Elke Koch and Werner Fischer, in particular, have extended traditional crystallography by the discovery and enumeration of surfaces which are useful for the description and understanding of structures and which supplement the traditional polyhedra as referents. Liquid crystals, mesoporous zeolites, photonic band gap structures and Fermi surfaces can be comprehended within such descriptions, but they may occur on all scales from chemistry to mega-engineering.

## **Crystal chemistry** and **informatics**

The development of gigantic computational power, and the appearance of the first generations of mathematicians able to use it, has begun to change crystal chemistry. It has been remarked that Linus Pauling, who formulated the principles of structural crystal chemistry, used only a perhaps a thousandth of the information now available, but nevertheless produced rules which have not required significant correction. Data bases have been compiled.

The IUC have adopted a somewhat retrograde definition of crystal depending on diffraction spots which gives an undue emphasis to Fourier analysis and periodicity. The most general definition, echoing work by G. Chaitin, might be that "a crystal is a structure the description of which is much smaller than the structure itself". Information has now entered explicitly into the structure of matter. Some structures composed of atoms contain information about other structures made of atoms. In the rush to unravel genetics the role of shape is overshadowed. The DNA and protein systems evolve together. Genomics is only half of the secret of life; the other half of the secret is shape[27].

## Recognition of higher level structure

N. V. Belov[28] made the perceptive comment that:

> The exclusion of a five-fold axis for crystals, as well recognised, results from the impossibility of reconciling it (and axes of order greater than 6) with the "lattice state" of crystalline matter. It would appear, then, that for small organisms the fivefold axis represents a distinctive instrument in their struggle for existence, acting as insurance against petrifaction, against crystallisation, in which the first step would be their "capture" by a lattice.

The golden number entered crystallography rather dramatically because it is the most irrational number, that is the furthest from a rational ratio. Thus, strongly icosahedral local order is able to prevail over the pressure for periodicity and produce the surprise of quasi-crystals. This represented a break with traditional crystallography although foreshadowed by the discovery of incommensurable magnetic structures and modulated structures.

The present challenge is to deal with materials which have hitherto been characterised as poorly crystallised but can now be seen to have order of a different kind. For example, crystals with incommensurate modulations gave X-ray powder diagrams which could not be satisfactorily indexed as crystals and were thus thought to be mixtures. Indeed a material now recognised to be quasi-crystalline was reported many years before the actual discovery[29].

In general, for crystal structure analysis of organic compounds and biomolecules, the structure of the molecule is primary and the crystallisation is simply a means to this end. In inorganic and biological materials (such as fibres, membranes and networks) the properties of interest are often at the level of the crystal aggregate. For example in zeolites, the pore structure is the major concern. Now, however, the assembly of complex components into crystals and other types of order is of great technical concern.

## Hierarchic structures

Fractal structures, where there are self-similarity operations, were proposed by Shubnikov[30]. These are clearly incompatible with atomicity, because of the infinity regress, but many real structures are hierarchic with perhaps six discernable levels, the rule of composition at each level being different. Bernal drew attention to the hierarchic universe proposed by Charlier where  the local surroundings could be everywhere the same but where the density remained small. Attempts to pack icosahedra hierarchically, giving clear rules for filling in the gaps recursively, led to a model for the quasi-crystals which were discovered about 1982. This model, depending on local interactions, has eventually prevailed over the global ordering model.

## Synthesis   On Growth and Form

Could X-ray diffraction be played backwards to produce periodic nodal surfaces like Lippmann films, where standing waves of light are used to produce periodic layers of silver atoms in a photographic emulsion as in an early form of colour photography ?

Methods of building structures, such atomic beam deposition, manipulation by atomic force microscopy, electron beam and X-ray etching have almost reached atomic resolution.  Chladni plates, investigated by Faraday, produce structures at nodes or anti-nodes with the wavelengths of sound waves. Nodal surfaces in three dimensions are at present being actively investigated[31] mathematically with potential applications in devices for photonics.

In crystals nodal surfaces are by way of being the materialisations of high-order structure invariants, sums of symmetrically related density waves where the sum of the reciprocal lattice vectors is zero. Triple invariants are central to the direct methods of crystal structure determination. Tortuously, Cyril Smith (1968) expressed the wave/particle duality as: "Matter is a holograph of itself in its own internal radiation".

There is great interest at present in **photonic band gap** materials, a bibliography obtainable on the Internet having some 2000 entries. The aim is the construction, for use with digital opto-electronics devices, of triply-periodic dielectric networks having an optical band gap at about 1.5 microns. It is not clear yet whether chemical, physical or engineering methods will be the most successful, but the question of synthesising, for example, opal crystals, has moved to the forefront, now for engineering purposes as well as for jewellery. The very early work of H. Zocher[32] and later S. Hachisu and the examination of *tipula iridescent virus*[33] might be recalled. Crystallography may occur at all scales.

Production of such large period structures might be done as liquid crystals, as micro-deposition on suitable substrates, by ion-beam or electron beam or laser beam manipulation or etching or by mechanical drilling.

The whole field of growth and form is now very active with the synthesis of shapes more general than those of crystals[34] and has a new coherence as nanotechnology.

Many of the themes mentioned here were first articulated in a paper[35] presented to the Yugoslav Centre for Crystallography in June 1975 where the situation was summarised as: "Crystallography is only incidentally concerned with crystals ... crystallography is rapidly becoming the science of structure at a particular level of organisation, being concerned with structures bigger than those represented by simple atoms but smaller than those of, for example, the bacteriophage. It deals with form and function at those levels, particularly with the way in which large-scale form is the expression of local force."

## Acknowledgments

On this special occasion it is appropriate to acknowledge, as well as my immediate colleagues, especially those who have given me a congenial home at Birkbeck, the long- range influences of three of the great polymaths and encyclopaedists who continue to affect us with their perceptions of science and civilisation. These are, Titus Lucretius Carus[36] (ca. 99-55 BC), Denis Diderot (1713-1784) and John Desmond Bernal (1901-1971). Modern crystallography has taken place within the Republic of Science, the community of those who seek to acquire "reliable knowledge" about the natural world by verifiable experimentation rather than by revelation and it has been a great privilege to have taken a small part in it.

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[2] Cicero, better known for his literary writings, was the editor of the text of Lucretius' "De rerum natura", ["On the Nature of Things", a title also used by William Bragg for a lecture series on the structure of matter at the Royal Institution] . He also found and restored the tomb of Archimedes in Sicily and perhaps also saw the anti-Kythera machine, a complex analogue astronomical computer, or something like it. Our school teaching has underestimated the scientific activities of antiquity.

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[3] Plato in particular, in spite of the reputed legend "let no one ignorant of geometry enter here", is supposed to have suppressed the works of Democritos and propagated the technology of state myths to which would be attributed the social order.

[4] George Sarton, doyen of historians of science, labels the influence of Plato's "Timaeus" as an evil one.

[5] Alan Sokal and Jean Bricmont, "Intellectual Impostures", Profile, London 1998.

[6] However, the social structure of the those dealing with crystallography is so coherent and is formalised by many national crystallographic societies and by the International Union of Crystallography, that a change of name would be quite undesirable, although the subject matter and techniques may change. See "Fifty Years of X-ray Diffraction", ed. Ewald, P. P., published by the IUC in 1992.

[7] Van't Hoff, J. H., "Stereo-isomerism", Encyc. Brit., (11th edn.), **25**, 890-895, (1910)

[8] Bernal, J. D., "Science and Industry in the Nineteenth Century", London, 1953.

[9] Newton was born, a posthumous child,, on Christmas day in the year (1642) that Galileo died.

[10] Tandy, P., "Crystallography and the geometric modelling of minerals: a reflection on the models in the Natural History Museum, London", Crystallography News (BCA), 15-23 (June 1999) and earlier in "The Geological Curator", 6 (9), 333-338, (1998). Groth, P., "Physikalische Krystallographie", Leipzig, (1895) (contains a large section of advertisements for crystallographic models).

[11] See the important essay "Models", by Ludwig Boltzmann in the Encyclopaedia Britannica, (11th edn. 1910).

[12] P. Redondi, in "Galileo, heretic" suggests that Galileo was induced to plead guilty to the heresy of heliocentricism so that the more serious crime of atomism (which would question the nature of trans-substantiation) should not be ventilated.

[13] There are about four different types of machine. It is used for making prototypes and models in the size range of 1cm to 30 cm. but is as yet not economic for serial production.

[14] Microcosmic salt, an ammonium sodium hydrogen orthophosphate, was so named because it is found in decomposing human urine, "the microcosmos".

[15] Blanchard, P., Alliage (Nice), no. 37/38, (1999). p.47.

[16] At the other end of the scale of sizes, the devices for using Global Positioning System, now extremely cheap through nanotechnology, apply the non-intuitive equations of general relativity.

[17] Nature, **383**, 772, (31 Oct. 1996).

[18] Rudyard Kipling, in "The Secret of the Machines", wrote "But remember please the Law by which we live, / We are not built to comprehend a lie, / We can neither love nor pity nor forgive, / If you make a slip in handling us you die." (Not really well-designed poetry, but like the first machines themselves!)

[19] See the essay on Hessen by Paul Josephson (forthcoming). Introducer of quantum mechanics and relativity into Russia, Hessen's fate showed the tight connections between science, technology, ideology and power.

[20] James Clerk Maxwell's essay on atoms (from the 9th edn.) is to be found quoted in the 11th edn. of the Encycl. Brit. under "molecule". The scale of molecular structure was then (about 1900) estimated at $10^{-8}$ cm.

[21] Zou, X., "Electron crystallography of Inorganic Structures", Stockholm University, (1995)

[22] Delone, B. N., Padurov, N. and Aleksandrov, A., "Matematicheskie Osnovy Strukturnogo Analiza Kristallov", ONTI, Leningrad-Moscow, (1934)

[23] William Kingdon Clifford (1845-1879) (whose tomb is in Highgate Cemetery) was also concerned with the application of mathematics to chemical structure as "chemico-algebraic theory".

[24] A Mathematica package "Clifford Algebra Calculations" has been prepared by Jose Luis Aragon who has also demonstrated crystallographic calculations in several papers: **joseluis@iec.csic.es**.

Gómez,A., Aragón, J. L. and Dávila, F., "A geometric algebra description of quasilattice planes and quasicrystal morphology"

[25] Lord, E. A. and Wilson, C. B., "The Mathematical Description of Shape and Form", John Wiley, (1984)

D'Arcy Wentworth Thompson, "On Growth and Form", Cambridge, (1917)

[26] Olaf Delgado Friedrichs, Andreas W. M. Dress, Daniel H. Huson, Jacek Klinowski and Alan L. Mackay, "Systematic enumeration of crystalline networks", Nature, 400, 644-647, (1999).

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[36] R. E. Latham's translation in Penguin Classics: "Lucretius: On the Nature of the Universe" (revised edition, 1994) provides understanding, but I happen to have the (second) edition of Thomas Creech (1659-1700), London, 1717, which is a marvel of scholarship, and of the technology of printing, and which provides direct access to the actual words of the author formulated more than two thousand years ago. Lucretius final words on chemical bonding: "When the textures of two substances are mutually contrary, so that the hollows in the ones correspond to full sections in the other and vice versa, then connection between them is most perfect. It is even possible for some things to be coupled together, as though linked by rings and hooks" is immediately followed by a horrific description of the medical and social effects of the plague in Athens. Both topics are still worth our attention.