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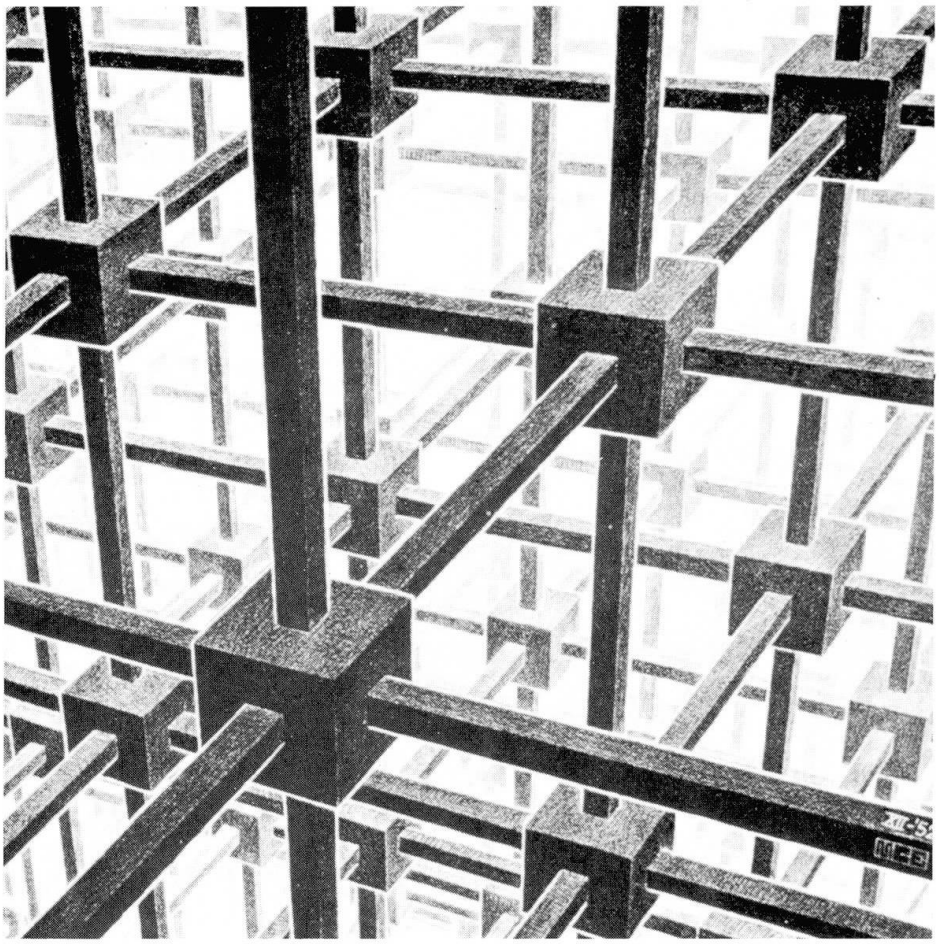
The symmetry of a point in a lattice: beginning and future

by *S.S. Hafner*[1]



The point in the lattice: from Paul Niggli 1915 to E.C. Escher 1975.

Reproduced from "Die Welten des M.C. Escher", Fig. 181 "Kubische Raumaufteilung"; 1952. Heinz Moos Verlag München 1971, second edition.

History

For many scientists, Paul Niggli was a petrologist of excellence with an exceedingly broad background, showing competence in fundamental chemistry and physics. In fact, his very first papers were concerned with geological topics. When he published his first crystallographical paper in 1915, which was on the formation of simple and isotypical crystals and the effect of external factors on the structure of crystals (NIGGLI, 1915), he had already written a large number of papers on fundamental petrological problems, especially on physical and chemical conditions of formation of magmatic and metamorphic rocks. In the year 1915, ho-

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wever, a new activity became apparent in Niggli's work: crystallography. It was an activity that was completely decoupled from his petrological interests at that time, at least for the first few years. It dealt with the symmetry-related description of the point lattice as base for the macroscopically homogeneous crystal. Niggli's reflections lead soon to the well known book "Geometrical crystallography of the discontinuum" (NIGGLI, 1919) which had unusual impact on crystallographers until present time. The manuscript was finished 1917, and the book appeared in 1919. It was the time soon after Max von Laue (1879–1960), Professor of Theoretical Physics at the University of Zürich 1912–1914, had performed diffraction of X-rays from the atoms in a crystal thus proving the existence of the crystal lattice by this experiment (FRIEDRICH, KNIPPING and VON LAUE, 1912; VON LAUE, 1914), and the time when William Henry Bragg (1862–1942) and William Lawrence Bragg (1890–1971) experimentally determined the first crystal structures using X-ray diffraction.

While Niggli's book was written during a revolutionary time for science, it included new ideas which turned out to be most fruitful for a more fundamental understanding of the structure of crystals in the following decades. Niggli's way of thinking developed naturally from classical crystallography of the 18th and 19th centuries. Before Laue's experiments, crystals were studied from outside only. It was Nicolaus Steno (1638–1686) who in his book "De Solido Intra Solidum Naturaliter Contento" (ODENSE UNIVERSITY PRESS, 1969; STENSEN, 1669/1967) came to the conclusion that plants grow from the interior to their surfaces; crystals, however, grow by deposition of material from outside onto the surface. The book was published 1669 as third part of his Dissertatio Prodomus. With his statement that careful study of the crystal surfaces would be needed to understand the construction and formation of a crystal, Steno was way ahead of his time:

> A crystal grows while new crystalline material is added to the exterior planes of the already formed crystal, so that there is no room at all here for the opinion of those who assert that crystals grow vegetatively, that they draw their nurrishment from the side on which they are attached to the matrix[1], so that the particles thus received from the fluid of the rock and transmitted into the fluid of the crystal are added internally to the several crystal particles (translated from Latin, ODENSE UNIVERSITY PRESS, 1969 p. 175).

Steno's observation that crystal surfaces exhibit only certain angles which are found to be always the same on different specimens, the law of angle invariance, was the basis for the following 250 years of mineralogical research. During that time mineralogists devoted themselves extensively to the minute description of the crystal faces and precise measurement of the angles between and over face edges. During the time of Auguste Bravais (1811–1863), the recognition of the symmetry relationships reflected by the faces and angles of a crystal eventually led to the conclusion that crystals consist of a lattice formed by very small particles which are separated from each other and periodically arranged. This was about half a century before Laue's diffraction experiment.

It was Niggli who was able to describe the periodical arrangement of points in a lattice in general terms using the principles of symmetry. His presentation developed mainly from the basis of the previous work of Arthur Moritz Schoenflies (1853–1928), at that time Professor of Mathematics at the University of Frankfurt, and by contacts with Arrien Johnsen (1877–1934), at that time Professor of Mineralogy at the Humboldt University of Berlin. References were also made to related studies of Evgraf Stepanovich v. Fedorow (1853–1919) and Leonhard Sohncke (1842–1897). However, papers of Schoenflies and Johnsen were cited frequently in the early crystallographical work of Niggli.

Niggli introduced new definitions which proved to be most fruitful for crystallographic research until our times: the position of a general point in the periodical lattice, its coordinates, its multiplicity (the number of symmetrically equivalent points), its symmetry, as well as the term "lattice complex"[2]. His work between 1917 and 1920 provided the principle ba-

[1] In the 16th century it was commonly assumed that crystals grow like plants, i.e. fluid moves from the ground through "roots" into the interior of the crystal.

[2] More detailed definitions on a mathematical basis were developed later by E. Hellner, W. Fischer and E. Koch (FISCHER and KOCH, 1983, and references cited therein).

sis for crystal structure determination from diffraction experiments in the following years.

After the discovery of electrons at the turn of the century, physicists were primarily concerned with the electronic structure of the atom in general. The question about the effective electron density distribution of an atom in a crystal was not yet discussed. Since considering points in the lattice 1915–1917 it was clear to Niggli that an atom in a crystal does not have to be a sphere. Its shape has to be consistent with the symmetry of the position it occupies. More than thirty years later, when more precise experimental methods were available the question of intrinsic electron density distribution in the crystal became subject of extensive research by physicists, chemists, and crystallographers. It was Niggli who had introduced the symmetry conception for that experimental work a long time before.

Niggli's approach to point position and lattice complex was not entirely remote from classical crystallography of the nineteenth century and the work of many contemporary mineralogists who were primarily concerned with description of crystal faces, measurement of edge angles, and morphology. He also paid special attention to the detailed morphology of the crystal, its "Habitus" and "Tracht" (NIGGLI, 1941), and he was more concerned than any other mineralogist at that time with discovering relationships between lattice complex and face forms.

The view of point symmetry from recent experiments

After the second world war, new physical methods were developed which allowed to probe multiplicity and symmetry of an atomic position directly in the crystal structure. Such methods are, for example, nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), various combinations of nuclear and electronic double resonance, and gamma ray resonance. Other physical methods like infrared absorption, electronic absorption in the visible and ultraviolet regions etc. were improved so that they could be used more successfully for studying crystallographical problems. In general, these techniques are complementary to the diffraction methods. They provide selected crystallographic information on a particular atomic species or small group of atoms in the crystal structure. Point symmetry considerations are especially important. While crystallographic applications have not yet been common during Niggli's lifetime they link to his early crystallographic work in a rather direct way. Three examples will demonstrate this.

CUPRITE

In a first example, the shape of the atoms in cuprite, Cu_2O, will be examined. Cuprite was one of the early minerals to be analysed structurally (W.H. and W.L. BRAGG, 1916, NIGGLI, 1922). A projection of its simple, cubic crystal structure is shown in Figure 1. Its space group is Pn3m, and Cu and O occupy the two lattice complexes F (position 4b, point symmetry $\bar{3}$m) and I (position 2a, point symmetry $\bar{4}3$m), respectively.

How are the electronic density distributions of Cu and O in Cu_2O with respect to the point symmetries of the atomic positions? Do they in fact deviate from spherical symmetry? This can be tested by NMR. The technique allows to measure the electric field gradient (second derivative of the electrostatic potential) at a nuclear position which is produced by the total charge distribution in a crystal structure. If the point symmetry of that position is cubic the electric field gradient will be zero. In the case of cuprite, ^{63}Cu and ^{66}Cu resonance yields a large field gradient as expected from point symmetry $\bar{3}$m of the Cu position indicating a significant deviation from the density distribution from spherical symmetry (KRÜGER and MEYER-BERKHOUT, 1952). The field gradient at the O position could be measured e.g. by ^{17}O NMR, but it is predicted to be zero because the point symmetry at that position is $\bar{4}3$m.

In recent years theoretical ab initio computations of the electron density distribution in crystal structures has made considerable progress. In the case of Cu_2O, the Schrödinger equation was solved (NAGEL, 1985; MARKSTEINER et al., 1986) e.g. for a nine-atom cluster of the crystal structure in local density approximation using the scattered wave method (NAGEL, 1985). The cluster consisted of two OCu_4 tetrahedra linked via a corner (cf Fig. 1). The results are shown in Fig. 2 and 3. The computed total density distribution is mapped for the plane (110) in Fig. 2. It shows that the densities for Cu and O are close to spherical symmetry, though some deformation can be observed in

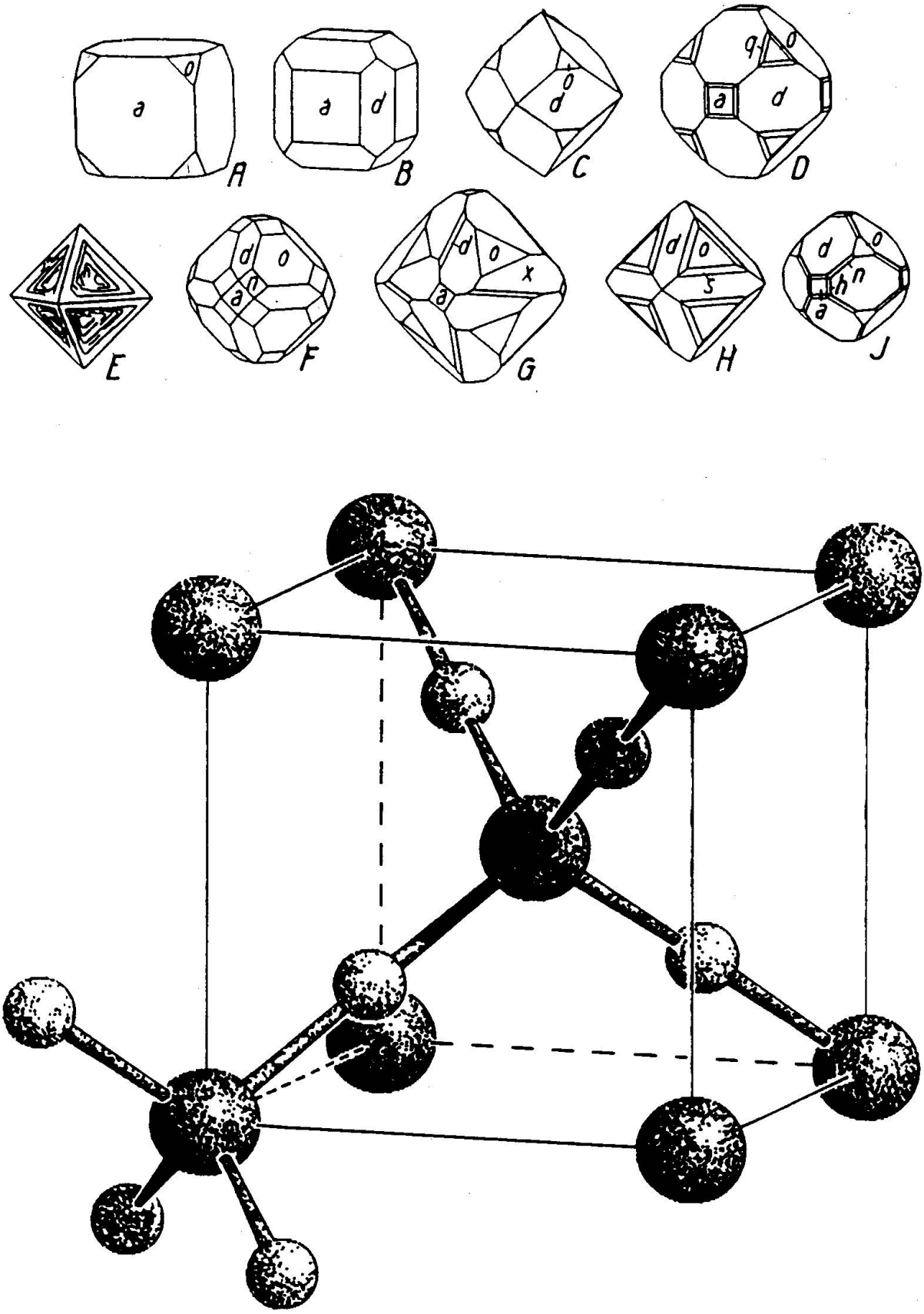

Fig. 1 Projection of the crystal structure of cuprite, Cu_2O. Large spheres: oxygen; small spheres: copper. The morphological drawings A–J on top are from NIGGLI (1926); a–x indicate the different face forms (cf. p. 218).

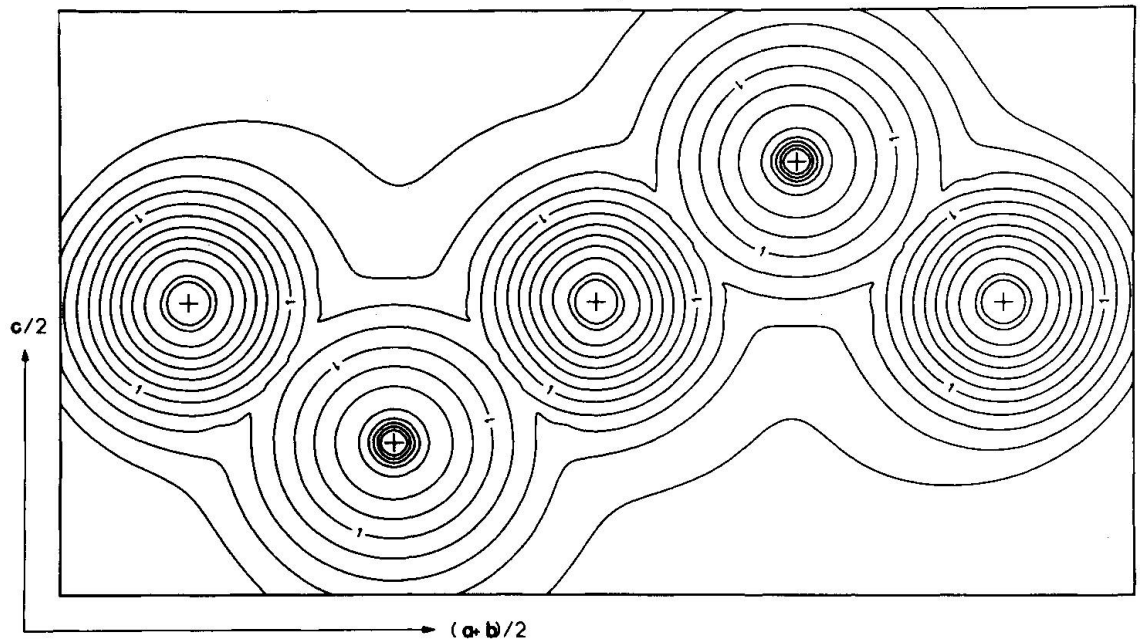

Fig. 2 Electronic charge density distribution in e/A^3 in the plane (110), total density; successive contour lines differ by a factor of 2. The position in the center of the Figure refers to Cu.

the projection. A plot of the difference between the computed density distribution of the free atoms and that of the cluster illustrates this in more detail (Fig. 3). A quite similar distribution was obtained from precise intensity analysis of X-ray diffraction data (RESTORI and SCHWARZENBACH, 1986) as shown in Fig. 4, which may be compared with Fig. 3. At first the lack of electron density on the line between anion and cation is surprising. Although the distance Cu-O is about ½ Å shorter than the sum of the ionic radii of Cu^+ and O^{2-} the density is redu-

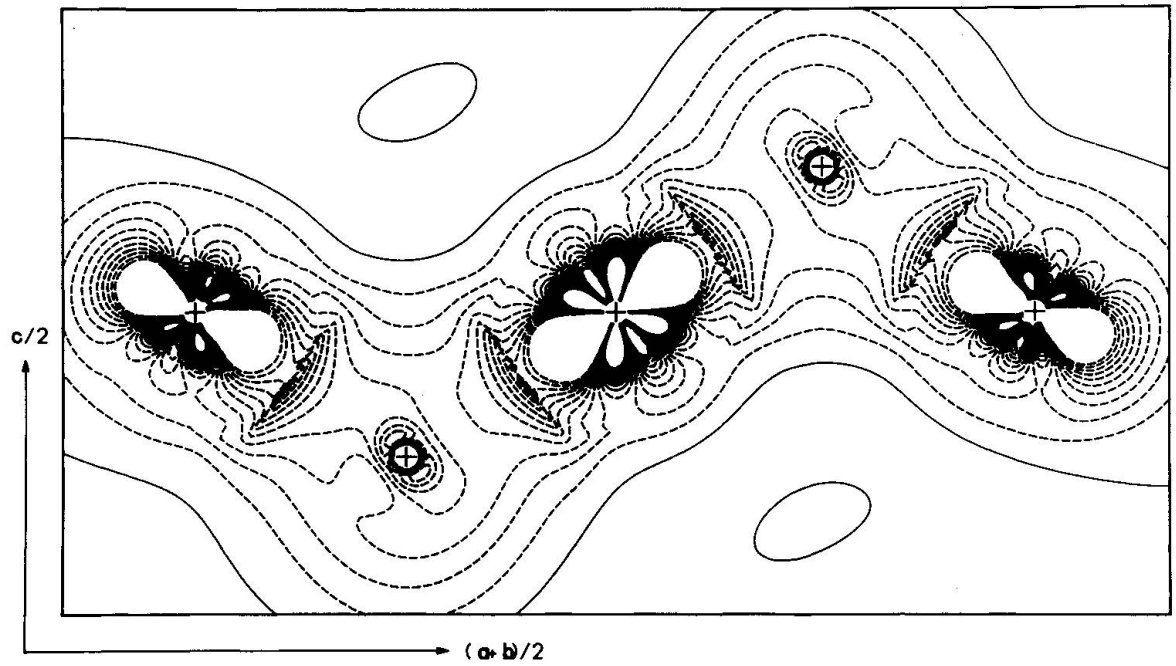

Fig. 3 Difference between the density computed for a nine-atom cluster and the density computed for the Cu^+, O^{2-}-ions in the plane (110). Negative contours are broken; increment is 0.05 e/A^3. Note the reduced electron density in Cu^+: net positive charge about 0.45 e, and enhanced density in O^{2-}-ions: net negative charge about 0.90 e.

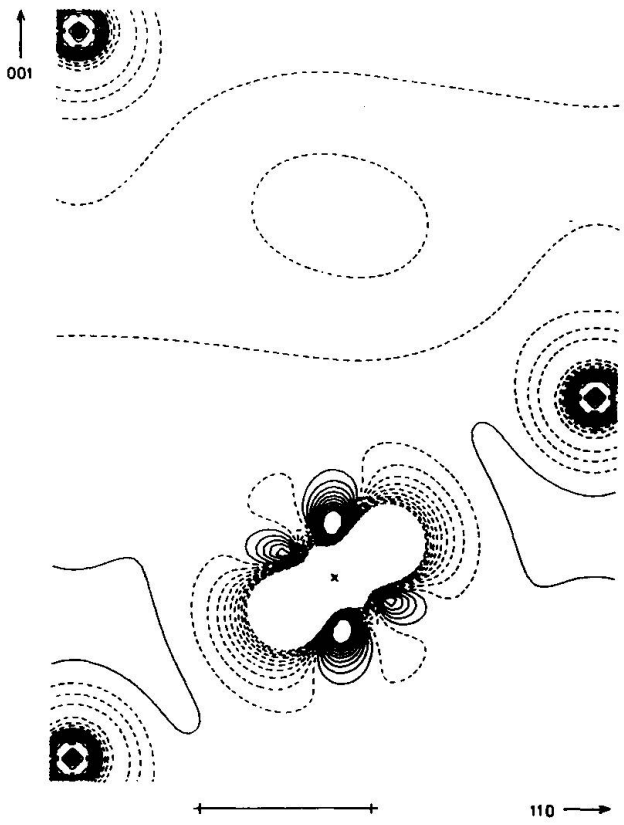

Fig. 4 Static model deformation map of RESTORI and SCHWARZENBACH (1986, Fig. 2(d), in the plane (110) as in Fig 3. Contours drawn between ± e/A^3, negative contours broken. The map is comparable to the one of Fig. 3.

ced between Cu and O, i.e. there is practically no hybridization of $3d_2^24s$ in the copper ion.

NIGGLI (1922) realized that considering symmetry alone, three cubic space groups are, in fact, equally possible for Cu_2O: Pn3, $P4_232$, and Pn3m. BRAGG (1916) had adopted the one of highest symmetry, Pn3m, whereas WYCKOFF (1983) chose the one of lowest symmetry, Pn3. The correct spacegroup can be deduced from the nuclear charge distributions at the atomic positions which determine the final electronic density distribution over the crystal structure. The nuclear spins of ^{63}Cu and ^{66}Cu are 3/2 and the nuclear charge distribution is, therefore, axially symmetric, i.e. consistent with the point symmetry of the Cu position of the space group with the highest symmetry. The nuclear charge distributions of the two main isotopes of O, ^{16}O and ^{18}O, are spherical symmetric. Thus, Pn3m is the correct space group for Cu_2O.

THE POSITIONS OF OXYGEN IN FORSTERITE, Mg_2SiO_4

In a second example the positions of the oxygen atoms in forsterite Mg_2SiO_4 will be studied. Forsterite is orthorhombic (space group Pnma). A projection of its crystal structure which was determined by BRAGG and BROWN (1926) is shown in Fig. 5. They concluded from that structure determination that the oxygen atoms occupy three distinct positions: two positions 4c (point symmetry m) and one position 8d (point symmetry $\bar{1}$). This result was confirmed by a direct analysis of the multiplicity and point symmetry of the oxygen positions by NMR of ^{17}O (FRITSCH et al., 1986; FRITSCH, 1987).

For the experiment the crystal is placed into an external magnetic field B. The resonance spectrum can be recorded at constant frequency and the magnitude of B is varied, or vice versa. In case of ^{17}O (nuclear spin 5/2, natural abundance 0.004 per cent), the spectrum consists of five different resonance lines, with their transition energies depending on the orientation of the crystal with respect to B.

Oxygen atoms which occupy a position of identical points give rise to one single resonance spectrum. If the position consists of equivalent points the spectrum will be generally split into n different spectra, where n is the multiplicity of the position. For special orientations of the crystal with respect to B, some or all spectra of equivalent points will coincide depending on the orientation of the symmetry elements which relate the points to each other. It should be noted that for magnetic resonance, the sign of the magnetic field is irrelevant, therefore points related by a center of inversion cannot be distinguished.

In Fig. 6 resonance lines of ^{17}O in forsterite are plotted for the rotations of the crystal around the crystallographic axes a, b and c (NIGGLI, 1926, Fig. 1.6.13; in that reference, Pbnm was chosen, not Pnma). Only lines 1, 2, 4 and 5 of the 5-line spectra were included in the figure. The axis of rotation was perpendicular to B. Spectra were recorded after steps of 1–5 degree. Fig. 6 allows identification of O at one 8d and 2 different 4c positions. The multiplicities of the oxygen positions are demonstrated by a small misalignment of the crystal of about one degree producing a general orientation of the crystal with respect to B and, therefore,

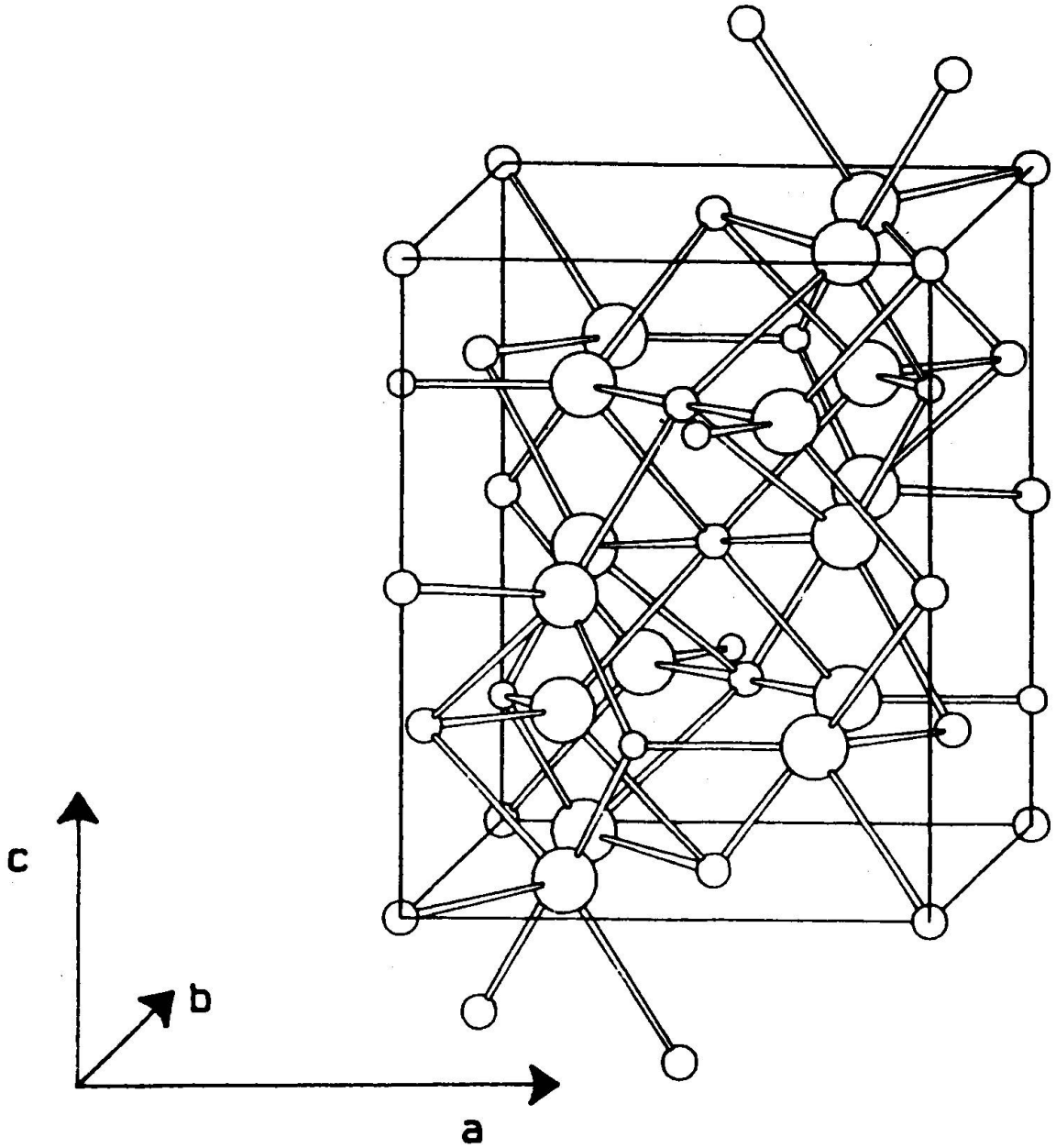

Fig. 5 Projection of the crystal structure of forsterite, Mg_2SiO_4. Large circles: oxygen at two positions 4c (point symmetry m) and one position 8d (point symmetry 1); medium circles: magnesium at positions 4a (point symmetry 1); small circles: silicon at position 4c of space group Pbnm.

splitting the maximum number of spectra. Number and symmetry relationships of all spectra observed are in agreement with the point symmetries of the three O positions of Pnma. The spectra also allowed determination of the electric field gradient tensors at those positions which will test future ab initio computations of the electron density distribution in the crystal structure of forsterite.

LOCATION OF Fe^{3+} IN FORSTERITE, Mg_2SiO_4

The third example deals with the position of a trace ion in a crystal structure: Fe^{3+} in forsterite. In this mineral Fe^{3+} may be substituted for Mg^{2+} and/or Si^{4+}.

The question of identification Fe^{3+} positions by determination of point multiplicity

and symmetry may be solved using paramagnetic electron resonance (EPR). A study of a synthetic forsterite crystal doped with a trace of Fe^{3+} was carried out by NIEBUHR (1975). The crystal was placed in an external magnetic field B and rotated around an axis perpendicular to B. A spectrum was taken every 1–5 degree. The axis of rotation was an arbitrary (noncrystallographical) direction parallel to (010). The frequency γ = 9.47 GHz was constant while the magnetic field B (abszissa) was varied. The spectra are shown in Fig. 7. Fe^{3+}-ions occupying a position of identical points produce one spectrum. If Fe^{3+} is located at a position of n equivalent points n different spectra are observed, n being the multiplicity of the position. In Fig. 7, two different types of Fe^{3+} lines can be recognized. A line which belongs to the first group is designated with 1 and one to the second group with 2 at the top of the figure. The first spectrum on top refers to the special orientation B parallel to crystallographic b. For general orientations of the crystal with respect to B, 1 is split into two different lines according to position 4c of Pnma while 2 is split into four different lines according to position 4a. As in case of ^{17}O NMR, a systematic analysis of the spectra for different orientations of the crystal with respect to B allows determination of multiplicities and point symmetries for the positions of the paramagnetic trace element. For Fe^{3+} in forsterite, it was found that this ion can be located at positions 4a and 4c of Mg as well as 4c of Si with varying preference. The same technique was also applied to identification of locations of several other paramagnetic trace ions in forsterite and other minerals.

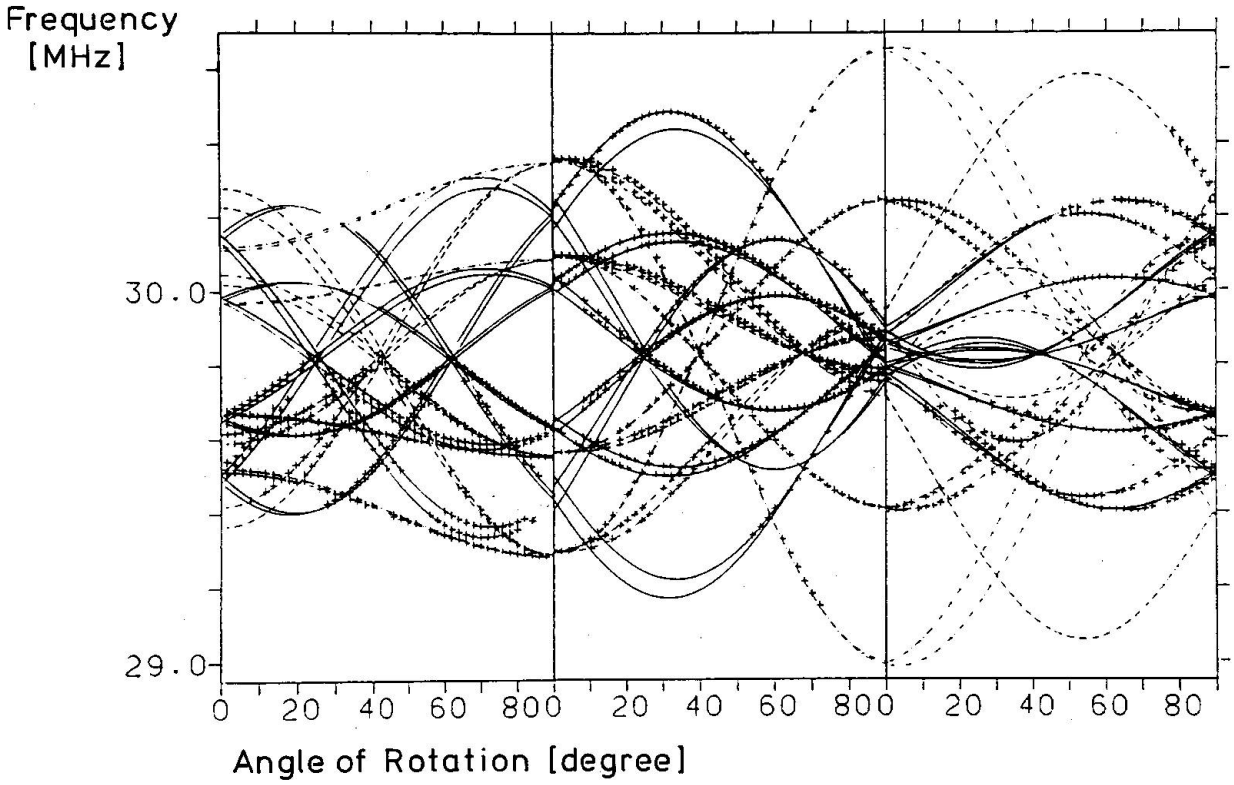

Fig. 6 NMR spectra of ^{17}O of a synthetic crystal of forsterite (FRITSCH, 1986, Fig. 1.6.13). The resonance frequencies of the lines 1, 2, 4 and 5 of the 5-line ^{17}O spectrum are plotted for constant magnetic field B. Left, center and right part of the figure: rotation around crystallographic a, b, and c, respectively. The axis of rotation was perpendicular to B. O1 at 4c1, O2 at 4c2, O3 at 8d of Pbnm. In case of general orientation with respect to B, the number of curves of a particular position refers to the multiplicity of the position. Coincidence of spectra occurs for special orientations of symmetry elements with respect to B. For example, O at 8d for general orientation produces 16 curves in Fig. 6. In (21), crystallographic a, b, and c refers to Pbnm, not Pnma.

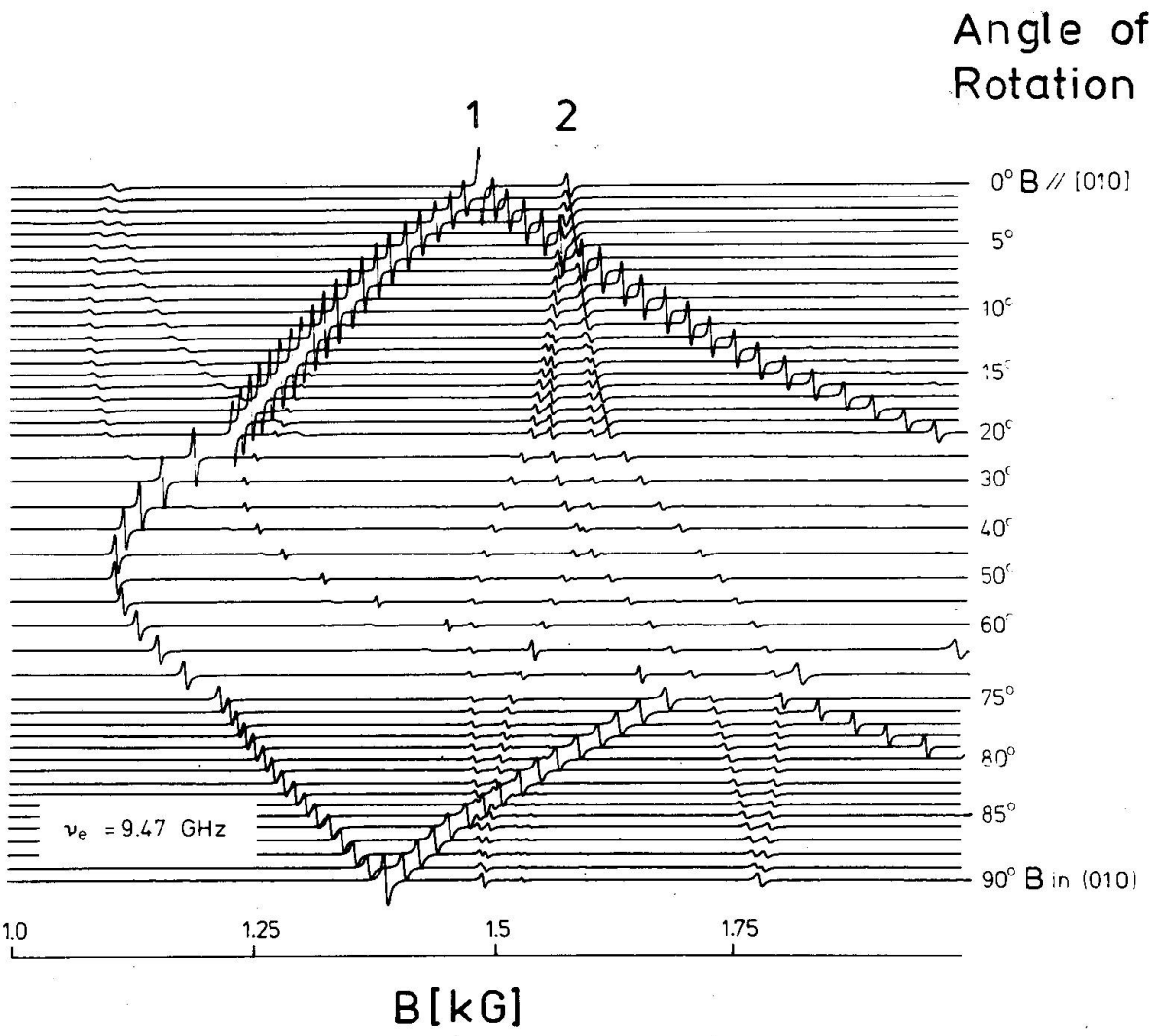

Fig. 7 Electron paramagnetic resonance (EFR) spectra of Fe^{3+} in forsterite. The crystal was rotated by 1–5 degree around a noncrystallographical axis in the plane (010 perpendicular to the magnetic field B. Note the splitting of the lines 1 and 2: coincidence for the special orientation of crystallographic b parallel to B and splitting into 2 and 4 different lines, respectively, for general orientations. For the orientation b parallel to (010), there is coincidence for 1 (position 4c) and splitting into two lines for 2 (position 4a).

Future

Paul Niggli's general symmetry considerations which began in 1915 and continued systematically in the years thereafter have over more than half a century been a basis for the most successfull development of crystal structure determination using diffraction techniques. The book "Geometrische Kristallographie des Discontinuums" has initiated three subsequent editions of the International Tables of Crystallography between 1920 and today. Niggli was perhaps the first crystallographer who paid special attention to the point in the lattice, its multiplicity, and its symmetry. The importance of his conception may not have always been recognized by others. Many new crystal structures have been described in a form that made it difficult for the reader to identify all atomic positions properly in terms of positional multplicity and symmetry.

With the discovery and subsequent development of physical techniques which allow to examine the properties of a point and its local environment directly in the crystal, Niggli's conception has gained importance. Applications of such techniques now already established are increasing, and promising experiments on new techniques are now being carried out. For example, magnetic muon spin rotation will permit to examine local properties of an interstitial point between atomic positions. At

any rate, it is easy to predict that properties in crystals will continue to be an important problem in research of the forthcoming decades. The author is indebted to J.J. Burckhardt whose book (BURCKHARDT, 1988) just appeared when this paper was beeing written.

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