Reports

Space Groups Not Always Derivable by Parallelohedra and Subdivision into Stereohedra

For the last several years I have expressed regret to my colleagues that there has not been available (even in Russian) an edition of the *Collected Works of Fedorov*. Nor have there been translations of the most important works of this ingenious crystallographer, except for those published in German by Fedorov himself. In 1949, Shubnikov and Shafranovskiĭ (*1*) edited a collection of reprints (*2*) and translations (*3, 4*) (from German into Russian) of five important papers. (Appended to this collection is a complete bibliography and an appreciation by Shafranovskii, Belov, and Bokii of the life and work of Fedorov.) These five papers have recently been superbly translated into English by David and Katherine Harker (*5*). In his introduction to the last paper, *A Theory of the Structure of Crystals*, which deals with parallelohedra, Harker remarks,

> Fedorov states that there are five space groups that cannot correspond to actual structures, in the same way that a crystal cannot have a five-fold symmetry axis. These space groups are: C_{2v}19–$Fdd2$, D_{2h}24–$Fddd$, T_d6 (not T_d 5!)–$I\bar{4}3d$, O^6–$P4_33$, and O^7–$P4_13$. Unfortunately, each of these space groups is now represented by several actual crystal structures. I have not been able to find the fault in Fedorov's derivation. It is possible that one or more of his assumptions about the necessary natures of parallelohedra and stereohedra may be too restrictive, or his geometrical insight may have overlooked a few possibilities. In any event, here is a subject for a research project. I think there is no question that our modern notion of *asymmetric units* corresponds to Fedorov's notion of *stereohedra*. Perhaps parallelohedra are not always necessary. I hope the solution will appear soon.

The solution to this problem has in fact been given by Fedorov himself in 1900 (*6*) and also in my 1935 doctoral dissertation (*7*). Fedorov corrected the result of his 1895 paper (*4*) [Monograph 5 of (*1*), and (*5*)] and demonstrated that all space groups except his 94*a*, $O6$–$P4_332$, and 95a, $O7$–$P4_132$ can be derived by consideration of parallelohedra and their subdivisions into stereohedra. Thus $4\phi''1$, C_{2v}19–$Fdd2$; 12χl, D_{2h}24–$Fddd$; and 22 (δ1), T_d6–$I\bar{4}3d$ are included among the set which can be so derived. The *Wirkungsbereiche* (*7, 8*) of *true* or *apparent translation lattices* are parallelohedra. A Wirkungsbereiche is the smallest convex polyhedron obtained by joining a point of a crystal space to all equivalent ones and constructing the planes which are the perpendicular bisectors of the line segments so constructed. In a *true translation lattice* (Fig. 1a), all points are equivalent by means of translations only. In an *apparent* translation lattice, equivalent points may also be obtained by rotations, rotation-inversions, mirror planes, screw axes, or glide planes (Fig. 1b). *If we disregard the orientation* of an asymmetric figure located at these points, the set of equipoints is identical to that in a *true translation lattice*. In both cases, the *Wirkungsbereiche* are parallelohedra. I have previously (*7*) designated such equipoints as *Hauptpunkte im Sinne Fedorow's* (HP*), and Fedorov (*6*) has shown that all space groups except $O6$–$P4_332$ and $O7$–$P4_132$ possess such HP*. I have again carefully examined all 219(+11) space groups and have confirmed Fedorov's result. It is clear that space groups without HP* cannot be derived by means of parallelohedra. Certainly Fedorov overemphasized the importance of the parallelohedra, perhaps because of the fact that each space group contains a (true) translation group as a subgroup; this fact does not, however, imply the existence of an HP* in each space group.

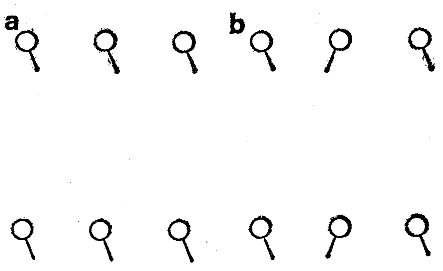

Fig. 1. (a) True translation lattice. (b) Example of an apparent translation lattice.

In most space groups the HP* are equipoints of highest symmetry (lowest multiplicity). However, equipoints of lower symmetry (higher multiplicity) can form HP* in the following 13 space groups: C_{2v}19–$Fdd2$, D_{2h}24–$Fddd$, $C_4$6–$I4_1$, C_{4h}6–$I4_1/a$, D_{2d}12–$I\bar{4}2d$, C_{4v}11–$I4md$, $D_4$10–$I4_12$, D_{4h}19–$I4/amd$, T_h4–$Fd3$, T_d6–$I\bar{4}3d$, $O4$–$F4_13$, $O8$–$I4_13$, and O_h7–$Fd3m$. [The space groups $C_1$1–$P1$, $C_2$2–$P2_1$, $C_3$2–$P3_1$, $C_3$3–$P3_2$, $C_4$2–$P4_1$, $C_4$4–$P4_3$, $C_6$2–$P6_1$, $C_6$3–$P6_5$, $D_2$4–$P2_12_12_1$, C_s2–Pc, C_s4–Cc, C_{2v}5–$Pca2_1$, and C_{2v}9–$Fdd2$ contain only equipoints (xyz) without point symmetry (*fixpunktfrei*); their asymmetric units (*Fundamentalbereiche*) are Euclidean space forms (*9*).] Only the 73 symmorphic space groups have HP* which form true translation lattices; all other space groups [except $O6$, $O7$] have HP* which form apparent translation lattices.

As I have shown in (*7*), the *Hauptpunkte im Sinne Weissenberg's* (HP) of each space group provide a more important concept, and a study of the papers of Weissenberg (*10*) remains important for the modern student. Unfortunately the mathematical proof of a certain theorem proposed in (*7*, pp. 37, 75) is still lacking. Otherwise the derivation of *all* space partitions into stereohedra would be possible in principle, by subdividing the Wirkungsbereiche of all HP's of all space groups according to their own symmetry.

I close by remarking that it is perhaps not generally known that in 1891 Fedorov gave the first complete and correct derivation of the 17 plane groups, by neglecting the third coordinate in the three-dimensional space groups. This paper (*11*) should also be translated into a Western language.

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Primordial Oil Slick

Abstract. *Calculations and some preliminary experiments suggest that an early methane atmosphere would have been polymerized by solar ultraviolet radiation in geologically short periods of time. An oil slick 1 to 10 meters thick could have been produced in this way and might well have been of considerable importance in the development of life.*

Numerous experiments have shown that amino acids and a large variety of the other building blocks of living organisms can be synthesized in electrical discharges if free oxygen is absent and if some reducing gases are present. These experiments suggest that the earliest terrestrial atmosphere was reducing. Methane and nitrogen may well have been its major components; water vapor, hydrogen, carbon monoxide, and ammonia were probably present in small quantities. A simplified model is presented in Fig. 1. Such an atmosphere would have responded to solar ultraviolet radiation and to lightning discharges quite differently than our present atmosphere. The effects of both energy sources on the chemistry of the present-day atmosphere are relatively small; on the other hand the rather drastic polymerizing effects of electrical discharges on mixtures of reducing gases have been amply demonstrated in a variety of experiments. Measurements suggest (*1*) that an input of electrical energy at the present rate would polymerize a methane atmosphere with an initial pressure of 1 atmosphere in 10^7 to 10^8 years.

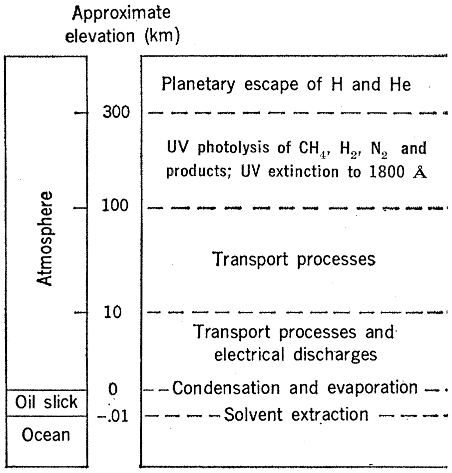

Fig. 1. Locale of some important processes in the primitive atmosphere-ocean system.

The effect of solar ultraviolet radiation on the present-day atmosphere is largely confined to dissociation and ionization reactions. In a predominantly methane-nitrogen atmosphere, methyl and methylene radicals are produced by ultraviolet light of wavelength less than 1450 Å. These radicals can combine to form heavier hydrocarbons. We propose that this process was rapid, that it was followed in the early atmosphere by the downward removal of the reaction products, and that these accumulated in an oil slick which could have been 1 to 10 m thick.

In the primitive atmosphere illustrated in Fig. 1, short-wavelength ultraviolet radiation would be primarily absorbed by methane at an elevation of 100 to 300 km; here methane and hydrogen will be the main reactive species. Figure 2 shows a partial reaction scheme for methane in the presence of ultraviolet light of 1200 to 1800 Å. Methyl and methylene radicals are produced from methane, and ethane is produced most efficiently by the combination of two methyl radicals. The reaction of a C_2H_5 radical with a CH_3 radical leads to the formation of propane, and two C_2H_5 radicals can combine to form butane. As their concentration increases, the photodissociation of the heavier hydrocarbons becomes important. At shorter wavelengths (<1018 Å) photoionization also occurs, but is expected to play a minor role. Ultimately, a steady-state distribution of species is reached in a closed one-phase system. A set of equations was developed to describe the time variation in the composition of such hydrocarbon gas mixtures, and the gas composition was then followed on a computer until a steady state was approached.

The parameters in our theory require a knowledge of the hydrocarbon photodissociation cross sections, P_i, as a function of carbon number, i, as well as the recombination rates, k_{ij}, and the branching matrix, α_{ij}. The rate constant for the recombination of the

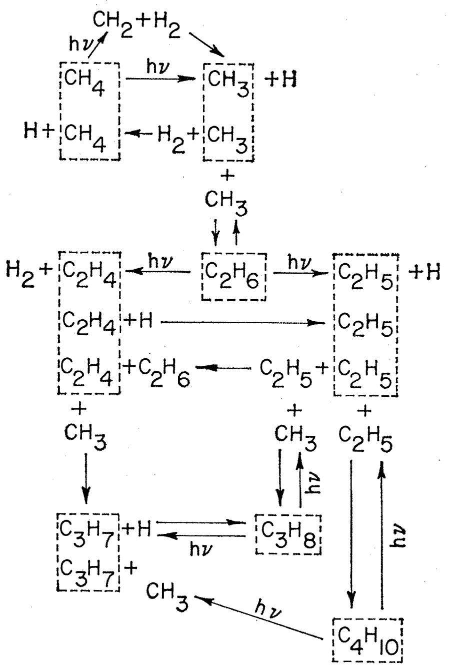

Fig. 2. Partial reaction scheme for polymerization of methane in the presence of 1200 to 1800 Å ultraviolet light (*4, 5, 13*).