

### Space-group Representation in Condensed Models of Inorganic Close-packed Structures

EARLIER I described some condensed models of inorganic close-packed structures<sup>1</sup>. These were based on standard transparent sheets of film, representing layers of the main types of close packing, in which the occupied holes could be marked out. An approximate three-dimensional representation was obtained by placing these sheets at equal distances in an appropriate supporting rack. It became apparent that the conventional symbols for the elements of symmetry of space groups could also be marked out on these sheets, completing the information contained in the models. The top layers of two of these models, olivine and spinel, are represented in Fig. 1a and b. When the layers are placed in the appropriate supporting rack, screw axes, inversion axes, glide planes, etc., can be easily visualized and related to the actual structure.

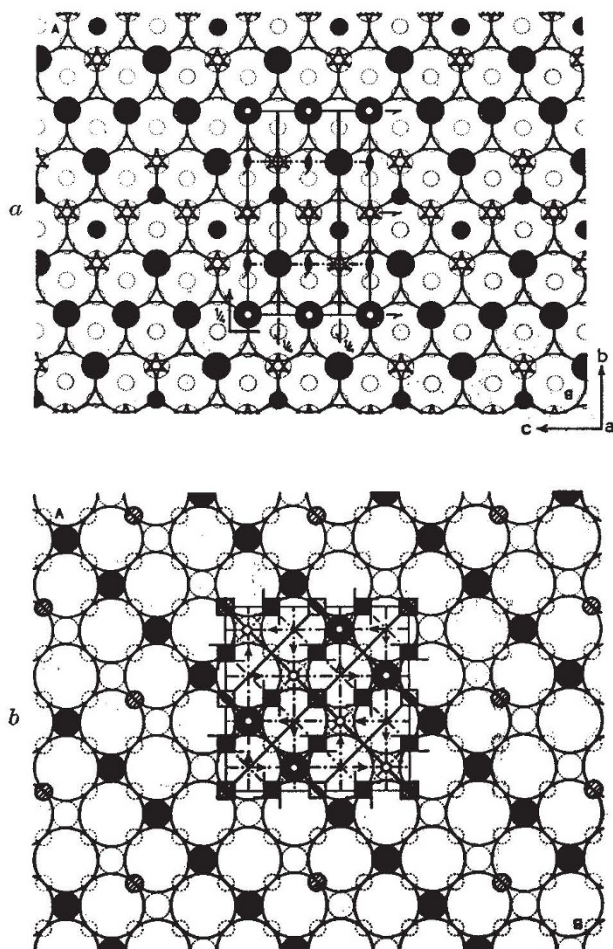


Fig. 1. Top layers of two examples of space-group representation in condensed models of close-packed structures. *a*, Olivine,  $Mg_2SiO_4$ , space group  $Pbnm$ ; oxygen (large open circles) in hexagonal closest packing; magnesium (large filled circles) in octahedral holes; silicon (small filled circles) in tetrahedral holes. *b*, Spinel,  $Al_2MgO_4$ , space group  $Fd3m$ ; oxygen (large open circles) in cubic closest packing ((001) face); aluminium (large filled circles) in octahedral holes; magnesium (small shaded circles) in tetrahedral holes. In the case of spinel, to facilitate the reading of the picture, only a partial representation of the space group is given (for example, triad axes, diad axes, etc., are not represented). The centres of symmetry that are marked out are at  $7/8$ ; those at  $5/8$  are omitted because they belong to the layer immediately underneath. The inversion tetrads that are at  $3/4$  are also omitted—they also belong to the layer immediately underneath.

A complete representation of the orthorhombic space group of olivine is easily achieved, but in the complex example of the cubic space group of spinel a partial representation is more satisfactory. Such a partial representation enables the location in this structure of the

complete representation which appears in the work of Buerger<sup>2</sup>.

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<sup>1</sup> Lima-de-Faria, J., *Z. Krist.*, **122**, 346 (1965).

<sup>2</sup> Buerger, M. J., *Elementary Crystallography* (John Wiley, New York, 1956).

### Ice Nucleation by Proteins and Surface Films

DURING an investigation of the icing characteristics of solid surfaces, Schaefer<sup>1</sup> observed that certain protein films induced supercooled water drops to freeze at temperatures near zero. The possible importance of proteins as a source of natural ice nuclei cannot be over-emphasized because proteins are able to concentrate irreversibly at water surfaces and thereafter find their way into the atmosphere in particles large enough to act as ice nuclei. The ocean surface, in particular, would be an immense source of air-borne protein<sup>2</sup>. Furthermore, protein films are of great fundamental interest because they possess the unique property that their state of compression, and therefore their geometric similarity to an ice lattice, can be varied continuously, thus providing a means of testing the relationship between 'fit' and nucleation temperature. It is therefore surprising that while several authors<sup>3-5</sup> have accepted proteins as ice nucleators, no confirmation or extension of Schaefer's work has been reported.

Schaefer observed ice formation on films of egg albumen and pepsin when these films were prepared in the form of 'dipped out' layers on a chromium plated glass slide. In the present work, this experiment has been repeated, the proteins (twice recrystallized, Mann Laboratories) being spread from solution on to iso-electric substrates as described by Langmuir, Schaefer and Wrinch<sup>6</sup>. Films of the types *PRA*, *PRB* and *PRAB* (terminology of Langmuir *et al.*) were prepared, and tested as ice nuclei by placing the film-coated slides in a cold stage and passing moist air over them until condensation appeared on the slide. On no occasion was any ice detected on the protein film unless the temperature was below  $-10^\circ C$ , this behaviour not being different from that of slides without the protein coating.

A possible reason for the failure of these protein films to nucleate ice was the lack of order resulting from the complex arrangement of amino-acids in the peptide chains. Therefore, a number of poly-amino-acids were tested as nucleators in the form of "dipped out" layers, the expectation being that the uniformity of the peptide chains might confer on the film enough two-dimensional crystallinity to promote nucleation. However, no ice nucleation was detected on either *PRA* or *PRB* films of the following polymers—poly-*L*-leucine (molecular weight of 12,000), poly-*DL*-leucine (mol. wt., 8,000), poly-*L*-alanine (mol. wt., 3,000), poly-*DL*-alanine (mol. wt., 2,500), and poly-*L*-tyrosine (mol. wt., 130,000) (supplied by Yeda Research and Development, Israel).

As cholesterol was known to be a good ice nucleator with an onset temperature of  $-5^\circ C$  (ref. 7), it was of interest to investigate its nucleating properties when deposited on chrome-plated slides using the technique of Langmuir, Schaefer and Sobotka<sup>8</sup>. Again no ice nucleation was obtained, even on 'built-up' layers of cholesterol up to 100 monolayers in thickness. This was perhaps to be expected because, although the packing of the interlayer spacing of the layer is almost identical with that of the cholesterol crystal<sup>8</sup>, the molecules of the outermost monolayer are all oriented with their hydrocarbon tails facing outward, whereas the equivalent plane of a cholesterol crystal has half the molecules oriented with the hydroxyl group outward<sup>9</sup>. Even a 'built-up' layer which had been