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NOTES AND NEWS

MICROFRAMEWORKS*

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The purpose of this paper is to call attention to those regular, repetitive features of crystalline bodies whose repeat distances are in general larger than the interatomic distances of the crystal structure, but not visible to the unaided eye. These I shall call *microframeworks.*

One of the reasons for interest in them is that they may result in the development of a new area of investigation in physics and chemistry since the properties of substances under the conditions that exist in some microframeworks will be different from their bulk properties. Secondly, as a result of this difference in properties and also because of their very small size and precise dimensions, microframeworks may be of technological interest.

These two points will be illustrated under the headings of several types of microframeworks: *micromolds*, *microsandwiches*, *microgrids*, *microcages*, *microsieves*, and *microjigs.*

1. *Micromolds*

Chrysotile asbestos has been described (Bates, Sand, and Mink, 1950) as composed of closely packed tubes. Noll and Kircher (1950) show electron micrographs of cross sections of these tubes and state that their outside diameter is 150–300 Å. Such a structure could serve as a precisely dimensioned tubular micromold whose tubes could be filled with the substance whose properties were to be studied.

Consider first magnetic properties. It is well known that the domain-wall energy of a ferromagnetic material is such that a wall cannot exist in a particle of about 200 Å diameter (Kittel, 1946). Such a particle, consisting of a single domain, has a high coercive field. A body made up of such particles, packed in a matrix would therefore be an excellent permanent magnet. If the particles consisted of parallel rods, the effect of shape anisotropy would be added and the body would be a better permanent magnet than any now known.

Williams and Sherwood (1958) attempted to fill chrysotile tubes with various magnetic materials and achieved a 600-fold increase of the coercive force in cobalt compared to that of the bulk material, but this is far short of what was expected from theory. This unsatisfactory result may support the conclusion of F. L. Pundsack (1956) whose density measure-

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* The substance of this paper was the subject of the retiring president's talk at the banquet of the American Crystallographic Association meeting in Milwaukee, June 26, 1958.

ments indicate that the supposed tubes of chrysotile asbestos are in fact filled with solid material. If this was true of the specimen which we tried to fill with the magnetic material, the volume filled could only have been the interstices between the rods, giving an inadequate amount of magnetic material present in the composite body.

If a tubular micromold was filled with a metal, the resistance of the microwires would be high because of their small diameter and a new type of resistor would result (Doucette, 1958). Since the "wires" would maintain their shape and size in spite of phase transformations, including melting, the changes of conductivity with changes of phase could be studied.

It is well known that metals in thin films do not have the same density, optical constants, and electric constants as bulk metals (Lewis, 1950) and that the epitaxial influence of the substrate may even result in a change of crystal structure of the deposited substance (Pashley, 1956). The study of properties of materials in micromolds is a new field of investigation where one may expect the discovery of new properties of materials. Since the material in a micromold is not in contact with air except for a negligibly small area, reactive materials can be investigated without the necessity of a controlled atmosphere. Although the tubular micromolds so far described have been crystals with spaces available for filling, microframeworks may also exist in which rod-like inclusions of a material different from the matrix may be selectively removed or replaced with the same end effect as that of a tubular micromold.

In addition to tubular or "one-dimensional" micromolds, lamellar or "two-dimensional" micromolds may be used. A filled lamellar micromold has the properties of a *microsandwich* which will be discussed below. A three-dimensional micromold would probably have to be filled as the crystal grew. The *microcage* discussed below is related to this.

2. *Microsandwiches*

Microsandwiches are layered structures on a very small scale whose adjacent layers differ from each other in composition or structure. Such microframeworks are called polycrystals (Donnay and Donnay, 1953) and may be composed of such different substances as pyrite and uraninite (King, 1957). In current microwave technology, components with closely-spaced thin metallic filaments have been needed (Reed, 1955). Microsandwiches with metallic layers, either originally present or introduced by selective replacement might find application in this field.

3. *Microgrids*

The construction of ruled gratings for optical diffraction is an exacting mechanical task. Microridges on crystal surfaces might, in favorable cases, serve as an optical grating or as a mold for a replica that could be used for an optical grating as suggested by Farney (1958). Slip planes, as in twinned calcite, produce such a ridged surface. Alternating development of faces, as on the cube face of pyrite and the prism face of quartz, if sufficiently regular, might provide a suitable microgrid. In some crystals, e.g., albite, polysynthetic twinning results in twin lamellae of uniform width. Selective etching of these would produce a microgrid.

The remaining three categories comprise small scale microframeworks, examples of which are already in use.

4. *Microcages*

A microcage is a crystal microframework that is used to trap something that would otherwise escape. The clathrate compounds are an example. In the quinol-rare gas clathrates, the gas atoms are mechanically trapped in quinol cages as close together as they would be if the gas were under a pressure of 91 atmospheres. The oil industry uses clathrate compounds to trap selectively petroleum derivatives whose boiling points are not sufficiently different from each other to allow separation by fractional distillation (Banerjee, 1958).

5. *Microsieves*

A microsieve is a crystal microframework which, because of the shape or size of openings in it, is useful for separating one substance from another. An example is the zeolites which have large (ca. 10 Å) cavities interconnected by smaller passages (ca. 4 Å in diameter). These have recently been used to separate straight chain hydrocarbons from branched chain hydrocarbons (Breck, 1958). They have also been called "molecular sieves."

6. *Microjigs*

A microjig is a crystal microframework in which something is held for processing in some way. Examples are the urea and thiourea crystals used by Brown and White (1958) to hold monomers end to end during electron-irradiation which results in their linkage into straight chain polymers.

The list of microframeworks given in this paper is not exhaustive. Others will be discovered or produced synthetically. It is hoped that mineralogists and crystallographers will pay special attention to potential microframeworks in the crystals they find or grow. These, in the hands of engineers, may make possible the construction of useful devices on a scale that would be prohibitively difficult for manufacturing processes. In the hands of crystallographers and physicists, microframeworks may be a new tool for the study of solids.

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SYNTHESIS OF SABUGALITE[1]

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In his paper on sabugalite, $HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$, Frondel (1951) stated that his efforts to synthesize this mineral had been unsuccessful.

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