Five-fold symmetry in chrysotile asbestos revealed by transmission electron microscopy

BARBARA A. CRESSEY

Department of Geology, University of Southampton, SO9 5NH, U.K.

AND

ERIC J. W. WHITTAKER

Department of Earth Sciences, University of Oxford, OX1 3PR, U.K.

Abstract

The structure of chrysotile, an important asbestos mineral, consists of layers curled concentrically or spirally into tubes. Published transmission electron microscope (TEM) images suggest that successive layers are generally stacked out of register with one another. However, a lattice model can be constructed in such a way that each layer can be stacked in register with the next, five times around the circumference, so that the structure exhibits a global 5-fold symmetry. We report here TEM observations confirming that chrysotile asbestos can form crystals with this structure, the first observation of five-fold symmetry in a natural crystalline material.

KEYWORDS: chrysotile, asbestos, transmission electron microscopy, five-fold symmetry.

Introduction

THERE is a continuing interest in the study of asbestos because of the health hazards associated with fibrous materials. Since asbestos fibres are very small, transmission electron microscopy (TEM) is the most appropriate method to study their morphologies and structures. Chrysotile, $Mg_3Si_2O_5(OH)_4$, is the most important asbestos mineral commercially. Its structure consists of layers curled concentrically or spirally into tubes. This structure was determined 40 years ago by X-ray diffraction (Whittaker, 1951; 1952; 1953; 1954; 1955*a,b,c,d*; 1956*a,b,c*; 1957) and was confirmed by imaging lattice fringes using high-resolution TEM (Yada, 1967; 1971). In the case of concentrically stacked layers, global 5-fold symmetry about the fibre axis is a necessary result of the long-range (though imperfect) order inherent in a cylindrical lattice with the lattice parameters of chrysotile. This is, of course, quite different from the 5-fold symmetry of quasi-crystals of intermetallic phases (on which there is now extensive literature—see for example Guyot *et al.*, 1991) which is based on local 5-fold symmetry axes without long-range order. We report here TEM observations which confirm that chrysotile asbestos can form crystals with 5-fold symmetry.

Chrysotile is one of the serpentine group of minerals, all of which have the approximate composition $Mg_3Si_2O_5(OH)_4$, and are sheet silicates with two components to each layer. One part is a sheet of silica tetrahedra in a pseudo-hexagonal network. Joined to this is a sheet of magnesium hydroxide octahedra, in which on one side, two out of every three hydroxyls are replaced by apical oxygens of the silica tetrahedra. A diagrammatic representation of this structure is shown in Fig. 1. What makes the serpentines such an interesting group of minerals is the fact that these two components have different dimensions, resulting in a structural mismatch which is compensated for, partially, in different ways by the different serpentine polymorphs. The silica layer has the smaller dimensions. In chrysotile the layers curl, concentrically or spirally, usually about the x axis or more rarely about the y axis. This structural arrangement produces smooth, silky fibres which are typically around 200 Å in diameter, and can be very long. At a radius of around 88 Å, the mismatch would be fully compensated in the y direction; for sheets inside or outside this radius, the mismatch is

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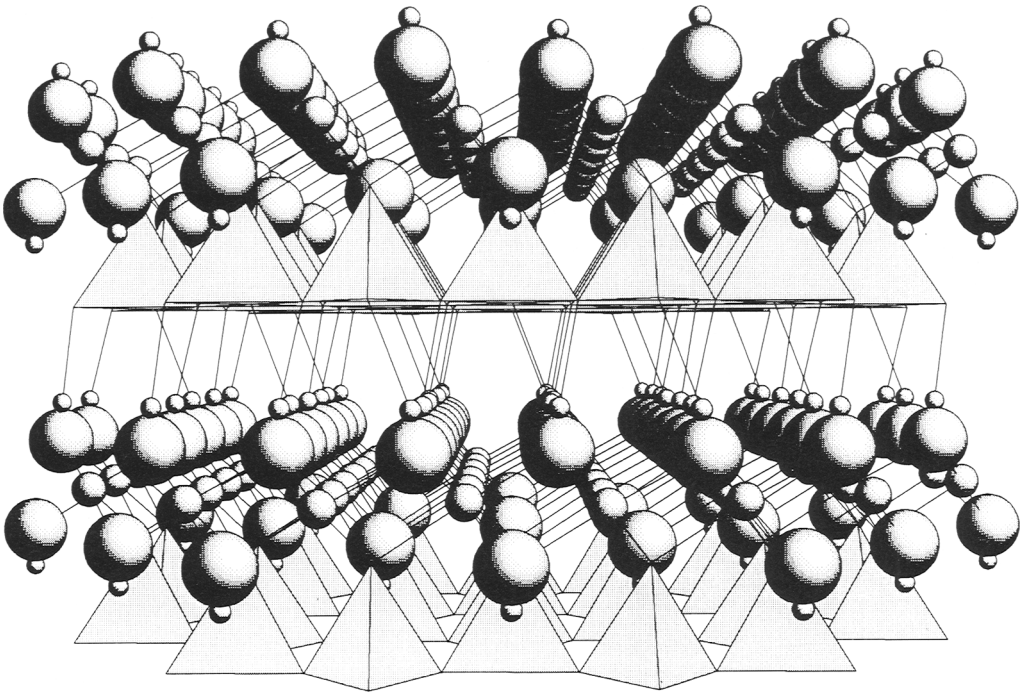

FIG. 1.Diagrammatic representation of the structure of two serpentine layers (without curvature). Pyramids represent SiO_4 tetrahedra. Mg atoms (intermediate-sized spheres) lie at the centres of octahedra of O atoms in (OH) groups or SiO_4 tetrahedra. (Large spheres O, and small spheres H).

over- or under-compensated. There is no compensation for the strain in the x direction in chrysotile.

Transmission electron microscopy

Previous studies. In Yada's TEM micrographs of chrysotile, the cylindrical wrapping of layers was clearly demonstrated by the images of (002) lattice fringes, 7.3 Å apart, corresponding with the spacing between the individual two-part layers. (The layer stacking arrangement in chrysotile has a 2-layer unit cell—hence the layer spacing is (002).) Radial (020) lattice fringes, which are 4.6 Å apart, were also resolved. (Radial lattice planes index as (020) because the structure is *C* face-centred.) Generally these planes are not straight, but zig-zag in direction as extra (out of register) unit cells are added around the circumference in successive layers, with the increasing radius of curvature.

This study. We have prepared chrysotile fibres for study by TEM by vacuum-impregnating fibre bundles in epoxy resin, then ion-beam thinning cut and polished slices, following standard procedures. Cross-sections of fibres were imaged using a JEOL JEM 2000FX TEM.

The specimen described here is from Nil Desperandum Mine, Shabani, Zimbabwe. It consists of fibres up to 4 cm long which, in hand specimen, appear similar to many other chrysotile asbestos fibres, except that they are more splintery than most.

In Fig. 2, we show a TEM image of cross-sections of chrysotile asbestos fibres (specimen BM 1929, 1974 provided by the Natural History Museum, London). In this orientation, with fibre axes exactly parallel to the electron beam, and with a slightly thicker part of the specimen than is ideal for high-resolution imaging, diffraction contrast makes the fibre sections appear completely dark. With increased exposure to the electron beam, the dark contrast breaks into radial bands,

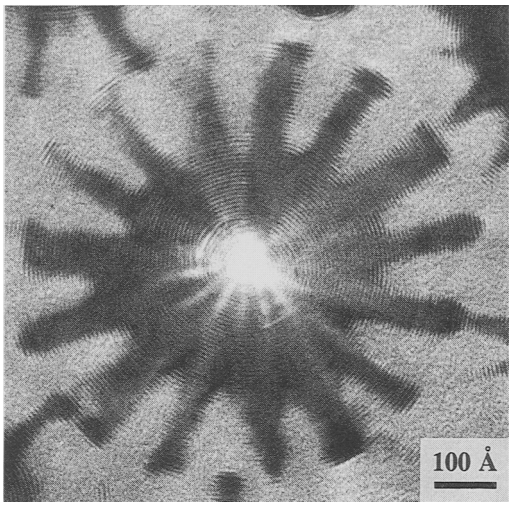

FIG. 2. Cross-section of a chrysotile fibre in the TEM, with fibre axis exactly parallel to the beam. Strong diffraction contrast, which initially made the section appear completely dark, has broken into 15 radial bands after a period of exposure to the electron beam has caused certain parts of the structure to become amorphous.

with the diffraction contrast being lost from the outside edge first and extending towards the centre with time, as is shown in Fig. 2. Dark diffraction contrast remains where (002) fringes are clearly visible and fades as the fringes disappear when these areas become amorphous under the beam. There are almost always 15 radial bands; the number 15 is very significant. As pointed out by Whittaker (1954), $2\pi\ d_{002} \approx 5b$. Although the b-parameter could be measured with only limited accuracy from the diffuse $0k0$ reflections, the relationship $2\pi\ d_{002} = 5b$ must be exact for a stack of closed cylindrical layers. This means that the relative positioning of successive layers will repeat five times around the circumference, and there must be 5-fold symmetry. This is true whether or not the layers are in register with each other anywhere, but if they are in register on one radial plane then they will be in register on five such planes.

Whittaker (1953) used a mask for optical diffraction in which the dots line up on certain radial planes, and in Fig. 3 we reproduce Whittaker's mask, marking with open circles those lattice points which line up radially. On the mask, the lining-up occurs ten times around the circumference. This is because the lattice points are separated by $b/2$ to allow for the effect of projection of the centred unit cell down a. If the structure were more susceptible to decomposition under the electron beam where the layers are out of step, then one could produce an effect similar to that in Fig. 2 but with only five spokes. However, the hydroxyl side of the serpentine layer has a repeat of only $b/3$, so there is local similarity of the arrangement of the basal oxygens of one layer with respect to hydroxyls of the next inwards 15 times per circumference. These 15 positions are marked on the digaram in Fig. 3. The areas between these 15 spokes, where layers are out of step and so hydrogen bonding between layers is not possible, probably produce 15 radial bands where decomposition under electron bombardment takes place more readily, as seen in Fig. 2.

Concluding remarks

Similar patterns of diffraction contrast have been observed in other samples, although sometimes showing less regularity. For example, many of the cylindrical fibres in the specimen described by Cressey and Zussman (1976) appeared to have many, possibly 15, dark radial contrast bands under appropriate conditions of alignment and exposure to the electron beam. In most of the fibre cross-sections in the present specimen we see the same pattern of diffraction contrast where the sections are of suitable thickness, though in some fibres it is less regular. In thinner regions, under conditions suitable to permit imaging of (020) lattice fringes, we see that these are frequently straight from centre to rim along certain radii, confirming that the layers are stacked in register with each other, though from these lattice images the 5-fold symmetry is not obvious. It is the overall pattern shown by strong diffraction contrast and a degree of beam damage that clearly demonstrates the 5-fold symmetry. Our interpretation of our observations is strictly applicable only to fibres consisting of closed cylindrical layers, and only to these if successive layers are so ordered as to be in register on a radial plane; if they are not in register in this way the 5-fold symmetry would not be made apparent by the beam damage. However a spiral latice mask (Whittaker 1955*b*) also shows a good approximation to radial alignment like that in Fig. 3, and it seems quite possible that fibrils with a cross-section of this form could also give similar effects. The development of 15 radial contrast bands may therefore not be limited to, or indicative of, fibrils with closed cylindrical layers.

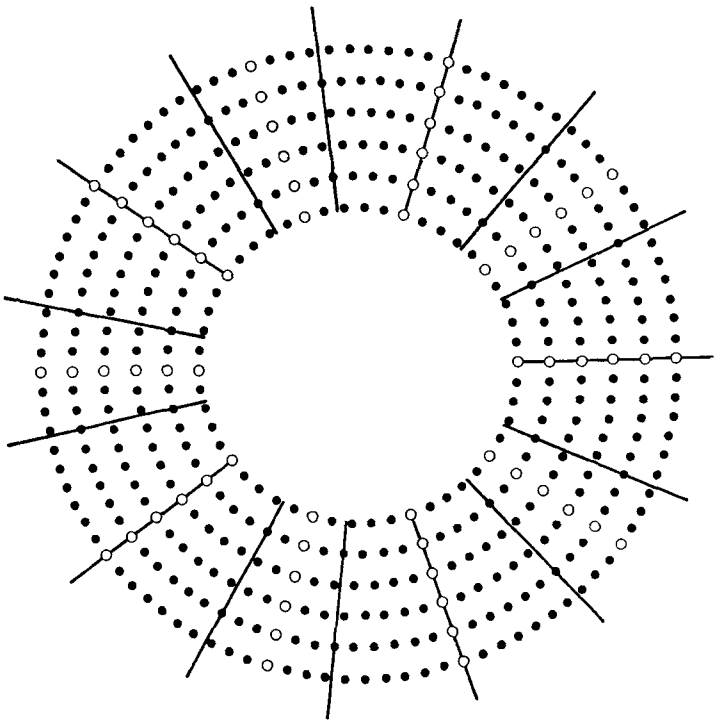

FIG. 3. A cylindrical array of points (after Whittaker, 1955*b*), representing a projection of chrysotile lattice cross-section. The points are separated circumferentially by *b*/2, and those marked with open circles are rows of points which exactly line up radially, in projection. Solid lines represent the 15 radial positions where local similarity of structure arising from the *b*/3 repeat of the hydroxyl layer could allow hydrogen bonding to occur between successive layers (see text for explanation).

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