

Order-Disorder Structures in Amesite

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The structures of an ordered and a disordered form of amesite have been reported independently in the literature. It is shown that the two structures are closely related to one another, the structure found for the ordered crystal being one of many ordered structures whose possible existence may be predicted from that found for the disordered crystal.

Introduction

Dornberger-Schiff (1956) states that 'an adequate description of structures exhibiting disorder phenomena cannot be expressed simply in terms of the language of classical crystallography'. Recent work on the structure of amesite illustrates this remark.

The structure of a disordered amesite crystal was originally described (Brindley, Oughton & Youell, 1951) in terms of a face-centred orthorhombic unit cell containing two types of layer, *X* and *Y*, which alternate throughout the structure. The diffuseness of reflexions with $k \neq 3n$ showed that there was some disorder in the stacking of the layers, with a randomness in the sequence of $\pm \frac{1}{3}b$ displacements. It was shown by comparison of calculated and observed intensities for reflexions with $k = 3n$, which were unaffected by the disorder, that, of the two geometrically possible stacking arrangements, I and II, which differ in their *ac* projection, the former is correct. This is the arrangement in which successive layers are stacked vertically above one another as seen in this projection. If there had been no *b*-axis displacements, the space group of this structure would have been $P6_3cm$, as stated in the paper. The attribution of a space group was, however, misleading, as it defines, not the disordered structure itself, but the simplest of the many ordered structures which may be derived from it. This point was not made sufficiently clear in the original paper.

Steinfink & Brunton (1956), in the course of their elegant and detailed examination of an *ordered* crystal of amesite, state that their data cannot be satisfactorily correlated with a structure derived from that of Brindley *et al.* assuming complete order and the space group $P6_3cm$. This, however, is not the only ordered structure which may be derived from that given by Brindley *et al.*, whose results referred explicitly to a *disordered* crystal. In fact, the ordered structure of Steinfink & Brunton, the hypothetical ordered structure of space group $P6_3cm$, and the actual disordered structure of Brindley *et al.* bear an interesting and altogether reasonable relationship to one another.

It is now realized that standard crystallographic nomenclature is not strictly applicable to structures showing disorder phenomena, and Dornberger-Schiff's suggested new nomenclature should help to clarify such problems.

It is relatively common in this type of layer mineral for many ordered structures to exist. They fit into the same general scheme as the disordered structures, and have a similar arrangement of atoms within the layers, but different, related, stacking sequences of the layers, e.g. zinc sulphide (Jagodzinski, 1949; Krumbiegel & Jost, 1955), β -wollastonite (Jeffrey, 1953), the chlorite minerals (Brindley, Oughton & Robinson, 1950), mica (Smith & Yoder, 1956), and cadmium iodide (Mitchell, 1956).

The basic atomic arrangement and the possible structural variations in amesite can best be clarified by describing the disordered structure more specifically than in the original paper, and then by deriving the relationships to be expected between the disordered and the possible related ordered forms.

The disordered form of amesite

A simpler description of the structure of the disordered crystal can be given in terms of one type of layer (Fig. 1) having the *X*-type arrangement of atoms relative to the three sets of axes labelled a_1b_1 , a_2b_2 and a_3b_3 , and the *Y*-type arrangement relative to the three sets $\bar{a}_1\bar{b}_1$, $\bar{a}_2\bar{b}_2$, $\bar{a}_3\bar{b}_3$. It follows that the structure is composed of identical layers stacked so that successive layers have $\pm 60^\circ$ rotations in the *ab* plane (equivalent to $\pm 180^\circ$ rotations because of the threefold symmetry of the layers) about an axis passing through an oxygen atom O_1 (Fig. 1); such layers can then take up any of three definite positions relative to one another, and this allows the formation of a disordered structure containing a random sequence of displacements of the layers by $\pm \frac{1}{3}b$ parallel to the three *b* axes. This threefold indeterminacy of position in the *b* directions causes the continuous streaks parallel to the c^* axis observed for reflexions with $k \neq 3n$, indexed in terms of the face-centred ortho-

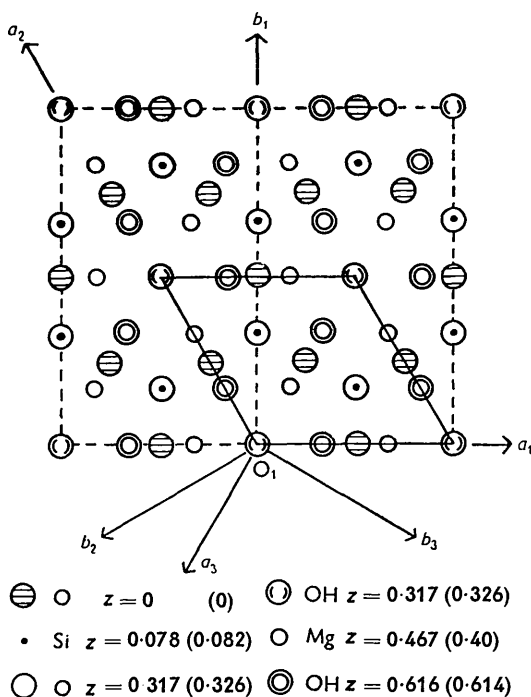


Fig. 1. Projection of one amesite layer on the layer plane (a_1a_2 projection); z coordinates are expressed as fractions of the height of one amesite layer. The values given by Brindley *et al.* (1951) are compared with those of Steinfink & Brunton (1956) (in brackets).

rhombic cell. If hexagonal indices are used then all reflexions with $(h-k) \neq 3n$ show disorder streaks (Fig. 2).

Thus the disordered structure has three-dimensional order within the layers only, together with certain restrictions on the stacking of the layers. Any one layer has a completely ordered three-dimensional

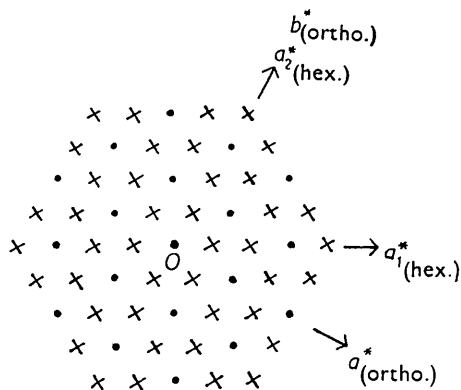


Fig. 2. Reciprocal lattice of amesite.

Dots: reflexions which are always sharp spots, and are unaffected by $\pm \frac{1}{3}b$ displacements of the layers. $k_{ortho.} = (h-k)_{hex.} = 3n$.

Crosses: reflexions which vary according to the sequence of $\pm \frac{1}{3}b$ displacements, and become continuous streaks parallel to c^* in disordered structures. $k_{ortho.} = (h-k)_{hex.} \neq 3n$.

atomic arrangement and all layers are identical in structure.

In Dornberger-Schiff's terminology the dimensions of the 'structural unit' are $a_1 = a_2 = 5.29$ kX., $e = 6.99$ kX. (the thickness of one amesite layer), $\alpha = 120^\circ$, and the symmetry of the layers (the A -symmetry) is $P(3)1m$. The stacking vectors are composed of two types, rotational and translational. The rotational vectors are:

$$S_1 = \frac{1}{3}\pi \text{ rotation about the } e \text{ axis,}$$

$$S_2 = -\frac{1}{3}\pi \text{ rotation about the } e \text{ axis,}$$

where the e axis is perpendicular to the plane of the layer and passes through an oxygen atom O_1 .

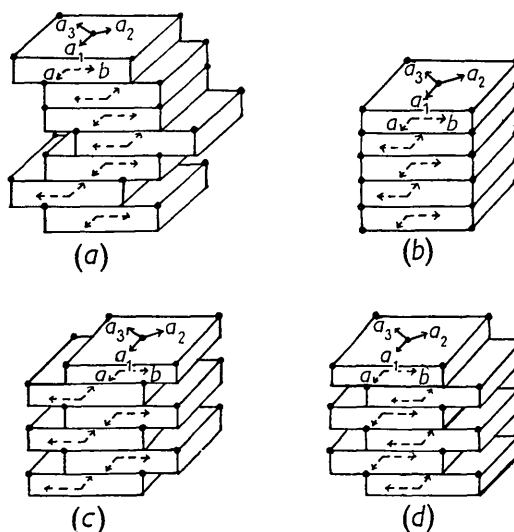


Fig. 3. Diagrammatic representation of the stacking of the layers in (a) a disordered structure; (b) the ordered sequence (1) with no b -axis displacements; (c) the ordered sequence (2) with regular $+\frac{1}{3}b$ displacements; (d) the ordered sequence (3) with regular $-\frac{1}{3}b$ displacements.

The translational vectors are:

$$S_3 = \frac{1}{3}a_1 + \frac{2}{3}a_2 + e (= +\frac{1}{3}b_1 + e)$$

$$S_4 = -\frac{1}{3}a_1 - \frac{2}{3}a_2 + e (= -\frac{1}{3}b_1 + e)$$

$$S_5 = \frac{1}{3}a_2 + \frac{2}{3}a_3 + e (= +\frac{1}{3}b_2 + e)$$

$$S_6 = -\frac{1}{3}a_2 - \frac{2}{3}a_3 + e (= -\frac{1}{3}b_2 + e)$$

$$S_7 = \frac{1}{3}a_3 + \frac{2}{3}a_1 + e (= +\frac{1}{3}b_3 + e)$$

$$S_8 = -\frac{1}{3}a_3 - \frac{2}{3}a_1 + e (= -\frac{1}{3}b_3 + e)$$

$$S_9 = e$$

where $a_1, a_2, a_3, b_1, b_2, b_3$ define axes *within* the layer being considered. Although the amesite layers themselves have only trigonal symmetry, their outermost sheets of atoms (upper and lower) are hexagonal networks, causing the stacking vectors to have hexagonal symmetry. It should be noted that the effects of the operations S_1 and S_2 on any one layer are indistinguishable owing to the trigonal symmetry of the layers; similarly $S_3 \equiv S_5 \equiv S_7$ and $S_4 \equiv S_6 \equiv S_8$. The mini-

num symmetry (the φ symmetry) of the family of structures formed by different sequences of these operations is $P(3)$, whilst the smallest possible unit cell which may be formed contains two amesite layers (in different orientations owing to the rotational vectors S_1 and S_2) and is 13.98 Å in thickness.

In a fully disordered structure the sequence of the translational vectors is completely random.

Related ordered structures

The possible existence of a variety of related ordered forms of amesite may be predicted. These ordered structures are composed of the same type of layer as the disordered structure and each layer is rotated by S_1 or S_2 ; but they have various *periodic* sequences of stacking vectors S_3 – S_9 . According to the complexity of these sequences, repeating units containing various numbers of layers can be formed.

If, as assumed, the stacking vectors are limited to those defined by S_1 – S_9 , then all the related amesite structures, ordered and disordered alike, would give identical patterns for reflexions with $k = 3n$. Only reflexions with $k \neq 3n$ would be affected by the structural variations, and these would vary both in position and intensity, the former according to the size and shape of, and the latter according to the arrangement of layers within, the resulting periodic unit.

Consider now the type of ordered structure examined by Steinfink & Brunton. The unit cell is hexagonal and contains two amesite layers. All the possible sequences of translational vectors giving this size of periodic unit may be examined. They are:

- (1) a translation of every layer by S_9 (i.e. no b -axis displacements),
- (2) a translation of every layer by S_3 (i.e. regular $+\frac{1}{3}b$ displacements),
- (3) a translation of every layer by S_4 (i.e. regular $-\frac{1}{3}b$ displacements).

Structures containing sequences (2) and (3) are enantiomorphous, because each layer has a mirror plane parallel to the a axis.

It should be remembered that these b -axis displacements are relative to a set of axes *within each individual layer*. As successive layers alternate between two orientations at 60° to one another, owing to the operations of the rotational vectors S_1 and S_2 , the sequence of b -axis displacements expressed in terms of a fixed set of axes for the structure as a whole is different from the sequence relative to the axes for the individual layers.

Let the two possible orientations of a layer relative to a chosen set of axes a'_1, a'_2, a'_3 for the whole structure be:

- X when $a'_1 \equiv +a_1, a'_2 \equiv +a_2, a'_3 \equiv +a_3$, and
 Y when $a'_1 \equiv -a_1, a'_2 \equiv -a_2, a'_3 \equiv -a_3$ (see Fig. 1).

(These are then the X - and Y -type layers described by Brindley *et al.* (1951).)

Thus sequences (2) and (3) have alternate $+\frac{1}{3}b'$ and $-\frac{1}{3}b'$ displacements relative to the fixed axes a'_1, a'_2, a'_3 . In sequence (2), layers in orientation X are translated by $+\frac{1}{3}b'$ and layers in orientation Y by $-\frac{1}{3}b'$, whilst in sequence (3) layers in orientation X are translated by $-\frac{1}{3}b'$ and layers in orientation Y by $+\frac{1}{3}b'$.

A comparison with the results of Steinfink & Brunton shows that the structure of the ordered crystal they examined has the second sequence of translational vectors, (or its enantiomorph, sequence (3)) whereas the ordered structure they assumed from Brindley *et al.*'s paper has the first sequence. It is now clear that both types of ordered structure bear a relationship to that of the disordered crystal, and therefore are equally in accord with it.

Whether the internal structure of the layers makes some sequences more favourable than others is still not clear. Only the relative positions of the Si–O nets in successive amesite layers are affected by the stacking sequences, but it is conceivable that certain arrangements of these nets may give a more stable structure than others. Again, while Steinfink & Brunton found a certain deviation from the 'ideal' structure of the layers in the ordered crystal examined by them, it remains a question to be answered whether this particular deviation occurs in *all* amesite crystals, or whether the layer structure 'adjusts' itself in different ways according to the stacking sequences of the layers. These points could be clarified only by a detailed survey of a varied selection of single crystals of amesite free from random sequences of $\pm\frac{1}{3}b$ displacements.

Note added in proof, 22 September 1957.—An example of the ordered form having space group $P6_3cm$, as described above, has since been discovered (private communication from Dr H. Steinfink).

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