CRYSTALLOGRAPHY

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Abstract

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ON THE CRYSTAL STRUCTURE OF HODGKINSONITE

The structure of hodgkinsonite was solved (1) exclusively by "direct" methods, without any preliminary considerations whatsoever. On the contrary, as a result of the deciphering, the repeatedly expressed supposition of a structural analogy between hodgkinsonite $Zn_2Mn[SiO_4](OH)_2$ and norbergite $Mg_2Mg[SiO_4](OH)_2$ was completely disproved. The very sharp difference between the two structural types is determined chiefly by the tendency of Zn toward fourfold coordination, once again confirmed in the example of hodgkinsonite, and only Mn in its octahedra can to some extent be likened to Mg. By analogy with a number of other Zn—Be silicates,* the principal structural detail in hodgkinsonite appeared to be metasilicate chains $[Zn_2O_6]_\infty$ with characteristic polarity; moreover, again by analogy with other Zn—Be silicates and Zn phosphates, the Zn metachains are encrusted with orthotetrahedra SiO_4. It was noted that these metachains may be regarded as cutouts from a two-layer closest packing, and the same was said of the corrugated "walls" of Mn octahedra. The entire structure is described within the framework of the monoclinic group $P\,2_1/a$, in the adopted mineralogical setting with angle $\beta = 95°25'$.

Fig. 1. Structure of hodgkinsonite as a closest packing of Mn octahedra and tetrahedra of two kinds: Zn (light) and Si (dark). The mineralogical cell (wavy lines) and the crystal-chemical cell (heavy lines) with two layers of close-packed polyhedra are indicated.

Fig. 2. *a*—lower layer of the hodgkinsonite structure; between the bordering chains of Mn octahedra, two ribbons of Zn (light) and Si (dark) tetrahedra extend in different orientations. *b*—upper layer of the same polyhedra.

But after a model of hodgkinsonite had been built from Pauling polyhedra, it became especially clear that the whole—entirely—structure of hodgkinsonite, like a very considerable number of Zn- and Be-silicates (and phosphates), represents a well-expressed closest packing. Descri-

The description of the structure of hodgkinsonite becomes exceptionally simple on passing to the cell shown (along with the generally accepted one) in Fig. 1. The relation between the axes of the "crystal-chemical" setting and the axes

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* For literature references, see (1).

Fig. 3

Figure 1: Fig. 3

of the mineralogical setting is given by the three equalities: $a' = a$, $b' = b$, $c' = -2a + c$.

The values calculated from this for the new axis $c' = 20.94$ Å and the new angle $\beta' = 146°11'$ (the excessively acute angle $\beta'' = 33°49'$) make the crystal-chemical cell not entirely convenient, but in the new cell the structure is described exceptionally simply: it consists of two layers of hexagonal closest packing, with a width (along the axis $c' = 20.94$ Å) of 6 polyhedra (6 oxygen diameters). In each of the two layers, between the outer zigzags of Mn octahedra (Fig. 2, *a*, *b*), there extend (parallel to the short axis *b*) two identical ribbons, in which pairs of Zn tetrahedra alternate with single Si tetrahedra. In one ribbon all (three, constituting a link) tetrahedra point "downward" with respect to the *bc* face that coincides with the plane of the drawing; in the other, upward. In the second layer (which is superposed on the first), the orientation of both the Mn octahedra and of the tetrahedra of both types changes (along the axis *b*).

Fig. 3. Linkage of tetrahedral motifs of the lower layer (left) with the analogous motif from the upper layer (right)

The seemingly isolated ribbons of each layer are joined by means of the ribbons of the overlying layer*. In Fig. 3 the entire left half of the polyhedra belongs to the lower layer, and the entire right half to the upper layer. At the junction a metasilicate chain is formed, to which attention was drawn in the first communication on the structure of hodgkinsonite. Recalculating the coordinates for the new cell according to the (contravariant) formulas $x' = x + 2z$, $y' = y$, $z' = z$, one can see the great similarity between the coordinates that follow from the closest-packing principle and the "experimental" coordinates. The isolation of the SiO_4 tetrahedron appears quite natural, taking into account the obligatory shortening of all its edges in comparison with the large tetrahedra around Zn and the octahedra around Mn.

We express our gratitude to Yu. N. Simakov, who constructed the polyhedral model, from which the crystal-chemical feature of hodgkinsonite emerged so clearly.

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1. L. P. Solov' eva, N. V. Belov, DAN, **152**, No. 2 (1963).

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* This layer is displaced relative to the lower one by one polyhedron (one oxygen diameter) to the left, which determines the very obtuse angle $\beta' = 146°$.