

The complete vibration spectra and the calculations with this model for other metals with the inclusion of long range forces are in progress.

REFERENCES

- Chevan L. 1968 *Phys. Rev.* **199**, 496.
 Cochran W. 1965 *Proceedings of the International Conference on Lattice Dynamics* ed. R.F. Wallis (New York, Pergamon Press), pp. 83.
 Joshi S. K. & Rajgopal A. K. 1968 *Solid State Physics*, Vol. 22, ed. F. Seitz and D. Turnbull (New York, Academic Press), pp. 159-312.
 Krebs K. 1965 *Phys. Rev.* **138**, A143.
 Langer J. S. & Vosko S. H. 1959 *J. Phys. Chem. Solids* **12**, 196.
 Lehman G. W., Wolfram T. & Dewames R. E. 1962 *Phys. Rev.* **128**, 1593.
 Overtone W. C. & Gaffney J. 1955 *Phys. Rev.* **98**, 969.
 Shukla M. M. & Closs H. 1973 *J. Phys. F. Metal Phys.* **3**, 1.
 Svensson E. C., Brockhouse B. N. & Rowe J. M. 1967 *Phys. Rev.* **155**, 619.

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Disorder in the crystal structures of some hexahydrated perchlorates

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Crystal structures of a number of hexahydrated perchlorates with general formula $M'(ClO_4)_2 \cdot 6H_2O$, where $M' = Mg, Mn, Fe, Co, Ni, Zn, Cd$ and Hg , were studied by West (1935), who discovered that as far as the dispositions of the ClO_4 groups and H_2O molecules are concerned, these structures totally resemble that of $LiClO_4 \cdot 3H_2O$. The only difference observed in case of the hexahydrate structures is in the distribution of the divalent metal ions amongst the available sites. $LiClO_4 \cdot 3H_2O$ crystals have space group $P6_3mc$, with $a = 7.71 \text{ \AA}$, $c = 5.42 \text{ \AA}$ and $Z = 2$ (West 1934). The metal atoms with coordinates $00\frac{1}{2}$ and $00\frac{3}{2}$ are at the centres of water octahedra, which form columns along the direction of the six-fold axis. Two neighbouring octahedra in a column share a sheet of three water molecules between them. The chlorine atoms, situated centrally in oxygen tetrahedra, lie on the three-fold axes. A group of four unit cells of this structure is shown in (001) projection in figure 1.

When a compound $M'(ClO_4)_2 \cdot 6H_2O$ crystallises with the above structure, the number of sites (centres of water octahedra) available for M' atoms is double

the number of such atoms present, and there are different possible ways of distributing the M' atoms amongst the available sites. West (1935) described two such arrangements :

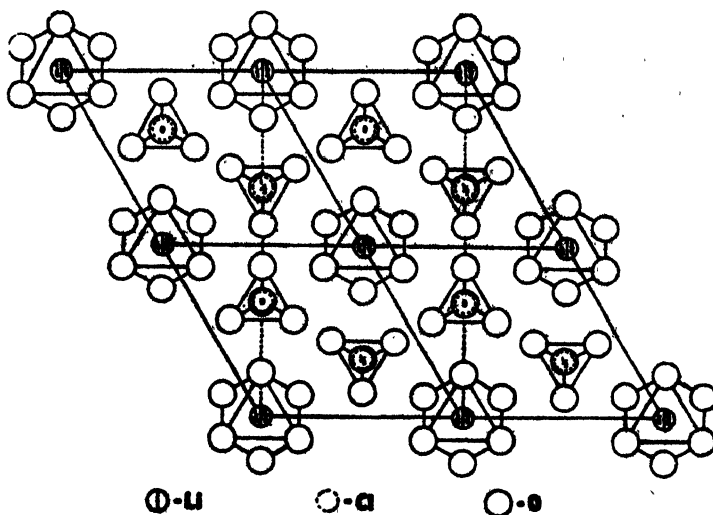


Fig. 1. Four unit cells of lithium perchlorate trihydrate structure, shown in (001) projection ; z -coordinates of the Li and Cl atoms are marked.

(1) All the metal atoms may occupy similar sites (say, those at $z = \frac{1}{4}$ level) in all the columns. In this case the cell dimensions remain unaltered but the symmetry reduces to $P3m1$. The Cd and Hg compounds are reported to have this structure.

(2) The metal atoms may occupy the sites at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ respectively in alternate rows, parallel to any one of the three equivalent axial directions in the plane perpendicular to the unique axis. Such an arrangement reduces the symmetry to $Pmn2_1$, and the orthorhombic cell, of dimensions $a = a_h$, $b = \sqrt{3}a_h$, and $c = c_h$ (subscript h refers to the hexagonal cell of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$), is shown in broken outlines in figure 1. Here the rows along which the metal atoms are at similar z -levels, are parallel to the X -axis. Evidently there are three equally probable orientations of this cell, with the a -axis coinciding respectively with the $[100]$, $[010]$ and $[\bar{1}\bar{1}0]$ directions of the hexagonal cell. Crystals of the Mg, Mn, Fe, Co, Ni and Zn compounds, reported to have this structure, grow as a special type of three-component twins, where the perchlorate-water structure is continuous throughout the bulk of the crystals, discontinuity at the twin boundaries being only in the distribution of the metal atoms. To emphasise this novel feature, the term *hemispherulites* rather than twin has been suggested by West for this type of crystals.

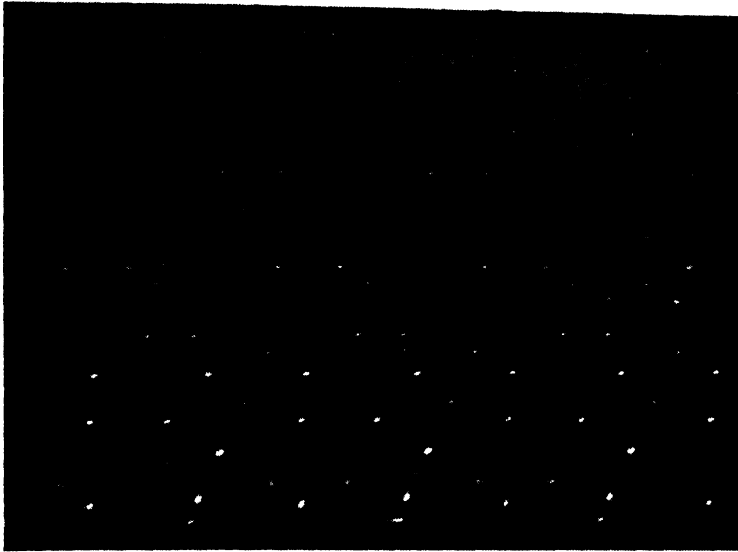


Fig. 2. First level Weissenberg photograph of zinc perchlorate hexahydrate crystal, taken about the *c*-axis.

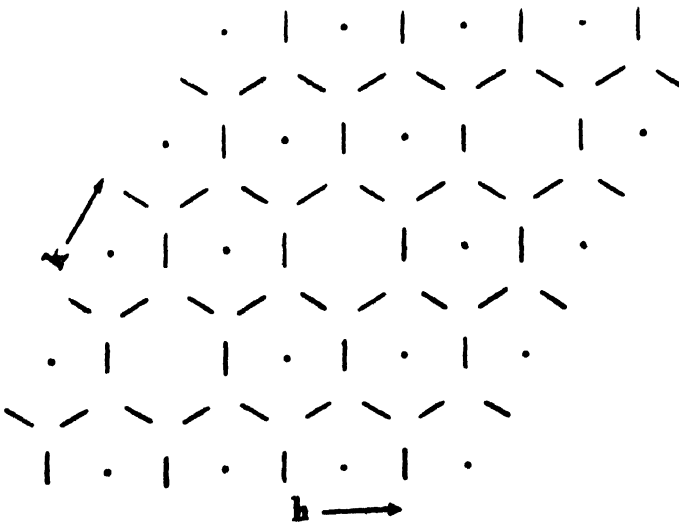


Fig. 3. A portion of the *hkl* level of the reciprocal lattice (idealised) derived from the photograph in figure 2.

In the X-ray photographs of the Zn compound, however, West (1935) observed some peculiarities. They displayed sharp spots corresponding to a cell of dimensions similar to that of the Li compound, and some weak diffuse spots corresponding to a doubling of cell-dimensions in the plane normal to the unique axis. In the basal Laue photographs, the diffuse spots were found to streak out into a continuous net of hexagons, each surrounding a sharp spot. These observations suggest a disordered nature of the structure of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Preliminary results of our investigations on this interesting structure are presented here.

Cell dimensions, determined from oscillation and Weissenberg photographs, are $a = 15.43 \pm 0.02 \text{ \AA}$, $c = 5.22 \pm 0.01 \text{ \AA}$. The cell volume is thus about four times that of $\text{Li}(\text{ClO}_4) \cdot 3\text{H}_2\text{O}$, and in this case $Z = 4$. In the c -axis oscillation photographs while only the usual sharp spots appear in the even layer lines, there are some diffuse spots (streaking along the layer lines) along with the sharp ones in the odd layer lines. From such a disposition of the diffuse spots it is evident that there is some indefiniteness in the periodicities in the plane normal to the unique axis.

The even layer Weissenberg photographs about c -axis consist of sharp spots only, with both h and k even. Spots with either h or k or both h and k odd, appearing in the odd-layer photographs only, are diffuse, and streak out to form a hexagonal network (figure 2).

An $hk0$ Patterson projection confirmed that the arrangement of the perchlorate tetrahedra and the water octahedra was exactly similar to that in the lithium compound. To study the nature of disorder, the hkl level of the reciprocal lattice was constructed from the first layer Weissenberg photograph (figure 3). Inspection of this diagram revealed that the directions of extension of spots with h odd, k odd and both h and k odd are reciprocal respectively to the $[120]$, $[\bar{2}10]$ and $[\bar{1}10]$ directions in direct space. These three are the directions of the b -axes of the orthorhombic cells of three different orientations postulated by West. Thus, although the Zn-compound has a hermaphrodite orthorhombic structure similar to the Mg-compound, there is some indefiniteness in periodicity along the b -axes of all the three components. A quantitative study on the probability of mistakes occurring along these directions is in progress.

Another member of the series, $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, is reported to undergo a reversible phase transition at low temperature (Chowdhury & Ghosh 1974). Preliminary examination of crystals of this compound prior to a low temperature study yielded some interesting results. It was found that even among the crystals from the same crop, there were two varieties, one showing diffuse spots

indicating disorder, and the other showing no such irregularities. While the ordered variety probably has a structure similar to that of the Mg compound, there are indications that the nature of the disordered structure may not be similar to that of the Zn-compound. In this case no mirror symmetry is observed perpendicular to the unique axis which may therefore have at best a three-fold symmetry. It is highly probable that the structure of this variety of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystals is a disordered variant of the trigonal structure of the Cd and Hg compounds. Detailed study of both these varieties as well as the low temperature phase has been taken up.

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REFERENCES

- Chowdhury B. K. & Ghosh D. 1974 *Physica Stat. Solidi*. **23a**, 649.
West C. D. 1934 *Z. Kristallogr.* **88A**, 198.
West C. D. 1935 *Z. Kristallogr.* **90A**, 480.