Zeitschrift für Kristallographie, Bd. 127, S. 73–93 (1968)

The crystal structure and crystal chemistry of valleriite

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(Received December 14, 1967)

Auszug

Die Struktur des Valleriits besteht aus zwei verschiedenen Schichtarten, die abwechselnd aufeinander folgen: aus brucitähnlichen Schichten $[Mg_{0,68}Al_{0,32}(OH)_2]$ und aus neuartigen Sulfidschichten der Zusammensetzung $[Fe_{1,07}Cu_{0,93}S_2]$. Eine solche Sulfidschicht besteht aus zwei ebenen dichtesten Packungen von Schwefelatomen. Alle der in dieser Schwefeldoppelschicht vorhandenen Tetraederlücken sind statistisch durch Fe- und Cu-Atome besetzt. Die Struktur als Ganzes erfordert eine große Überzelle; sie kann aber mit Hilfe von zwei getrennten Unterzellen beschrieben werden: einer zu den Sulfidschichten gehörenden rhomboedrischen Unterzelle mit $a = 3{,}792 \pm 0{,}005$ Å und $c = 34{,}10 \pm 0{,}05$ Å, Raumgruppe $R3m$; und einer zu den Hydroxidschichten gehörenden hexagonalen Unterzelle mit $a = 3{,}070 \pm 0{,}006$ Å und $c = 11{,}37 \pm 0{,}02$ Å, Raumgruppe $P\bar{3}m1$. Die Struktur wurde für die beiden Unterzellen getrennt verfeinert unter Benutzung von zwanzig $10l$-Reflexen des Sulfidteilgitters ($z_{\text{Fe, Cu}} = 0{,}3083 \pm 0{,}0002$, $z_{\text{S}} = 0{,}03791 \pm 0{,}0003$) und von zwölf $10l$-Reflexen des Hydroxidteilgitters ($z_{\text{OH}} = 0{,}4704 \pm 0{,}0005$, bezogen auf $c = 34{,}10$ Å). Der endgültige Zuverlässigkeitsindex für alle Reflexe einschließlich von elf $00l$-Werten beträgt $R = 0.068$. Die Gitterkonstanten a der beiden Unterzellen stehen im Verhältnis 21 : 17. Daher lautet die Gesamtformel für den Valleriit $1{,}526\,[Mg_{0,68}Al_{0,32}(OH)_2] \cdot [Fe_{1,07}Cu_{0,93}S_2]$, $\{(21/17)^2 = 1{,}526\}$. Dieses Ergebnis stimmt gut mit den analytischen Daten überein und erklärt die ungewöhnlichen Eigenschaften sowie die Vorkommensart des Valleriits. Valleriit gehört zu der Gruppe der Doppelschichtstrukturen, in denen brucitähnliche Schichten, die wegen eines teilweisen Ersatzes von Magnesium durch Aluminium (oder Eisen usw.) eine positive Ladung tragen, regelmäßig mit negativ geladenen Schichten anderer Art abwechseln.

Abstract

The crystal structure of valleriite has been determined to consist of alternate interlayering of layers of two kinds: a brucite-like layer of composition $[Mg_{.68}Al_{.32}(OH)_2]$; and a novel sulfide layer of composition $[Fe_{1.07}Cu_{.93}S_2]$.

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The sulfide layer consists of two sheets of sulfur atoms in close-packed association, with all of the tetrahedral sites occupied at random by Fe and Cu atoms. The structure as a whole requires a large superlattice, but can be defined in terms of two separate sublattices: one rhombohedral with hexagonal axes $a = 3.792 \pm .005$ Å and $c = 34.10 \pm .05$ Å, space group $R\bar{3}m$, corresponding to the sulfide layers; and one hexagonal with $a = 3.070 \pm .006$ Å and $c = 11.37 \pm .02$ Å, space group $P\bar{3}m1$, corresponding to the hydroxide layers. The structure was refined in terms of the two sublattices separately using twenty $10l$ counter-measured data (Mo$K\alpha$) for the sulfide substructure ($z_{\mathrm{Fe,Cu}} = 0.3083 \pm .0002$, $z_{\mathrm{S}} = 0.3791 \pm .0003$) and twelve $10l$ data for the hydroxide substructure ($z_{\mathrm{OH}} = 0.4704 \pm .0005$, referred to $c = 34.10$ Å). The final reliability index for all reflections including eleven $00l$ data is $R = 0.068$. The a axes of the two subcells are in the ratio of 21:17, hence the overall composition of valleriite is $1.526\,[\mathrm{Mg_{.68}Al_{.32}(OH)_2}] \cdot [\mathrm{Fe_{1.07}Cu_{.93}S_2}]\,\{(21/17)^2 = 1.526\}$. This result is in good agreement with analytical data and accounts well for the unusual properties and occurrence of valleriite. Valleriite belongs to a well established group of minerals which have structures where brucite-like layers bearing a positive charge through extensive substitution of magnesium by aluminum (or iron, etc.) are interleaved by negatively charged layers of another kind.

Introduction

Valleriite was first described and named by Blomstrand (1870) on the basis of his study of material from Nya Kopparberg, Sweden. It is a soft, flaky mineral with a texture like that of graphite, and has a dull, bronzy luster. Its most striking characteristic is its unusual chemical composition, consisting of approximately 65 wt.% copper iron sulfide and the remainder of magnesium aluminum hydroxide. This feature, difficult to reconcile with ordinary principles of chemical affinity, has been a major stumbling block to its acceptance as a mineral species up to the present time. Even though good specimens showed no lack of homogeneity, many mineralogists have preferred to regard the material as an intimate interlayering of two separate phases on a submicroscopic scale. On the other hand, chemical analyses of samples obtained at such widely distant sources as Sweden and South Africa show a similarity of composition that is remarkable if the material is to be regarded as a mixture.

The identity and character of valleriite have in the past been obscured by its formerly almost universal confusion with another mineral with very similar physical properties but quite different chemical composition and mode of occurrence—mackinawite. Mackinawite was first clearly defined by Kouvo, Vuorelainen and Long (1963) as a tetragonal polymorph of troilite, FeS. Berner (1962) showed that it is isostructural with the synthetic compound FeSe.

In 1964, EVANS *et al.* made a crystallographic and petrographic study of the two minerals, giving definitive data by which they may be distinguished. They showed conclusively that they are distinct species, and that at least since 1930 most of the frequent reports of occurrence of valleriite probably were actually occurrences of mackinawite. These authors maintained that analyzed valleriite is a mixture of two phases, and that the copper sulfide phase is probably a dimorph of chalcopyrite, $CuFeS_2$. The magnesium aluminum hydroxide phase could not be identified with any previously known substance.

Up to the time of the study of EVANS *et al.* (1964), only two conclusively verified localities for valleriite were known; Kaveltorp in Sweden, and Loolekop and Palabora in South Africa. Recently valleriite has been positively identified from Greece (PANAGOS and RAMDOHR, 1965), Cyprus (ANTUN, EL GORESY and RAMDOHR, 1966), and Canada (CHAMBERLAIN and DELABIO, 1965). The latter two reports are illustrated with good pictures of polished sections showing valleriite. A description of an excellent study of valleriite and mackinawite from the Soviet Union (Noril'sk, Monchegorsk, and Khalilovsk) has also been published by GENKIN and VYAL'SOV (1967).

The feature common to all reported occurrences of valleriite is the indication that it is formed from other copper ores, such as cubanite ($CuFe_2S_3$) and chalcopyrite ($CuFeS_2$), during a serpentinization process, presumably at low temperatures ($< 250\,^{\circ}C$). ANTUN *et al.* (1966) have observed that cubanite is replaced by valleriite more easily than chalcopyrite, and also that occasionally the outermost rim of the valleriite is converted to chalcopyrite.

Taking a strong lead from the close crystallographic similarity between smythite Fe_3S_4 (ERD, EVANS and RICHTER, 1957) and the valleriite sulfide phase, EVANS continued his search for the crystal structure of the latter. Owing to the poor quality of the crystals only about 40 independent intensity data could be measured, but it was hoped that a structure could be found, since at most seven structure parameters would need to be determined. As in smythite, the problem was essentially one-dimensional, and consisted of finding the sequence of sulfur and metal atoms along a single three-fold symmetry axis in the rhombohedral unit cell. An exhaustive search for a structure that would satisfactorily explain the observed intensities, during which hundreds of models were tested, proved of no avail.

The key was finally provided by an application of the structural principles found to form the basis of the crystal structure of koenenite determined by LOHSE *et al.* (1963; also ALLMANN *et al.*, 1968). This mineral proved to consist of a coherent interlayering of sheets of sodium magnesium chloride and magnesium aluminum hydroxide. ALLMANN and LOHSE (1966) have proposed that such an alternating layer structure may be the basis of the structure of valleriite. When the hypothesis of an interlayered structure for valleriite in which the magnesium aluminum hydroxide component is incorporated coherently with the sulfide component was tested, the correctness of such a structure was immediately apparent from an impressive agreement of observed and predicted intensities. The determination, refinement and crystal chemical properties of the structure of valleriite so deduced form the subject of this paper.

Crystallography of valleriite

No discrete single-crystal diffraction patterns could be obtained from any specimens of valleriite from Sweden (Kaveltorp). Newly obtained, rich samples from Loolekop, South Africa, recognized to be identical with the Swedish mineral mainly by means of x-ray powder patterns, have provided crystals large enough to give clear Buerger precession patterns. Although the patterns are usually multiple and smeared through crystal distortion, especially by twisting around the hexagonal *c* axis, a discrete crystal lattice can be clearly recognized. The photographs of the $hk0$, $h0l$ and hhl nets are reproduced in Fig. 1. The crystal used to make these patterns is an irregulalry shaped plate approximately 0.60 × 0.35 mm in size and 0.025 mm thick. From it all of the single-crystal data used for this work were obtained.

Except for a few diffraction effects that belong to a second crystal rotated approximately 17° about the *c* axis with respect to the main crystal, all of the effects can be attributed to Bragg reflections from a structure corresponding to the Laue group $\bar{3}m$. The $h0l$ net of its reciprocal lattice (Fig. 1*b*) shows certain special features that can immediately be associated with the crystal chemistry of valleriite. The pattern consists of a series of rows of spots parallel to c^*, indicated by the symbols 0_{SH}, 1_{S}, 2_{H}, 3_{S}, 4_{H} and 5_{S} (S stands for sulfide and H for hydroxide as will become apparent below). The spacing of the reflections within each row is the same for all rows and corresponds to 11.37 Å, but the reflections in different rows are not in horizontal or sloping register with one another. Also, the spacing of rows along the a^* direction is not regular.

One obvious way to interpret this pattern calls for two hexagonal reciprocal lattices in parallel orientation, one containing the rows with subscript S and one containing those with subscript H. The S direct lattice is evidently rhombohedral with a hexagonal *c* axis three times the single-row spacing, but the H lattice is primitive with *c* axis equal to the single-row spacing. The two direct cells may then be defined as follows (assuming the highest possible space-group symmetry in each case):

Lattice	S	H
Space group	$R\bar{3}m$	$P\bar{3}m1$
a	3.792 ± .005 Å	3.070 ± .006 Å
c	34.10 ± .05 Å	11.37 ± .02 Å.

The similarity of the S lattice to that of smythite (Erd, Evans and Richter, 1957), which has the same symmetry and a rhombohedral unit cell with hexagonal $a = 3.47$ Å and $c = 34.5$ Å, is striking, and suggests the presence of a close-packed stacking of 12 sulfur atoms in the hexagonal cell as in that case. The *a* axis of the H lattice, on the other hand, corresponds well with a lattice containing close-packed oxygen layers as in brucite, for which the hexagonal $a = 3.13$ Å. It is natural to associate the S lattice with the sulfide portion of the chemical analysis and the H lattice with the hydroxide portion. But while the *a* axes of the two lattices do not seem to be related to each other, their *c* axes are essentially equal, except for a factor of 3.

A second way to interpret the *h*0*l* net can be based on a single superlattice. Such a lattice would be primitive or rhombohedral hexagonal, Laue group $\bar{3}m$, and have a *c* axis of 34.10 Å. In order to index all of the *h*0*l* rows rationally, the *a* axis must be very large. To find it, we must find the rational ratio between the *a* axes of the S and H lattices given above. The ratio $a_S : a_H$ $(= p:q)$ is nearly 4:3, but not exactly (by inspection of Fig. 1*b*, it is apparent that row 4_H is not exactly midway between rows 3_S and 5_S). We shall discuss the question of the proper ratio later, but for the moment, let us accept $p:q = 21:17$. The superstructure will then be defined as follows:

Space group	$R\bar{3}m$, $R3m$ or $R32$
hexagonal *a*	$64.46\ \text{Å} = 17a_S = 21a_H$
hexagonal *c*	$34.10\ \text{Å} = c_S = 3c_H$
hexagonal cell volume	122,720 Å^3.

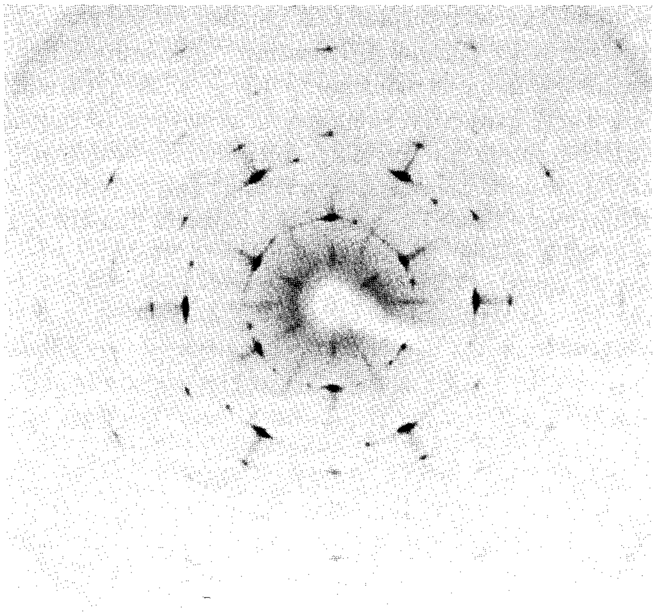

Fig. 1*a*

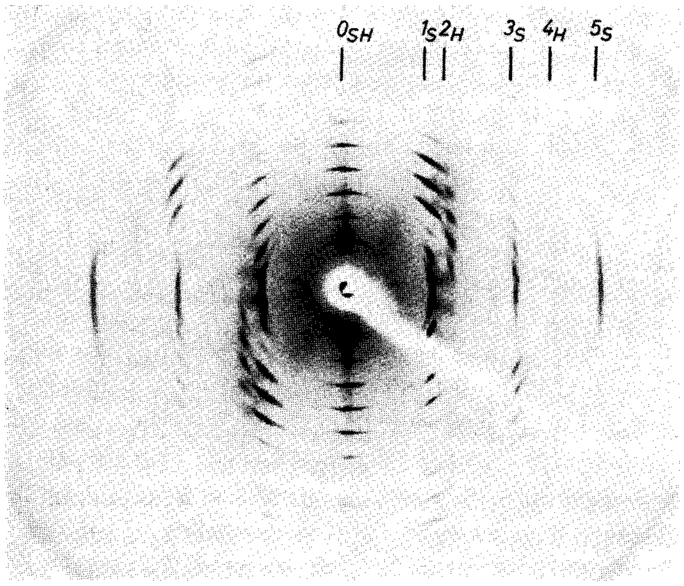

Fig. 1*b*

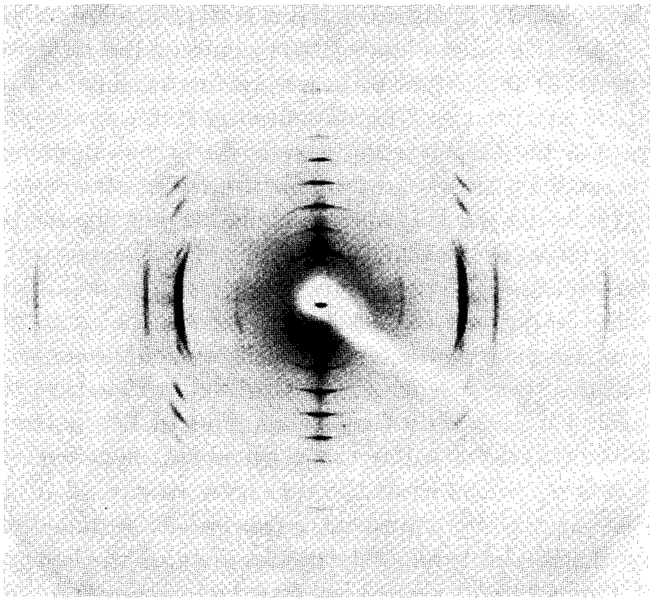

Fig. 1c

Fig. 1. Buerger precession photographs (Mo*K* radiation) of three nets of the valleriite lattice: (*a*) *hk*0, (*b*) *h*0*l* and (*c*) *hhl*

It can be shown that if *p* is a multiple of 3, a rhombohedral superlattice will account for all observed reflections, but if it is not, the superlattice must be primitive. The lattices S and H now become sublattices of this superlattice, and the sulfide and hydroxide chemical components are incorporated into one coherent structure. Diffraction effects from only a very few of the planes in this lattice will be produced, however, and these will emphasize sublattices corresponding to the lattices S and H mentioned above.

The structure determination of the mineral koenenite by ALLMANN, LOHSE and HELLNER (1968) gives strong support for the second interpretation described above. Koenenite is described by PALACHE, BERMAN and FRONDEL (1951) as a hexagonal mineral of composition $Mg_5Al_2(OH)_{12}Cl_4$, but 16 to 18 percent of alkali chlorides found in the analyses was ignored in this formula. ALLMANN *et al.* found the structure to consist of alternating layers of two kinds: one like that in brucite with composition $[Mg_7Al_4(OH)_{22}]^{4+}$; and one with a $CdCl_2$-like structure with composition $[Na_4(Ca,Mg)_2Cl_{12}]^{4-}$. Because of the poor fit between the hydroxide layer and the chloride layer, the relationship between them in the (001) plane of the structure seems at first to be irrational, but nevertheless it is fixed and remains coherent throughout the structure. The diffraction patterns show only reflections corresponding to two sublattices in the very large superlattice required to define the whole structure: one corresponds to the hydroxide layers, which are in simple hexagonal sequence along the c axis; the other corresponds to the chloride layers, which are in rhombohedral sequence.

A simple test proved that valleriite has an analogous structure, consisting of alternating brucite-like layers and sulfide layers of a new type. Intensities were calculated for the twelve measured $00l$ reflections for such a model. With the cations (Cu and Fe) located in octahedral sites between the sulfur sheets, the agreement with observed intensities was poor, but when the cations were located in the tetrahedral sites, agreement improved ($R = 24\,^0/_0$). A one-dimensional Fourier synthesis clearly showed the elements of the layer structure (see Fig. 3, curve P) and yielded improved values for the three structure parameters, which gave a reliability index of $R = 15\,^0/_0$. Thus, the coherent superlattice model was definitely established as the correct one.

Determination and refinement of the structure

X-ray diffraction intensities for valleriite were obtained with a General Electric Co. single-crystal goniostat, using a scintillation counter and strip chart recordings of the counting rate. The radiation used was Zr-filtered Mo$K\alpha$. The intensites were measured by integrating the recordings with a polar planimeter. Because of the poor quality of the crystals, the peaks were broad and sometimes poorly shaped, and reproducibility was only fair. In this way, 47 independent reflections were measured. The data were corrected in the usual way for the Lorentz-polarization effects, but no corrections were made for anomalous dispersion or extinction.

Attempts were made to estimate absorption corrections on the assumption of an infinite, thin plate, but such corrections could not be reconciled internally with the data (by measurement of equivalent reflections) nor made to effect any improvement of intensity agreement in the structure analysis. Such a correction changes slowly at high angles to the plane of the plate, but drops abrubtly toward zero (for the absorption factor A) below a grazing angle of about 10°.

It is apparent from the precession patterns (Fig. 1) that crystal distortions such as bending extend well beyond this range, so that the absorption correction becomes meaningless. Therefore, no correction at all was applied. Such distortions may be expected to affect the intensity measurements in a systematic way, but it seems safe to assume that the effect will for the most part vary monotonically with Bragg angle for the reflections that were measured, and that the error introduced will appear mainly in the temperature parameters.

The crystal-structure model assumed for the refinement is shown in Fig. 2. The top view in this figure shows a portion of the hydroxide layer superposed on the sulfide layer. A plane is passed through this structure as shown by the line trace *XX*, and all the atoms lying on this plane are shown in the lower view in the figure, taken normal to the section plane. Here the sequence of alternating hydroxide layers and sulfide layers is apparent, all layers having a common origin on the [001] axis at the left. The hydroxide layers have a simple hexagonal sequence and, if the sulfide layers are ignored, can be defined by the dashed-lined unit cell (lattice H). The sulfide layers follow a rhombohedral sequence and, ignoring the hydroxide layers, can be defined by the full-lined unit cell (lattice S).

There are two possible ways of arranging the hydroxide layers with respect to the sulfide layers,

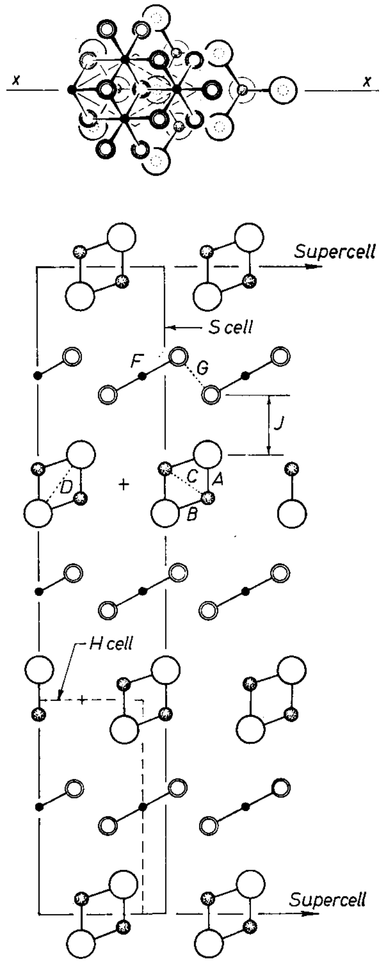

Fig. 2. The crystal structure of valleriite, showing arrangement of atoms in a (110) plane through the origin, represented by *XX* in the top view. The top view shows a portion of the hydroxide layer superimposed on a portion of the sulfide layer. Large open circles, S; double open circles, OH; shaded circles, (Fe,Cu); small black circles, (Mg,Al)

corresponding to a reversal in the z direction. The correct one (shown in Fig. 2) was easily determined by inspection of the $h0l$ precession pattern (Fig. 1*b*).

To define and refine the structure of valleriite as a whole in terms of the superlattice would require the placing of 247 atoms in the asymmetric unit of the hexagonal-rhombohedral cell given above (assuming space group $R\bar{3}m$), corresponding to 648 positional parameters. Instead of this obviously impractical approach, we must make the important assumption that each layer retains its ideal form undisturbed by the irregular contacts it makes with neighboring layers. The whole structure can then be defined in terms of only three variable structure parameters subject to refinement, one z parameter each for (Fe,Cu), S and (OH). The calculations can then also be carried out entirely in terms of the simple sublattices. The reason for this simplification is that, in such an idealized superstructure, only those reflections will have nonzero intensity that correspond to one or the other sublattice. Reflections corresponding to the sulfide substructure will receive no contribution from the hydroxide component; those corresponding to the hydroxide substructure will receive no contribution from the sulfide component. Only the $00l$ series of reflections will receive contribution from layers of both types.

The treatment can then proceed for the sulfide and hydroxide layers independently (each based on its own group of sublattice reflections), except for the $00l$ reflections and the determination of the relative scattering powers of the two sublattices. The ratio of scattering powers is determined by the relative dimensions of the two sublattices, in particular, the ratio of their parallel hexagonal a axes. This ratio is best measured from the Buerger precession patterns. These yield $a_S = 3.792 \pm .005$ Å and $a_H = 3.070 \pm .006$ Å. To fit together in a coherent structure, these values must have a rational relationship to each other; that is,

$$a_S : a_H = p : q = r : 1$$

where p and q are integers, and $r = 1.235 \pm .004$. The nearest appropriate values of p and q are the following:

p	q	r	r^2
5	4	1.250	1.563
16	13	1.231	1.515
21	17	1.235	1.526
26	21	1.238	1.533

The ratio 5:4 is clearly eliminated, but evidently we cannot choose with complete certainty among the remaining three ratios, or others involving higher values of p and q. We choose 21:17 as giving the best fit to our data. As noted earlier, this ratio is consistent with a rhombohedral superlattice, and in fact is the only one that is. Such a superlattice has the attractive feature that there is crystallographically only one kind of sulfide layer and one kind of hydoxide layer, rather than two or three kinds of each as would be required by a primitive superlattice. On the other hand, in terms of lattice energies, this fact may well be irrelevant to the stability of the actual structure.

Structure-factor calculations were then carried out for each type of layer separately on the basis of its respective subcell. When combining the results, basing our structure-factor calculations on one unit of the sulfide layer contained in one layer in one hexagonal subcell, we have multiplied the contribution of the corresponding structural unit in the hydroxide subcell by the factor $r^2 = 1.526$, to compute the $00l$ structure factors and establish a common relative scale for the other reflections.

Of the 43 nonequivalent, nonzero structure amplitudes measured, 20 are $10l$ reflections of the rhombohedral sulfide sublattice (S), 12 are $10l$ reflections of the hexagonal hydroxide sublattice (H), and 11 are $00l$ reflections common to both substructures. Refinement was carried out by full-matrix least-squares analysis on these three separate groups of reflections using unit weigths. The results are shown in detail in Table 1. None of the separate results differs from the indi-

Table 1. *Refinement of the valleriite crystal structure*

All of the z parameters are given in terms of $c = 34.10$ Å, and their standard deviations in terms of the last significant figure

Parameter	Reflection group			Accepted average
	20 $(10l)_S$	12 $(10l)_H$	11 $(00l)_{SH}$	
z(S)	.3793 ± 4		.3789 ± 6	.3791 ± 4
z(Fe,Cu)	.3082 ± 2		.3085 ± 3	.3083 ± 2
z(OH)		.4708 ± 5	.4699 ± 9	.4704 ± 5
B(S) [Å^2]	1.08 ± .45		1.80 ± .51	1.4 ± .5
B(Fe,Cu)	2.49 ± .27		2.21 ± .35	2.4 ± .3
B(Mg,Al)		2.98 ± .42	1.12 ± .62	2.1 ± 1.0
B(OH)		3.45 ± .59	.91 ± .69	2.2 ± 1.5
R	5.5	4.5	5.4	6.8%

cated accepted average by more than twice the standard deviation as found for each determination. The internal agreement for the z parameters is within $\pm$ .014 Å for S, $\pm$ .007 Å for (Fe,Cu), and $\pm$ .017 Å for OH. When all of the data are listed together with a single scale factor and assuming r^2 to be fixed at 1.526, as shown in Table 2, the reliability index for the 43 observed reflections is $R = 6.8\,^0/_0$. If the sulfide-to-hydroxide volume ratio r^2 is allowed to vary and its best value determined separately by a least-squares calculation, we obtain $r^2 = 1.497 \pm 0.025$, which is not significantly different from the assumed value of 1.526.

Table 2. *Observed and calculated structure factors for valleriite*
[F(000) is based on one formula unit]

A. Sublattice S:

($\underline{h}$	0	$\underline{l}$)$_S$	F_o	F_c
1	0	31	15.2	-15.7
		28	23.4	-22.7
		25	20.1	-19.5
		22		- 2.5
		19	22.8	24.0
		16	43.0	48.2
		13	53.9	56.6
		10	42.4	42.2
		7	9.1	10.6
		4	22.1	-21.3
		1	41.4	-37.0
		-2	37.1	-34.3
		-5	22.6	-24.5
		-8	18.5	-19.8
		-11	20.3	-21.3
		-14	22.8	-21.9
		-17	15.0	-14.6
		-20		1.0
		-23	20.2	18.7
		-26	29.5	30.1
		-29	31.7	29.5
		-32	16.8	18.0

B. Sublattice H:

($\underline{h}$	0	$\underline{l}$)$_H$	F_o	F_c
1	0	30		1.2
		27		- 1.0
		24		2.7
		21		- 6.6
		18	12.1	12.6
		15	18.7	-19.4
		12	23.4	24.7
		9	23.0	-26.2
		6	21.7	22.4
		3	13.3	-14.1
		0		4.6
		-3		2.1
		-6		- 3.5
		-9		- 0.3
		-12	6.1	6.7
		-15	11.0	-12.6
		-18	16.1	16.0
		-21	13.8	-16.2
		-24	11.7	13.8
		-27	9.0	-10.1
		-30		6.2

C. Basal reflections:

(0	0	$\underline{l}$)$_{SH}$	F_o	$F_{c,S}$	$F_{c,H}$	$F_{c,S}+F_{c,H}$
0	0	0		87.3	45.8	133.1
		3	31.1	73.1	-40.2	32.9
		6	55.7	26.5	27.2	53.7
		9	29.5	-17.0	-12.7	- 29.7
		12	37.4	-38.4	2.3	- 36.1
		15	36.6	-37.7	2.0	- 35.7
		18	29.7	-26.1	- 1.1	- 27.2
		21	20.6	-15.0	- 2.7	- 17.7
		24		- 9.7	6.7	- 3.0
		27	21.8	- 9.2	- 9.6	- 18.8
		30		- 8.5	10.5	2.0
		33	17.6	- 3.5	- 9.7	- 13.2
		36	15.0	5.3	7.7	13.0
		39		13.4	- 5.3	8.1
		42	17.5	16.1	3.0	19.1

The largest inconsistencies are found for the thermal parameters B, especially for the hydroxide layer. The larger B values for this layer obtained for the $(10l)_H$ reflections than for the $(00l)_{SH}$ reflections suggests a larger "thermal vibration" normal to the c axis than parallel to it. In this structure, however, we had best keep the term "thermal vibration" in inverted commas, because it will also incorporate all of the local atomic positional adjustment along the irregular contacts between the sulfide and hydroxide layers throughout the supercell. The four B parameters thus have little specific individual significance.

There is some uncertainty regarding the actual composition of the layers, especially the sulfide layers. In the hydroxide layer a composition of $[Mg_{.70}Al_{.30}(OH)_2]$ was assumed initially on the basis of the available analyses. On the other hand, the analyses all indicate some departure from stoichiometry in the sulfide layer, especially in the Fe:Cu ratio. Changes in the amounts of Fe and Cu assumed to be present have a small but definite effect on the other parameters

Table 3. *Interatomic distances and angles in valleriite*

Vectors are defined in Fig. 2; N is the number of vectors originating at first atom

Atoms	Vectors	N	Distances	Type
(Fe,Cu)—S	A	1	2.41 ± .02 Å	apical (c)
(Fe,Cu)—S	B	3	2.30 ± .02	basal
(Fe,Cu)—(Fe,Cu)	C	3	2.77 ± .01	
S—S	D	3	3.81 ± .03	shared tetrahedra edge
S—S	a_S	6	3.792 ± .005	unshared edge
(Mg,Al)—(OH)	F	6	2.04 ± .02	
(OH)—(OH)	G	3	2.69 ± .04	shared octahedra edge
(OH)—(OH)	a_H	6	3.070 ± .006	unshared edge
S—(OH)	J		3.11 ± .03	closest approach
			Angles	
S—(Fe,Cu)—S	$A \frown B$		107°57′	at shared edge
S—(Fe,Cu)—S	$B \frown B'$		110°58′	at unshared edge
(OH)—(Mg,Al)—(OH)	$F \frown F'$		81°30′	at shared edge

derived in the structure analysis. For the final structure-factor computations the composition was assumed to correspond to the formula $[Fe_{1.07}Cu_{.93}S_2] \cdot 1.526[Mg_{.68}Al_{.32}(OH)_2]$ as being most consistent with the analytical data. This composition leads to a calculated density of 3.21 g cm^{-3}, in fair agreement with 3.09 g cm^{-3} observed by HILLER (1939), and 3.14 g cm^{-3} observed by BLOMSTRAND (1870). The problem of composition is further discussed below.

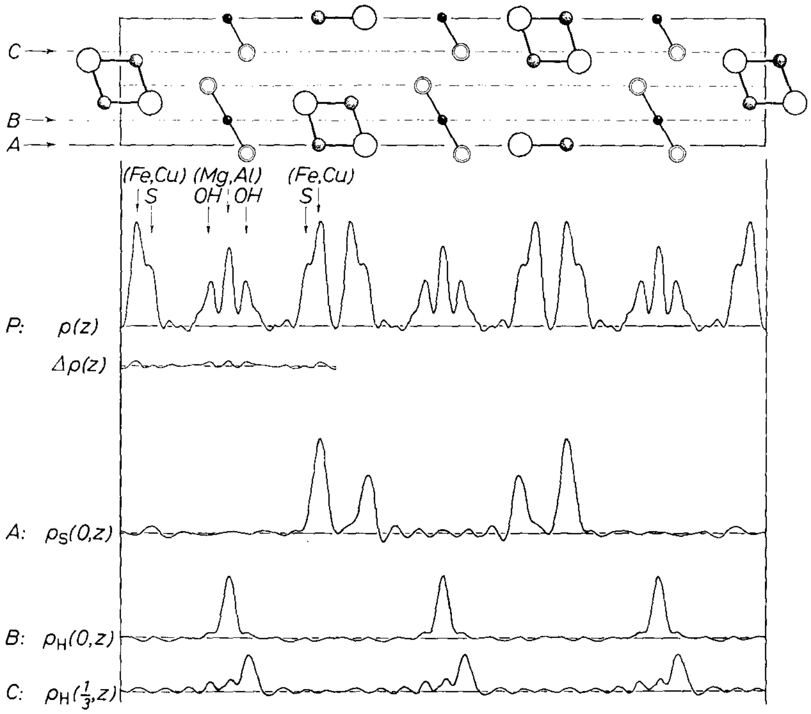

Fig. 3. Fourier syntheses of the electron density in valleriite along various lines parallel to the c axis, as indicated by the letters A, B and C at the left. The drawing of the structure at the top is drawn as in Fig. 2. The synthesis P is a projection of the whole unit cell onto the c axis

The significant interatomic-distance vectors in the crystal structure of valleriite are indicated in Fig. 2 and their lengths are listed in Table 3.

For illustrative purposes, electron density along certain lines through the structure is shown in Fig. 3. In this figure the structure as represented in Fig. 2 is shown at the top; the electron density of the whole structure is projected on the c axis in the curve P [based on $F(00l)$ only] and the corresponding synthesis of the residuals is shown in the adjacent curve below. For the remaining curves, the $F(00l)$ terms were split into sulfide and hydroxide components, and these appropriately combined with the $F(10l)$ terms gave the line syntheses along various axes in the substructures as shown.

The hydroxide layer

It is well known that trivalent aluminum ions cannot replace divalent magnesium ions in the brucite crystal structure to any appreciable extent. Evidently, a substitution process in which the insertion of Al^{3+} in some sites is compensated by vacancies in other sites is not permitted. But the recent structure studies on koenenite (LOHSE *et al.*, 1963; ALLMANN *et al.*, 1968), sjögrenite (ALLMANN and LOHSE, 1966), and valleriite, as well as earlier studies on chlorite (PAULING, 1930), all show that atom-for-atom substitution of Al^{3+} for Mg^{2+} in the $Mg(OH)_2$ layer can readily take place if the excess positive charge is compensated by interleaving other layers with negative charge. This process is accompanied by a shrinkage in the dimensions of the $Mg(OH)_2$ layer, although it is not possible as yet to relate this change quantitatively to the composition of the layer. The change is clearly shown by the numerical value of the hexagonal *a* axis, which for valleriite (Mg:Al = 0.68:0.32) is 3.07 Å, for koenenite (Mg:Al = 0.64:0.36) is 3.05, and for brucite is 3.147 Å. The change is better illustrated by the apparently linear relationship between the fraction of Al^{3+} replacing Mg^{2+} and the metal-oxygen distance. The pure Mg—OH bond in several structures has been found to be close to 2.07 Å; in the chlorite corundophillite, where the hydroxide layer is assumed to have the composition $(Mg_{.84}Fe_{.06}Al_{.10}(OH)_2]$, the bond is 2.05 ± .02 Å (STEINFINK, 1958); in koenenite where the layer is $[Mg_{.64}Al_{.36}(OH)_2]$ the bond is 2.02 ± .01 Å (ALLMANN *et al.*, 1968); in valleriite the bond is 2.04 ± .02 Å. When better data become available, it may become possible to use this relationship to estimate the degree of substitution in the same manner as the (Si,Al)—O distance is used to determine the extent of aluminum substitution in silicate tetrahedra.

The sulfide layer

The sulfide layer found in valleriite is a novel one, consisting of two sheets of sulfur atoms lying close-packed one on the other, with *all* of the tetrahedral sites between them occupied by metal atoms.

The structure of this layer is illustrated in Fig. 4, compared with the tetragonal layer found in mackinawite (BERNER, 1962). In the former, each tetrahedron shares three edges with its neighbors, while in the latter, each tetrahedron shares four edges. Thus, the valleriite sulfide layer represents an unusually dense packing of cations (each with three metal neighbors at 2.77 Å), though not as dense as that in mackinawite (four metal neighbors at 2.60 Å).

We may recall that the high-temperature form of digenite has nearly the antifluorite structure, that is, a cubic close-packing of sulfur atoms with 90% of the tetrahedral sites occupied by Cu atoms (MORIMOTO and KULLERUD, 1963). If the portion of this structure between two adjacent sheets of sulfur atoms parallel to the cubic (111) plane is isolated, the sulfide layer of valleriite is obtained. Furthermore, if the structure between two adjacent sulfur sheets parallel to the (100) plane is isolated, the sulfide layer of mackinawite is obtained. In these comparisons, no distinction is made between Cu and Fe atoms.

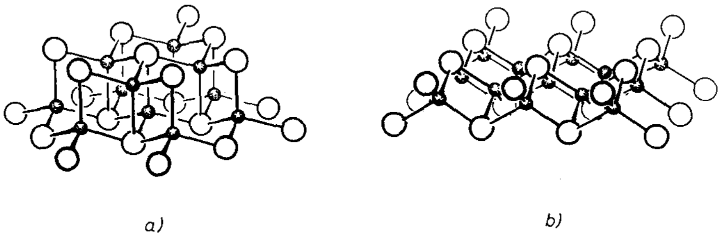

Fig. 4. The sulfide layer occurring in valleriite (*a*) and in mackinawite (*b*)

Concerning the charge on the sulfide layer, all information must come from our knowledge of the hydroxide layer. The fixed ionic valencies of Al^{3+}, Mg^{2+} and $(OH)^-$ enable us to determine the positive charge per unit $[Mg_{.68}Al_{.32}(OH)_2]$ to be 0.32. Multiplying this value by $r^2 = 1.526$, we know then that the charge of one unit of $[Fe_{1.07}Cu_{.93}S_2]$ must be -0.49. From this it is tempting to try to proceed with some estimate of the valencies of Fe and Cu (assuming, say, that the valency of S is -2), but surely no definite conclusion can be reached. We may suggest that the average valency of the metal atoms is $+1.75$, but that the electrons corresponding to this value are delocalized over all the metal sites, in accord with the metallic appearance of the mineral.

The chemical composition of valleriite

Only two localities have yielded sufficient amounts of reasonably pure valleriite for chemical analysis: Kaveltorp, Sweden, and Loolekop, South Africa. Five analyses of Swedish material and one of South African material have been recorded in the literature. These are summarized in Table 4A, where they are listed exactly as originally

Table 4. *Chemical analyses of valleriite*

	1	2	3	4	5	6	7
A. Original Analyses							
Fe	26.34	24.03	22.60	21.47	21.2	20.0	20.6
Cu	17.77	14.37	18.89	18.67	17.6	19.8	20.3
S	22.54	24.96	21.82	22.31	21.4	21.6	22.1
MgO	10.51	19.25		17.87	16.2	16.0	14.4 + 2.0
Al_2O_3	5.16	6.54		6.09	8.1	8.5	8.6
CaO	0.25			0.93	1.7	1.3	(1.3)
H_2O	10.77			12.16	12.2	10.8	9.4 + 0.6
Remainder	0.88	2.81		1.85	1.8	3.3	(SiO_2) 2.0
Total	94.22	91.96	63.31	101.35	100.2	101.3	101.3
B. Mole Ratios							
Fe	1.342	1.105	1.189	1.105	1.137	1.061	1.070
Cu	0.796	0.581	0.874	0.845	0.830	0.923	0.930
S	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Mg	0.742	1.227		1.274	1.205	1.176	1.038 + 0.144
Al	0.288	0.329		0.313	0.476	0.494	0.488
Ca	0.013			0.047	0.090	0.069	
O(r^2)	1.053	1.556		1.587	1.681	1.672	1.526 + 0.144
H_2O	1.701			1.941	2.030	1.777	1.526 + 0.096

1. Nya Kopparberg, C. W. Blomstrand, analyst; remainder: Na_2O, 0.61; K_2O, 0.27 (Blomstrand, 1870).
2. Kaveltorp, Pitzler, analyst; remainder: gangue, 2.81 (Ramdohr and Ödman, 1932).
3. Kaveltorp, R. Blix, analyst (Ramdohr and Ödman, 1932).
4. Kaveltorp, M. Bendig, analyst; remainder: MnO, 0.10; SiO_2, 1.75 (Hiller, 1939).
5. Kaveltorp, B. Ingram, analyst; remainder: insol. + SiO_2, 1.8 (Evans *et al.*, 1964).
6. Loolekop, B. Ingram, analyst; remainder: insol. + SiO_2, 3.3 (Evans *et al.*, 1964).
7. Theoretical for the composition:
   $[Fe_{1.07}Cu_{.93}S_2] \cdot 1.526\,[Mg_{.68}Al_{.32}(OH)_2]$, 94.5% + $Mg_3Si_2O_5(OH)_4$ (serpentine), 4.2% (+ CaO, 1.3%).

reported. Since in the structure of valleriite some of the Al^{3+} charge is balanced ionically by the sulfide layer while in the reported analyses it is all balanced by oxygen as Al_2O_3, the excess oxygen assumed will lead to an analytical sum $> 100\%$. For 8% Al_2O_3, the excess will be 1.3%, which is roughly consistent with that found in the best analyses (nos. 4, 5 and 6).

To interpret the analytical data, two assumptions must be made, based on the crystal-chemical properties found to be appropriate for this mineral from the structure analysis just described. They are as follows:

1. Al and Mg are incorporated in a brucite-like layer structure in which all sites are filled.

2. The mole ratio of S to Al+Mg must be $2:r^2 = 2:1.526$.

In finding the mole ratios, the values for the oxides are converted to the ratios for the metals and normalized so that the mole equivalent of S is 2.000. These data are given in Table 4B. To give the whole composition an amount of oxygen must then be added according to the relation

$$x\mathrm{Mg}^{2+} + y\mathrm{Al}^{3+} + (x+y)\mathrm{O}^{2-} + (x+y)\mathrm{H_2O} = [\mathrm{Mg}_x\mathrm{Al}_y(\mathrm{OH})_{2(x+y)}]^{y+}.$$

It is apparent from the second assumption stated above that on this basis $r^2 = x+y$. The values shown (for O) are not consistent with the expected value of 1.526, assuming that an error in the analytical values of Table 4 of 0.1 corresponds approximately to an error of 0.02 in $(x+y)$. This violation of the structural evidence in all probability lies in the deficient quality of the sample. All the most complete analyses show the presence of SiO_2 as well as excess H_2O. Since valleriite is removed from a matrix of serpentine, one explanation of the observed anomalous variation in $(x+y)$ may lie in a high value for Mg resulting from serpentine impurity in the sample. Another possibility is that the structure may actually contain a small amount of a chlorite-like component, consisting of random magnesium-silicate layers distributed in such a way that they produce no distinctive diffraction effects. In either case, the measured density would be somewhat lower than that expected for pure valleriite, as has been observed.

The role of calcium is also uncertain. Calcium could either be incorporated into the hydroxide layer, or be present as an impurity, in the form of carbonate, for example. Since its inclusion would further increase the observed value of r^2, we have omitted it from further consideration. It is clear, then, that we cannot depend on the chemical analysis to give a confirmatory value of r^2, or to tell the exact composition of the components of the structure of valleriite. But if we assume that the calcium is excluded from the hydroxide layer, and subtract enough magnesium to make $(x+y) = 1.526$, we may establish a provisional composition for the hydroxide-layer unit as $[Mg_{.68}Al_{.32}]^{+.32}$.

Table 4 shows that generally, especially in the better analyses, the molar sum Cu+Fe approaches closely to 2.0, and that there is always an excess of iron over copper of about 20⁰/₀. There is no apparent structural control over the ratio Fe:Cu, since in the structure as we have defined it these atoms play the same role in random distribution. The ratio is probably determined in some unknown way by the requirements of electrostatic charge needed to balance the charge of the hydroxide layer. For the Loolekop sample, we may write the composition of the sulfide layer unit as $[Fe_{1.07}Cu_{.93}S_2]^{-.49}$.

With the composition of the Loolekop material defined as stated above, and assuming the presence of 4.2⁰/₀ serpentine, a theoretical analysis may be calculated and is shown in the last column of Table 4.

Yund and Kullerud (1966) unsuccessfully sought for valleriite in the synthetic system Cu—Fe—S, before the essential role of magnesium and aluminum hydroxides in this phase was understood. These authours also heated valleriite from Kaveltorp in silica glass tubes at 400 ° to 450 °C and, in addition to residual valleriite, obtained chalcopyrite, water, and some optically transparent phases containing Al and Mg oxides, but found no excess sulfur. Thus it appears that the sulfide portion of valleriite at elevated temperatures will transform entirely to chalcopyrite, which at these temperatures embraces a wide composition range.

The hybrid layer structure of valleriite and other minerals

Our study of valleriite shows that it belongs to a group of minerals which may be said to have structures that are "hybrids" between the hydroxide-layer structure of brucite and some other layer structures. In the hybrid structure the hydroxide layers acquire an electrostatic charge through partial replacement of the divalent cation such as Mg^{2+} by a trivalent cation such as Al^{3+}. The layers are then interleaved in a one-to-one fashion with the other layer type, whose negative charge balances that of the hydroxide layer. Some of these hybrid phases have been summarized by ALLMANN and LOHSE (1966). Below are listed the minerals presently known to belong to this group.

Valleriite	$1.526[Mg_{.68}Al_{.32}(OH)_2] \cdot [Fe_{1.07}Cu_{.93}S_2]$
Koenenite	$1.78[Mg_{.64}Al_{.36}(OH)_2] \cdot [Na_{.65}Mg_{.35}Cl_2]$
Sjögrenite Pyroaurite	$8.0[Mg_{.75}Fe_{.25}(OH)_2] \cdot [CO_3(H_2O)_4]$
Mannassite Hydrotalcite	$8.0[Mg_{.75}Al_{.25}(OH)_2] \cdot [CO_3(H_2O)_4]$
Stichtite Barbertonite	$8.0[Mg_{.75}Cr_{.25}(OH)_2] \cdot [CO_3(H_2O)_4]$
Chlorite	$3.0[Mg_{.67}Al_{.33}(OH)_2] \cdot [Mg_3(AlSi_3O_{10})(OH)_2]$
Lithiophorite	$[Al_{.67}Li_{.33}(OH)_2] \cdot [MnO_2]$.

In these formulations, the positively charged hydroxide-layer unit is represented within the left-hand brackets, the negatively charged layer unit in the right-hand brackets, and the coefficient is r^2, the structural ratio of the former to the latter. Some variation of the compositions from those shown is permissible with appropriate provision for interlayer charge balance. From the examples of valleriite and koenenite, we learn that chemically quite different layer species will form hybrids with the hydroxide layer, and also that coherent hybrid structures can be formed even when the geometrical fit between the layers is very poor.

The detailed crystal chemistry of this group of minerals and related synthetic compounds will be reviewed in another place.

Acknowledgments

We wish to thank Dr. GUNNAR KULLERUD of the Geophysical Laboratory, Washington, D. C. for many helpful discussions; it was he who first noted that valleriite might be based on a structural principle similar to that of koenenite. We also wish to thank Professor J. D. H. DONNAY for his support of the portion of this work done under a National Science Foundation grant (GP 4947) to the Johns Hopkins University.

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