Crystal structure of jerfisherite

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(Presented by Academician N. V. Belov, April 1, 1975)
(Submitted March 28, 1975)

Dokl. Akad. Nauk SSSR **223**, 343–346 (July 1975)

PACS numbers: 61.50.Q, 61.10.F

The object of this investigation was to study jerfisherite single crystals obtained from pegmatites of the Khibinsk massif (M. N. Sokolova). The results of a chemical analysis (wt.%)[1] were the following:

K	Na	Cu	Fe	Mg	Mn	S	Σ
8.55	0.55	11.80	42.05	1.55	0.09	33.66	98.61

leading to the following approximate formula for the mineral:

$$K_{2.93}(Cu_{2.48}Na_{0.32})_{2.80}(Fe_{10.040}Mg_{0.81})_{10.85}S_{14.00}.$$

A comparison between the chemical composition of these crystals and those studied earlier[2–4] showed that all samples had a characteristic deficit of S atoms and a high K content, the other elements fluctuating as follows (%): Cu (0.05-11.8), Ni (0-4.2), Fe (42.5-51.9). X-ray microanalysis indicated quite clearly that up to 1.4 wt.% Cl atoms penetrated into the material.[6]

For purposes of structural analysis we used an unfaced single-crystal fragment of jerfisherite ≈ 0.1× 2.0 × 0.1 mm^3 in size. The mineral crystallizes in the cubic system, the edge of the cell being a_0 = 10.465±0.001 Å, in good agreement with published values.[1–3] The experimental set of intensities (250 independent reflections) was obtained in an automatic Hilger–Watts diffractometer (graphite monochromator, Mo$K\alpha$ radiation, ω scanning).

TABLE 1. Coordinates of the Atoms in Jerfisherite

Atoms	x/a	y/b	z/c	B_j	Atoms	x/a	y/b	z/c	B_j
Fe, Cu (24*m*)	0.131_8	0.369_1	0.131_8	0.96	K (6*f*)	0.500	0.500	0.201_2	1.12
S_1 (12*h*)	0.500	0.250	0.000	0.96	Cl (1*b*)	0.500	0.500	0.500	0.99
S_2 (6*e*)	0.000	0.250	0.000	0.78	Mg (1*a*)	0.000	0.000	0.000	0.78
S_3 (8*g*)	0.272_5	0.272_5	0.272_5	0.90					

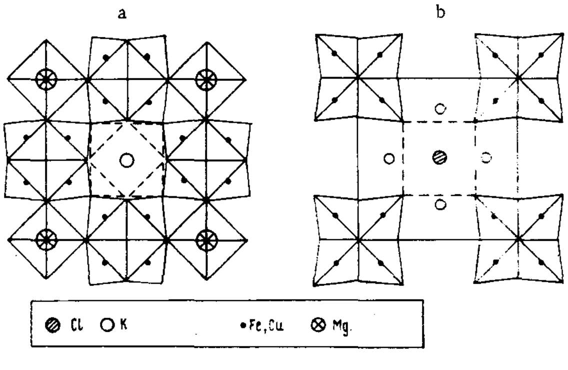

Fig. 1. Projection of the structure of jerfisherite on (001). a) Layer section of the close packing at a level of 0 ≤ z ≤ $^1/_4$ (S atoms); b) the same at a level of $^1/_4$ ≤ z ≤ $^1/_2$ (S atoms).

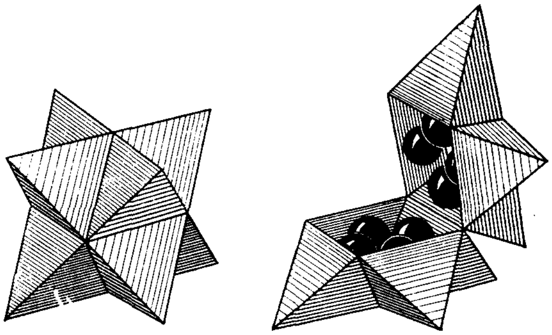

Fig. 2. Cluster of eight Fe tetrahedra according to N. V. Belov.[5]

The absence of any systematic extinctions leads to the x-ray group m3mP–, including three Fedorov groups: the centrosymmetrical group O_h^1–Pm3m and two acentric groups O^1–P432 and T_d^1–P$\bar{4}$3m. A decision in favor of holohedry was made at the next stage in the analysis of the structure.

The peak distribution1) of the three-dimensional Patterson function P(uvw) indicated a regular positioning of the atoms in the cell, with the populated levels lying $a/8$ apart. The first version of the structural model was based on a close packing of S atoms. A series of electron-density (ordinary and difference) syntheses enabled us to find the positions of the tetrahedral cations (Cu, Fe) and magnesium in the octahedra, as well as to locate the Cl atoms and confirm the occupation of some of the 32 close-packing positions (multiplicity 6) by K atoms (instead of S).

Refinement (by the method of least squares) of the coordinates and thermal parameters of the atoms (without allowing for absorption, owing to the irregular shape of

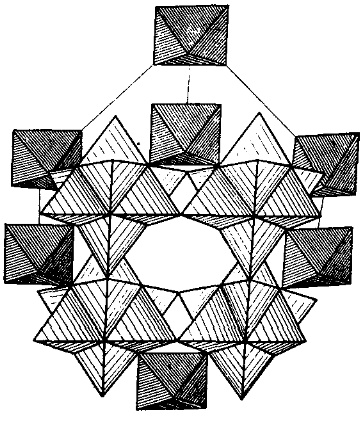

Fig. 3. Jerfisherite. Axonometry of the structure. Features distinguished include the Mg octahedra at the cell vertices and clusters on its "facade."

TABLE 2. Interatomic Distances in the Structure of Jerfisherite, Å

$S_1-(Fe, Cu)$	2.29_8	S_1-S_3	3.71_4
$S_2-(Fe, Cu)$	2.31_6	S_1-K	3.35_8
$S_3-(Fe, Cu)$	2.30_1	S_3-K	3.44_7
S_2-Mg	2.62_6	$Cl-K$	3.12_7
S_1-S_2	3.69_3	$(Fe, Cu)-(Fe, Cu)$	2.76_0

the sample) led to a variance factor of $R_{hkl} = 0.073\%$, with $B_{tot} = 0.91$ Å^2.

Initially the analysis was carried out within the framework of the acentric Fedorov groups P432 and $P\bar{4}3m$. An increase in the multiplicity of the positions (on the threefold axes) from 4 to 8 (UMNK-R-70) suggested passing to the more symmetrical Fedorov group Pm3m.

Since the composition of jerfisherite excludes the possibility of the xyz positions (multiplicity 24) being completely occupied by atoms of any one kind, we assumed a statistical distribution of Fe and Cu over the points of this regular system (with corresponding averaging of the f curve).

The final coordinates of the basis atoms are given in Table 1, and the corresponding interatomic distances in Table 2. The structure of jerfisherite is illustrated in Figs. 1-3.

The sulfur atoms lie on the levels 0, $1/4$, $1/2$, $3/4$ in the positions of the close-packed anions, but not quite completely. In the layers situated at the levels $z = 1/4$ and $3/4$ one S atom (in the middle of the layer) is missing in each case; at the level of $z = 1/2$ four S atoms are absent (Fig. 1), and these six empty positions in the cell are occupied by K atoms. The Mg atom lies at the cell origin (000), and in the connecting piece at the center of the cube ($1/2$, $1/2$, $1/2$) is the Cl.

The nonequivalent (from the steric point of view) replacement of S by K distorts the close packing, the layer being slightly corrugated owing to displacement of the K atoms from the positions of close packing (Fig. 1). Altogether the K cation is surrounded by nine ligands. Eight atoms form a distorted Thomson cube (K−S = 3.447 and 3.358 Å), in which the K is displaced to one of the square faces, the one closest to the Cl atom; the latter enters into the coordination sphere of the K atom, the K−Cl distance being 3.127Å; conversely, the large Cl anion is clad octahedrally with K atoms.

The Fe atoms together with the Cu atoms occupy the tetrahedral spaces in the close packing. The Fe, Cu tetrahedra are grouped in clusters of eight tetrahedra, each with an Me−Me distance of 2.76 Å as in the case of pentlandite[5]; according to N. V. Belov[5] these tetrahedra are adjacent to an empty octahedron and have faces in common with it (Fig. 2). Whereas in pentlandite there are four clusters, in jerfisherite there are only three; they center the edges of the cell (Fig. 3), the vertices of the cell being occupied by Mg octahedra, while the octahedra in the centers of the faces remain empty, and the pentlandite symmetry of Fm3m is reduced to Pm3m.

In accordance with the results of the structural analysis, the contents of the jerfisherite cell for Z = 2 (original units) may be written in the form $K_6Mg(Fe, Cu)_{24}S_{26}Cl$

The authors wish to thank Corresponding Member of the Academy of Sciences of the USSR G. B. Bokii, Yu. T. Struchkov, and N. G. Bokii for their interest in the work and useful consultations.

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1) All calculations involved in the solution of the structure were based on the "Rentgen-70" program written for the BÉSM-4 computer in the Computing Center, Academy of Sciences of the USSR.

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