weak bond, have a certain deficiency of these forces (Table VI).

[1)] $a = 7.189(3)$; $b = 12.693(5)$; $c = 7.188(2)$ Å; $\alpha = 93.17(3)^\circ$; $\beta = 106.83(3)^\circ$; $\gamma = 93.13(3)^\circ$; $P\bar{1}$; $Z = 2NaIn(SeO_4)_2 \cdot 6H_2O$.

[2)] Since for O_{13} and O_{14} the coordination number is 3 + 1 (H), then according to Shannon and Prewitt,[6] the ionic radius of these atoms was taken as 1.38 Å.

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Close packing and cation arrangement in the jerfisherite structure

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Jerfisherite is an example of nonstandard realization of the scheme of close packing in sulfides. The authors discuss the coordination environment of the atoms in the structure as a consequence of the unusual close packing.

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Jerfisherite, $K_6Na(Fe, Cu, Ni)_{24\pm x}S_{26}Cl$ (Ref. 1), is a sulfide[1)] of complex and unusual chemical composition with a constant, fairly high (up to 10%) potassium content and varying amounts of iron (35.49–51.9%), copper (0.05–15.32%), and nickel (0–19.81%). Recent investigators have found that the lattice contains chlorine (up to 1.4%). The Khibiny specimen also contains sodium (0.81%).

In the first chemical analysis, which was taken as a basis for deciphering the structure of jerfisherite,[4] Mg was found (1.56–1.76 wt.%). Later analysis with a microprobe did not confirm the presence of Mg, but the Na content reached 0.8%. Evidently the relatively large sample of the chemical analysis specimen contained a fine impurity of some foreign Mg-containing mineral.

For structural analysis[5] we used an unfaced single-crystal fragment of jerfisherite from the alkaline pegmatities of the Khibiny massif. The specimen from the Khibiny pegmatites can be regarded as unique in the sense that only this specimen was found to have high copper (15.98%) and sodium (0.81%) contents with practically no Ni (most analyses of jerfisherites revealed no sodium at all).

A preliminary x-ray analysis revealed that the mineral is cubic with $a_0 = 10.45$ Å. In this unit cell we were able to assign unambiguous indices to the powder pattern (Fe Kα radiation, 2R = 143 mm). The value of the parameter a_0 calculated from the powder pattern (with metallic silicon as standard) was 10.465 ± 0.001 Å. The preliminary data on the symmetry, unit-cell parameter, and space group were refined on a Hilger–Watts automatic diffractometer.

The experimental set of intensities (250 independent reflections) was registered in the same diffractometer (Mo Kα radiation, ω scanning, graphite monochromator).

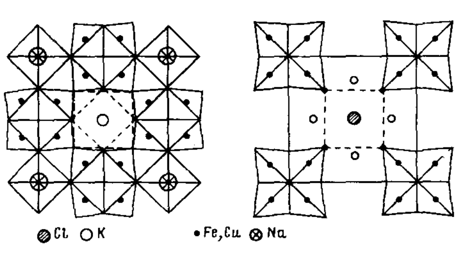

FIG. 1. Structure of jerfisherite projected on (001). a) Part of layer of close packing at level $0 \le z \le 1/4$; b) the same at level $1/4 \le z \le 1/2$.

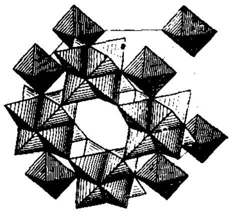

FIG. 2. Jerfisherite: axonometry of structure. Showing octahedra at vertices of cell and clusters on its "facade".

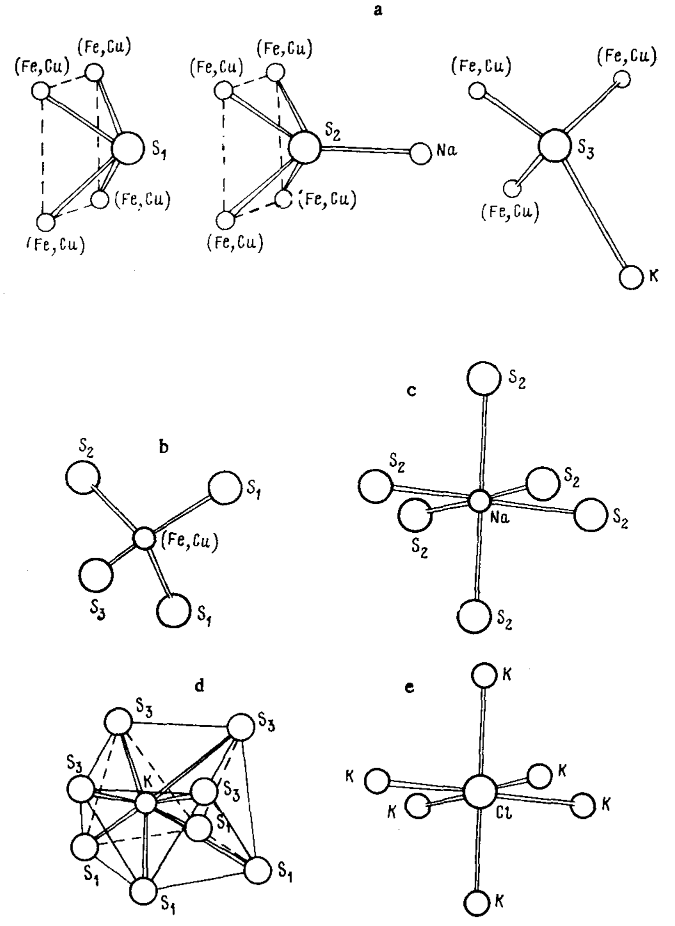

FIG. 3. Coordination of atoms in jerfisherite. a) S; b) Fe, Cu; c) Na; d) K; e) Cl.

All the calculations in the process of solution of the structure were made by means of the "Rentgen-70" program on a BÉSM-4 computer.

The absence of systematic extinctions satisfies the requirements of three space groups, Pm3m, P$\bar{4}$3m, and P432. A definite decision in favor of the centrosymmetric group Pm3m was possible only in the later stages of refinement of the structure.

The main difficulties in interpreting the structure of jerfisherite were associated with the absence of a heavy atom (and with the similarity between the scattering curves for the different species of atoms in the mineral) and with the marked pseudosymmetry: The characteristic reticular pattern of peaks in the three-dimensional Patterson function P(uvw) indicated a regular arrangement of atoms in the unit cell with the populated levels spaced 1/8*a* apart. The first variant of our model of jerfisherite was based on close packing of sulfur atoms.[5]

A series of electron density syntheses enabled us to fix the positions of the Cu and Fe atoms in tetrahedra of S atoms and the sodium atom (at the origin) in an octahedron of S atoms; the Cl atom was located in an octahedron of K atoms (Fig. 1), and we established that the potassium atoms (six in all) also occupy some of the close packing positions. This model of the structure was refined by the method of least squares in the isotropic approximation to R = 0.07 for B_{tot} = 0.91 Å^2. We made parallel refinements of the structure on the basis of two groups, the acentric P$\bar{4}$3m and the centrosymmetric Pm3m but the differences between the position parameters and the values of R for the centrosymmetric and acentric groups were so small that they did not yield a reliable criterion for choosing the space group. However, the increase in multiplicity of the xxx positions from four to eight was indirect evidence in favor of the higher-symmetry space group Pm3m. Since the chemical analysis data for jerfisherite eliminated the possibility of complete population of the xxz positions (multiplicity 24) by atoms of the same species, we assumed a statistical distribution of Fe and Cu atoms over the points of this regular system (with corresponding averaging of the *f* curve) in the space group Pm3m. Thus from the results of the structural interpretation we can write the formula of jerfisherite in the form $K_6Na(Fe, Cu)_{24}S_{26}Cl$. The final values of the coordinates and thermal vibration parameters of the basis atoms are listed in Table I, and the corresponding interatomic distances are listed in Table II.

In the structure of jerfisherite (Figs. 1 and 2) we must first note the nonstandard realization of the close-packing scheme, in which the lattice points are occupied by 26 S^{2-} anions and six large K^+ cations. The 26 sulfur atoms lie on the levels 0, 1/4, 1/2, 3/4 in the positions of the anions of the close packing in three regular systems of points. However in the cubic unit cell (*a* = 10.465 Å) of compounds of the sulfide class, in the case of ideal close packing there are 32 points. In jerfisherite at the levels z = 1/4 and z = 3/4 one atom is "withdrawn" from the middle of the layer, and four sulfur atoms are missing from the layer at the level z = 1/2. These six sulfur vacancies are occupied by potassium atoms. The simultaneous participation of anions and cations in the formation of the packing leads to its distortion, which is expressed in corrugation of the layers (due to the difference between the dimensions of the S^{2-} and K^+ ions). Replacement of sulfur atoms by potassium in some of the positions makes the packing less close and causes the appearance of gaps in the center of the structure, into which the large Cl^- anions fit. This deformation of the close packing is due to a shift of the S_3 atoms by 0.02 Å along the three coordinate axes, i.e., the sulfur ions shift toward the positively charged potassium cations and the distance between the close-packed sites (which would be 3.70 Å for sulfur atoms alone) is reduced to the distance $K-S_3$ = 3.44 Å. The other shortened distance between the packing sites, S_1-K = 3.35(8) Å, is due to the large interstitial Cl^- anion, which separates the K^+ cations. Structural deficit of sulfur is shown by the published chemical analyses to be characteristic of all jerfisherites, and is due to the arrangement of the potassium atoms, six of which com-

TABLE I. Atomic Coordinates in Jerfisherite Structure.

Atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
Fe, Cu (24*m*)	0,131 (8)	0.369 (1)	0,131 (8)	0.96
S_1 (12*h*)	0,500	0.250	0,000	0.96
S_2 (6*e*)	0.000	0,250	0,000	0,78
S_3 (8*g*)	0,272 (5)	0,272 (5)	0,272 (5)	0.90
K (6*f*)	0,500	0.500	0.201 (2)	1,12
Cl (1*b*)	0,500	0.500	0.500	0.99
Na (1*a*)	0,000	0.000	0 000	0.78

TABLE II. Interatomic Distances (in angstroms) in Jerfisherite Structure

Atom	Distances	Atom
$S_1-(Fe, Cu)$	2,29(8)	S_1-S_3
$S_2-(Fe, Cu)$	2.31(6)	S_1-K
$S_3-(Fe, Cu)$	2.30(1)	S_3-K
S_2-Na	2.62(6)	$Cl-K$
S_1-S_2	3.69(3)	(Fe, Cu–Fe,

plete the close packing. As a result, the packing consists not only of polyhedra of anions but also of mixed polyhedra of anions and cations, and naturally these remain unoccupied.

A consequence of the unusual close packing will be that the atoms S_1, S_2, and S_3 have different coordination environments (Fig. 3a). The nearest neighbors of S_1 are four metal atoms (Fe, Cu) forming the base of a square pyramid with atom S_1 at its apex. Atom S_2 is surrounded by four of the tetrahedral (Fe, Cu) atoms and one octahedral (Na), forming a coordination polyhedron in the form of a square pyramid with (Fe, Cu) atoms at the corners of its base and an Na atom at its apex. The nearest neighbors of atom S_3 are three metal atoms (Fe, Cu); if, however, a potassium atom is included in the coordination environment of S_3 we get a strongly distorted tetrahedron. The fact that the temperature factor for S_2 (0.7886 Å^2) is smaller than those for S_1 and S_3 (0.9644 and 0.9006 Å^2) is correlated with the dependence, established for a number of structures, between the coordination number of the anion and the corresponding temperature factor.[6]

Although mixed anion-cation packing is a rather rare phenomenon in crystal chemistry, the tendency for large cations (K^+, Ca^{2+}) to participate in the creation of a packing framework together with anions has been noted by N. V. Belov[7] for perovskite, barylite, and other compounds.

Mixed anion–cation packing reduces the number of purely anionic polyhedra and correspondingly the number of gaps for possible accommodation of cations. Atoms of Fe and Cu occupying tetrahedral gaps (Fig. 3b) are grouped in cubic clusters like those in pentlandite. The distances Me–Me = 2.76 Å are similar to those in the structures of metallic iron (2.50 Å) and metallic copper (2.55 Å).

The clusters are formed as a result of metal atoms occupying sets of eight tetrahedra joined by common faces to one empty octahedron. In this case each tetrahedral cation forms three metal–metal bonds; these must be due to the semimetallic properties of the mineral. In jerfisherite the clusters center all the edges of the unit cell and each of them belongs simultaneously to four cells (see Fig. 2).

We have noted that the atoms S_3, being attracted toward the K atoms, are shifted from the ideal close-packing positions (the relative coordinates change from 0.250 to 0.272(5)). The metal atoms occupying the tetrahedra for which one vertex is the S_3 atom are also shifted (see Table I), tending to occupy an energetically preferable position. The Na atom lies at the origin in an octahedral environment of sulfur atoms (Fig. 3c).

Since the subject of our structural investigation was a specimen not containing Ni, the position of the Ni was not found experimentally. Nevertheless, it would be interesting to consider the possibility of accommodating Ni in jerfisherite containing this element. The fact that in pentlandite it occurs preferentially in the metallic clusters suggests that Ni might occupy a similar structural position in jerfisherite. However, we cannot altogether eliminate the possibility that some of the Ni or Fe atoms might occur in an octahedral position in specimens not containing Na. Attempts to obtain a confirmation of the different variants of population of the tetrahedral and octahedral positions by Fe and Ni atoms in pentalandite by refining several models with different distributions of Fe and Ni cations among two regular systems of points (4b) and (32f) did not yield definite results, because the values of the R indices and atomic coordinates were identical for all the models tested, in view of the smallness of the differences between the atomic scattering curves of Fe and Ni.[8]

The six large K^+ cations occupy position 6f (close-packing sites). Replacement of S^{2-} by K^+ liberates some space in the packing and facilitates displacement of potassium from the ideal close-packing sites (0.5, 0.5, 0.25) to the position with coordinates (0.5, 0.5, 0.2); the potassium atoms lie at the vertices of a regular octahedron around the chlorine atom. The interatomic distance K–Cl (3.127 Å) is approximately equal to the sum of ionic radii of potassium and chlorine, as is in typical ionic compounds. Thus each potassium cation is surrounded by nine ligands. The seven S atoms (Fig. 3d) form a distorted Thomson cube ($K-S_3$ = 3.447 Å, $K-S_1$ = 3.358 Å) in which the K atom is shifted toward the square face nearest the Cl atom. The latter can also be included in the coordination sphere of the potassium (K–Cl distance is 3.127 Å) (Fig. 3e).

1) Jerfisherite was first found in meteorites[2] in the form of grains measuring up to 0.4 mm in concretions with the usual meteorite minerals. This was the first discovery of a natural sulfide containing potassium as one of the main components. In terrestrial conditions this mineral was first found in the Talnakh deposit.[3] Here it occurs in the form of fine segregations in close association with other sulfides.

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