POSITIONAL ORDERING AND DISORDERING OF ATOMS IN CRYSTAL STRUCTURES OF SYNTHETIC MELANTERITES
$Fe_xMg_{1-x}SO_4 \cdot 7H_2O$ (x =0,92 И 0,89)
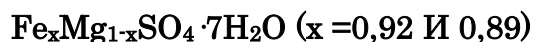
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ABSTRACT

Single crystals of two solid solutions of melanterite with compositions $Fe_{0,92}Mg_{0,08}SO_4\cdot7H_2O$ $Fe_{0,89}Mg_{0,11}SO_4\ 7H_2O$ were obtained and studied by X-ray diffraction. The crystals are monoclinic and are built from $[(Fe+Mg)(H_2O)_6]^{2+}$, octahedra located in two crystallographically independent positions M(1) and M(2), as well as the SO_4^{2-} anion and the crystallization molecule H_2O, combined into a three-dimensional island structure due to intermolecular H-bonds. The O atom of one of the aqua ligands with planar trigonal coordination around the M(2) position is disordered over two positions. Partial ordering of the Mg atom in the M(1) and M(2) positions is observed: the occupancy of Mg in the M(2) position is greater than in the M(1) position. The X-ray reflection arrays of both crystals contain reflections forbidden by the symmetry of the space group. $P2_1/c$,, which are observed in a wide range of $\sin\theta/\lambda$ values, and their number increases with increasing amount of Mg in melanterite.

Keywords: solid solutions, melanterite, epsomite, isomorphism, isodimorphism, symmetry-forbidden X-ray reflections.

INTRODUCTION

Iron sulfate $FeSO_4 \cdot 7H_2O$ is dimorphic: it crystallizes in a stable monoclinic modification (space group $P2_1/c$) and is called melanterite, as well as in an orthorhombic modification (space group $P2_12_12_1$) and is called tauriscite [1, 2]. Tauriscite is unstable under normal conditions and precipitates only from solutions that contain metal impurity atoms, for example, magnesium. Magnesium sulfate $MgSO_4\cdot7H_2O$ is also dimorphic: it usually crystallizes in the orthorhombic modification (space group $P2_12_12_1$), and is called epsomite. $MgSO_4\cdot7H_2O$ crystals in the monoclinic modification (space group $P2_1/c$) precipitate from solutions that contain some impurity metal salts, for example, iron(II) sulfate [3, 4].

Synthetic crystals of melanterite and epsomite were first studied by X-ray structural photomethod in [5, 6], and later using automatic X-ray diffractometry in [7-9]. In a melanterite crystal, Fe^{2+} cations are located in two crystallographically independent octahedral positions

M(1) and M(2). In solid solutions of this mineral, partial ordering of impurity atoms along the indicated positions is observed: an impurity metal cation replaces the Fe^{2+} atom in the M(1) position to a greater extent than in the M(2) position. This is explained by the larger size of the coordination cavity in the M(2) position compared to the M(1) position [7-9].

The purpose of this work is to discuss the results obtained during X-ray diffraction analysis of two melanterite crystals: $Fe_{0,92}Mg_{0,08}SO_4 \cdot 7H_2O$ (I) and $Fe_{0,89}Mg_{0,11}SO_4 \cdot 7H_2O$ (II). Possible local changes in the structure in crystals I and II, indicating those forbidden in the space group, are also discussed. $P2_1/c$ reflections.

1. EXPERIMENTAL PART

Crystals (I) and (II), obtained from productive solutions of sulfuric acid treatment of waste from a polymetallic enterprise, are green in color and prismatic in shape. The crystals are hygroscopic and gradually disintegrate in the air. For this reason, in order to protect them from atmospheric moisture, the crystals were coated with an epoxy layer. X-ray experiments of single crystals with dimensions of 0.3×0.2×0.2 mm were carried out on an automatic diffractometer XCalibur, Ruby ($\lambda CuK\alpha$-radiation, room temperature, graphite monochromator, ω-scanning for both diffraction experiments, as well as for crystal I : $6.52 \leq 2\theta max \leq 124.72^o$, $-14 \leq h \leq 16$, $-5 \leq k \leq 7$, $-11 \leq l \leq 12$, 3567 reflections with $I \geq 2\sigma(I)$ and for crystal II: $6,54 \leq 2\theta max \leq 150.94^o$, $-17 \leq h \leq 17$, $-8 \leq k \leq 7$, $-13 \leq l \leq 12$). Empirical corrections for absorption, Lorentz factor, and polarization were introduced using the CrysAlisPro program [10]. The main crystallographic data and conditions of the X-ray diffraction experiment are given in Table. 1, the parameters of unit cells are given in Table 2, and the most important interatomic distances and bond angles are given in Table. 3.

Primary processing of experimental data by the XPREP program in both cases suggests monoclinic space groups. P2/c and Pc. The average values of the statistical parameter $<|E2-1|>$ are 1.073 (I) and 1.068 (II), which is higher than the value of 0.968 for centrosymmetric crystal structures. This overestimation of the parameter values is apparently due to the presence of pseudosymmetry in structures I and II. In the array of X-ray reflections of both crystals, reflections are observed that are forbidden by the symmetry of the space group. $P2_1/c$. Their number correlates with the amount of magnesium replacing iron atoms: in the array of reflections of the first crystal, their number is 256, and in the second case - 420 before reflection averaging. Most of the forbidden reflections are observed in the reflection arrays of both crystals. Forbidden reflections with odd indices l are observed among reflections h0l throughout the entire range of $\sin\theta/\lambda$ variations. These reflections, weak in intensity but indicated, indicate a violation of the slip plane. The violation of symmetry centers at Wyckoff positions 2a, 2b, 2c and 2d is indicated by symmetry-forbidden reflections with an odd sum of indices k+l among reflections hkl. Among the serial reflections 0k0, only the forbidden reflection 010 is observed; other reflections with high indices k are beyond the threshold of observability. The bulk of the observed reflections of crystals obey the rules of systematic extinctions of the space group. $P2_1/c$, and this means that the crystal structure mainly obeys the symmetry of this space group. For this reason, the crystal structures were deciphered and refined in the space group. $P2_1$/with the SHELXL-97 program in the full-matrix anisotropic approximation for all non-hydrogen atoms [11, 12]. To reproduce the projection of the crystalline package, the Olex 2 program was used [13]. At the initial stage of structure refinement, positions M(1) and M(2) were occupied by an

Fe atom and the structures were refined in an anisotropic approximation to divergence factors $R_1 = 0.0575$ and $R_w = 0.0642$ in the first and $R1 = 0.0715$ and $Rw = 0.0788$ in the second case. Further, in order to determine the occupancies of the M(1) and M(2) positions, they were occupied by atomic mixtures of Fe+Mg and were refined in the isotropic approximation with reflection arrays trimmed to $\sin\theta/\lambda=0.32$. The obtained population values were recorded during the final refinement of the structures using full arrays of reflections in full-matrix least squares in an anisotropic approximation up to the divergence factors $R_1=0.0562$ and $R_w=0.0640$ in the first and up to $R_1=0.0687$ and $R_w=0.0772$ in the second cases accordingly. In both cases, residual electron densities of low intensity remain on the difference Fourier synthesis map at a distance of ~0.5 Å from the M(1) and M(2) positions. They were included in the structure refinements as a possible disordered position of the Mg atom; however, when the structure was refined, the Mg atom occupied in these positions does not remain near the center of the coordination octahedron, and for this reason was excluded from consideration. However, the possibility of disorder in the position of the Mg atom in the M(2) position is indicated by the asymmetry of the anisotropic displacement ellipsoid of the M(2) atom: the ratio of the length of the major semi-axis of the atomic ellipsoid (Fe+Mg) to the minor is 4.8. In the first structure, this situation is not observed, probably due to the small fraction of magnesium substitution of the iron atom. The regularity of the SO4 tetrahedron and the H_2O molecule was ensured by applying restrictions on the S–O and O...O interatomic distances in the tetrahedron and the O–H and H...H distances in the water molecule. The ellipsoid of anisotropic displacement of one of the O atoms of the SO_4 anion has the shape of a highly elongated ellipsoid. It was not possible to establish the positional disorder of this atom. Restrictions were imposed on the anisotropic displacement parameters of this atom, but it was not possible to completely eliminate the asymmetry of the ellipsoid. In the second structure, in positions M(1) and M(2), one O atom of the aqua ligands also had elongated displacement ellipsoids. The possibility of positional disorder of the O atom of aqua ligands in the M(1) and M(2) positions was tested by dividing the position of the O atoms into two nearby positions.

A similar situation was in the crystal structure of the $CoSO_4$ $7D_2O$ crystal, studied by neutron diffraction [18], however, in that structure, an elongated ellipsoid was observed at the O atom of the D_2O ligand in the M(2) position and it was found that this atom was disordered in two positions. Assuming that in the structure we studied there may be disorder in the positions of the O atom of both aqua ligands, in the isotropic approximation, the positions of each atom were divided into two closely spaced positions and then the coordinates and occupancies of these atoms were isotropically refined. The coordinates of the H atoms bonded to each O atom were refined isotropically. Complete crystal structure data have been deposited in the Inorganic Structure Data Bank (CSD No. 1904521 and 190522).

Table 1 Experimental data, crystallographic characteristics and refinement of crystal structures of I and II.

Chemical formula a	$(Fe_{0,92}Mg_{0,08})SO_4 \cdot 7H_2O$	$(Fe_{0,89} Mg_{0,11})SO_4 \cdot 7H_2O$
M	275,81	274,55
Radiation; l, Å	CuK_α; 1,5418	
m, mm–1	14,232	13,815
T, K	293	
Sample size, mm	0,3 × 0,2 × 0,2	0,3 × 0,2 × 0,2

Diffractometer	Xcalibur, Ruby	
Scan type	ω	
Accounting for absorption	Empirical, taking into account spherical harmonics	
Tmin, Tmax		
qmax, deg	62,36	75,47
Limits h, k, l	-14 ≤h≤ 16, -5 ≤k≤ 7, -11 ≤l≤ 12	-17 ≤h≤ 17, -8 ≤k≤ 7, -13 ≤l≤ 12
Syngony, sp. gr., Z	Монокл., $P2_1/c$, 4	триклинная, 4	Монокл., $P2_1/c$, 4	триклинная, 4
a, b, c, Å	14,051(3), 6,4994(13), 11,018(2)	14,034(3), 6,4970(13), 11,016(2)
a, b, g, deg	90, 105,62(3), 90	90, 105,55(3), 90
V, A3	969,1(3)	967,7(3)
Dx, g/cm3	1,89	1,88
Number of reflections: measured(N1)/independent(N2)	3311/1543	7646/1663
Rint / s I > 2s(I) (N2)	0,0641/1266	0,0916/1955
Method for refining OLS using F2	МНК по F^2	
Number of specified parameters	128	180
S to F2	1,098	1,068
R1/wR2 to N1	0,0641/0,1580	0,0808/0,2259
R1/wR2 to N2	0,0563/0,1511	0,0721/0,2066
Extinction coefficient	0,008(1)	0,009(1)
Drmin/Drmax, e/A3	-1,162/0,982	-2,398/1,798
Programs	CrysAlisPro [13], SHELX-97 [14]	

Table 2 Parameters of unit cells of crystals I, II, melanterite and epsomite

| Состав	a, Å	b, Å	c, Å	β, град	V, Å³
$Fe_{0,93}Mg_{0,07} SO_4 \cdot 7H_2O$	14,051(3)	6,499(1)	11,018(2)	105,62(3)	969,1(3)
$Fe_{0,87}Mg_{0,13} SO_4 \cdot 7H_2O$	14,034(3)	6,497(2)	11,016(5)	105,55(6)	967,7(3)
$FeSO_4 \cdot 7H_2O$ [5]	14,072(10)	6,503(7)	11,041(10)	105,57(5)	973(1)
$MgSO_4 \cdot 7H_2O$ [6]	11,868(10)	11,996(1)	6,857(7)	-	976(2)

2. RESULTS AND THEIR DISCUSSION

Crystal structures of I and II are isomorphic to the structure of melanterite and are built from $[M(H_2O)_6]^{2+}$ cations (where M = Fe + Mg), located in two crystallographically different positions (2a and 2d with symmetry), as well as SO_4^{2+} anions and one crystallization water molecule, united into a three-dimensional structure by intermolecular H-bonds (Fig. 1).

Substitution of the Fe2+ cation with ionic radius rion=0.78 Å by the Mg2+ cation with ionic radius rion=0.72 Å leads to a decrease in the unit cell parameters of melanterite in the sequence $FeSO_4 7H_2O \rightarrow (Fe_{0.92}Mg0.08)SO_4\ 7H_2O \rightarrow (Fe_{0.89}Mg0.11)SO_4\ 7H_2O$. In structure I, with a magnesium population of 0.08, the volume of the unit cell decreases by 0.40%, and in structure II, with a magnesium population of 0.14, by 0.54% (Table 2). The reduction in unit cell parameters occurs mainly along the crystallographic axes a and c. In both structures, partial ordering of the Mg2+ cation is observed in the M(1) and M(2) positions: the occupancy of the M(2) position by the Mg2+ cation is greater than in the M(1) position. The occupancies of the positions have the following values: M(1)=0.94Fe+0.06Mg in I and M(1)=0.92Fe+0.08Mg in II, and the

occupancy of the M(2) position is equal to M(2)=0.92Fe+0.08Mg in I and M(2)=0.86Fe+0.14Mg (in II) (Table 2). For disordered aqua ligands, one of the M–O distances is smaller than the second. For each structure, the distances M(1)–Ow and M(2)–Ow, respectively, have close values. The differences in the values of the M–Ow distances reflect the occupancy of the positions by Fe and Mg atoms and lie within the sum of the ionic radii of Mg^{2+} (c.n. 6) and O^{2-} (c.n. 3) and Fe^{2+} (c.n. 6) and O^{2-} (part 3). The shortest values are equal to the sum of the Mg^{2+} and O^{2-} ions, and the longest distances are the sum of the ionic radii of Fe^{2+} and O^{2-}. The average value of the M(1)–Ow distances is 2.104 (for I) and 2.099 Å (for II), and the M(2)–Ow distances are 2.116 (I) and 2.104 (II) Å. In both structures, the average M(2)–O distance is comparatively larger than the M(1)–O distance. This difference is explained by the participation of one of the aqua ligands coordinating the M(2) atom in three H-bonds: two as an H-donor and one as an H-acceptor (Table 5). The remaining aqua ligands participate in only two H-bonds. In both structures, the metal coordination octahedra are distorted due to the Jahn-Teller effect.
 The influence of this effect on the configuration of the coordination octahedra of melanterites Fe^{2+}, Co^{2+} and Ni^{2+}, as well as in solid solutions containing Cu^{2+}, was studied in detail in [14, 15] and the authors came to the conclusion that Jahn-Teller distortions are not the only factor determining the type of metric of metal sulfate crystals.
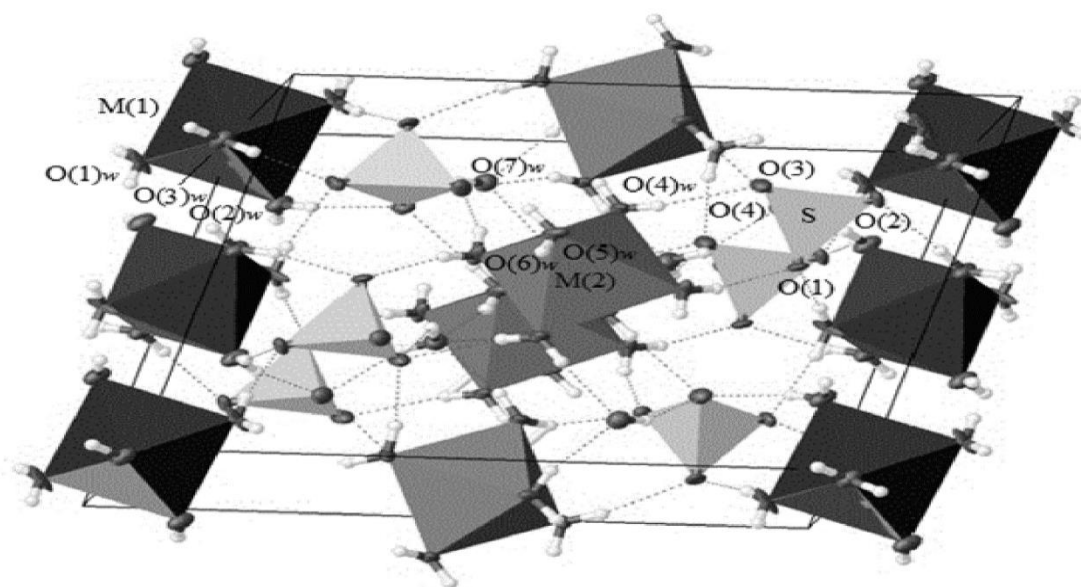
Rice. 1. Crystal packing of $[M(H_2O)_6]^{2+}$ octahedra and SO_4^{2-} tetradra in crystals 1 and 2.

The coordination octahedra $[M(1)(H_2O)_6]^{2+}$ and $[M(2)(H_2O)_6]^{2+}$ in the structures are located in planes that are parallel to the crystallographic planes (100) and spaced from each other by half a period a/ 2 (fig.). SO_4^{2-} anions and a crystallization water molecule located between the layers, forming H-bonds with each of the layers, contributing to the formation of a three-dimensional structure. Among the H-bonds of the SO_4^{2-} anion, the triple H-bond is especially important, which is formed between three O atoms of the SO_4 tetrahedron and three aqua ligands located on one of the faces of the $[M(1)(H_2O)_6]^{2+}$ octahedron. The angle between the faces of the tetrahedron and octahedron is 6.4º. In epsomites, only a double H-bond is not formed between polyhedra. The formation of a triple H-bond between the SO4 tetrahedron and the $[M(H_2O)_6]^{2+}$ octahedron depends on the geometric parameters of the octahedron face.

. Table 3

The most important bond lengths (d, Å) and bond angles (ω, deg) in structures I and II, as well as melanterite [4]

bond	I	II	melanterit
d(M(1)–O)	2,061(3); 2,123(3); 2,128(3)	2,051(7); 2,091(6), 2,124(3); 2,129(4)	2,068(5); 2,136(5); 2,144(5)
	2,104 (cp.)	2,098 (cp.)	2,116 (cp.)
d(M(2)‑O)	2,086(3); 2,096(3); 2,169(3)	2,039(16); 2,097(3); 2,110(6); 2,170(3)	2,096(5); 2,109(5); 2,188(5)
	2,117 (cp.)	2,104 (cp.)	2,131 (cp.)
d(S–O)	1,458(3); 1,468(3); 1,474(3); 1,478(3)	1,472(3); 1,474(3); 1,471(3); 1,468(3)	1,488(4); 1,481(4); 1,466(4); 1,462(4)
$\omega(O_w–M(1) – O_w')$	89,0(1); 92,37(13); 94,1(1)	88,4(2); 96,3(2); 91,6(3); 96,5(3)	90,5(2); 92,9(2); 94,0(2)
$\omega(O_w–M(2) – O_w')$	90,4(1); 91,1(1); 92,0(1)	96,8(5); 91,4(2); 92,0(1); 88,6(2)	90,5(2); 91,0(2); 94,4(2)
ω(O‑S‑O')	110,4(2); 108,7(2); 110,2(2); 110,0(2); 108,7(2); 108,9(7)	110,3(2); 110,0(2); 108,6(2); 109,0(2); 108,7(2); 109,9(2)	108,4(3); 108,7(3); 109,7(3); 110,1(3); 110,(3); 109,9(3)

CONCLUSIONS

As a result of the studies of two magnesium‑containing solid solutions of melanterite, it was established that: 1) the arrays of X‑ray reflections of crystals I and II contain a few space groups forbidden by symmetry. P2₁/c reflections, taking into account which leads to the loss of the plane of symmetry c and a decrease in the symmetry of the sp. gr. P21/c to its maximum subgroup P21. 2) as a result of the substitution of $Mg^{2+} \rightarrow Fe^{2+}$, there is a reduction in the parameters of the unit cell of crystals and the sizes of the coordination octahedra of atoms (Fe+Mg), 3) the occupancy of magnesium in the M(2) position is greater than in the M(1) position, 4) between the coordination octahedron $[M(1)(H_2O)_6]^{2+}$.

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