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THE SURFACE OF AN IDEAL CRYSTAL OF ALUNITE IN MATHEMATICAL CLOSE-UP. Part I. Qualities and surface concentrations of defect ions

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ABSTRACT

By means of computer techniques and on the basis of X-ray diffraction parameters of an ideal crystal of alunite, calculations were made of the concentration of various types of surface defect ions for characteristic planes of a basic aluminum–potassium sulfate with the alunite structure.

In many transformations to which crystalline substances are subjected, such as, for instance, thermal decomposition reaction, chemisorption processes etc., the state of the substance's surface on the molecular scale is of great importance. On this scale the mathematical description of the distribution of surface species is possible and seems to be a proper one, because, first of all, such an approach makes it possible to understand better the processes occurring on the crystal surface (together with topochemical reactions).

The inspiration to take up such studies on basic aluminum–potassium sulfate with the alunite structure (which is obtained as the intermediate product during acidic processing of alumina) was the complex character of its thermal decomposition.

In this paper, we formulate a base model of the structure of a basic aluminum–potassium sulfate by using data taken from the literature, and we have developed

(1) a set of algebraic expressions forming an algorithm for calculating the coordinates x, y, z of all the lattice points of the ideal alunite crystal in any declared section of space

(2) a program which, by means of an IBM PC XT computer, allows calculation of the coordinates of lattice points and enables us to analyze the environment of a selected ion

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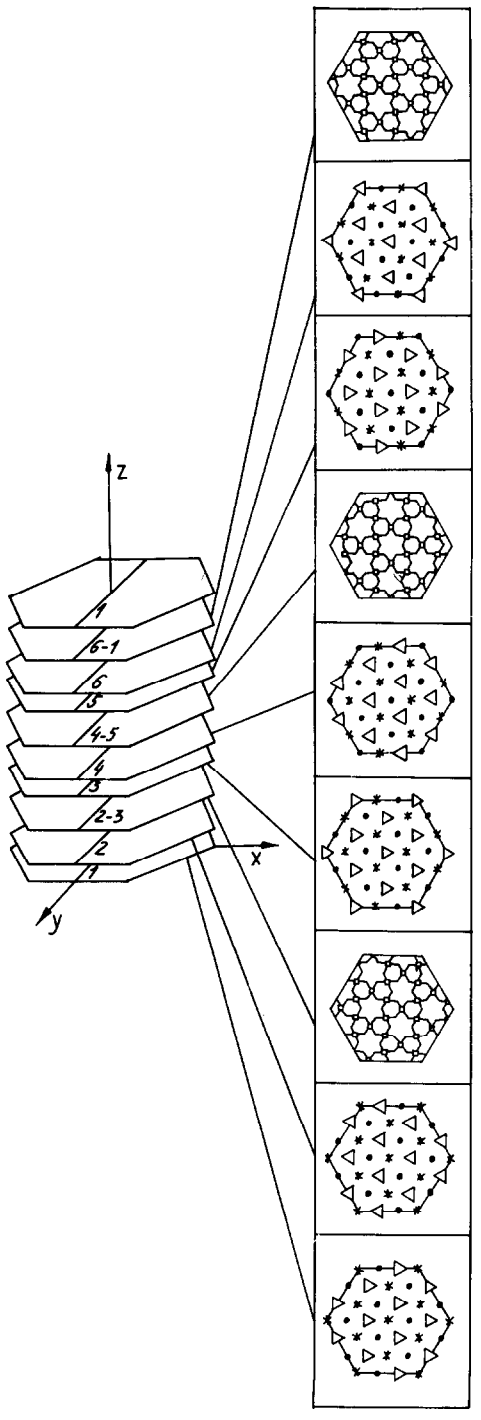


PLANE 6–1 $z = 15.45$ Å
□ aluminum
⟩ hydroxyl ($z = 15.45$ Å $\pm \delta$)

PLANE 6 $z = 13.56$ Å
◁ base of tetrahedron SO_4^{2-}
● top of tetrahedron SO_4^{2-}
* potassium under the plane 6 ($z = 12.56$ Å)

PLANE 5 $z = 11.56$ Å
▷ base of tetrahedron SO_4^{2-}
● top of tetrahedron SO_4^{2-}
* potassium over the plane 5 ($z = 12.56$ Å)

PLANE 4–5 $z = 9.67$ Å
□ aluminum
⟩ hydroxyl ($z = 9.67$ Å $\pm \delta$)

PLANE 4 $z = 7.78$ Å
◁ base of tetrahedron SO_4^{2-}
● top of tetrahedron SO_4^{2-}
* potassium under the plane 4 ($z = 6.78$ Å)

PLANE 3 $z = 5.78$ Å
▷ base of tetrahedron SO_4^{2-}
● top of tetrahedron SO_4^{2-}
* potassium over the plane 3 ($z = 6.78$ Å)

PLANE 2–3 $z = 3.89$ Å
□ aluminum
⟩ hydroxyl ($z = 3.89$ Å $\pm \delta$)

PLANE 2 $z = 2.0$ Å
◁ base of tetrahedron SO_4^{2-}
● top of tetrahedron SO_4^{2-}
* potassium under the plane 2 ($z = 1.0$ Å)

PLANE 1 $z = 0$
▷ base of tetrahedron SO_4^{2-}
● top of tetrahedron SO_4^{2-}
* potassium over the plane 1 ($z = 1.0$ Å)

Fig. 1. Basic model of alunite structure.

(3) a program which allows calculation of the number of ions on the crystal surface, on the basis of Miller coefficients, and segregation of the ions according to the quantity and quality of voids in their coordination polyhedra.

All the above activities were repeated for the anatase modification of titanium dioxide, and the chemisorption abilities of the surface, as well as its crystal shape and grain dimensions, were calculated. The calculated values of these parameters for the ideal crystal were compared with earlier published results of experimental research work [13].

BASE MODEL OF ALUNITE STRUCTURE

The alunite structure has been studied by the X-ray diffraction method and is described in the literature [1–8]. In the paper by Hendricks [1] it was accepted that the elementary cell, which includes three molecules of $KAl_3(OH)_6(SO_4)_2$ is a prism with a rhomboid base. The angles of the rhombus forming the base of the prism are 60° and 120°. Along the prism height, which is the triangle symmetry axis, there occur in turn two different regions: the first is filled with the ions SO_4^{2-} and K^+ and looks like a slice 0.2 nm thick; the other is filled with the ions Al^{3+} and OH^- and looks like a slice 0.375 nm thick. There are three such sequences within one elementary cell; they differ from one another in the linear shift and (or) the angular shift from the x and y axes of the cartesian coordinate system. Bonds between slices are formed by interaction of Al^{3+} ions and the oxygen of the SO_4^{2-} group and by interactions of K^+ and OH^- ions. Figure 1 shows the base model of the alunite structure with nine designated conventional planes and the distribution of ions near these planes.

ALGORITHM FOR CALCULATING THE x, y AND z COORDINATES OF ALUNITE

The base model of the alunite structure is written in the form of 342 algebraic expressions enabling the calculation of the x, y, z coordinates of the center of any ion—all the lattice points (Table 1) in the cartesian coordinates. The z axis of this system is in line with the triangle symmetry axis of the crystal and the x axis is aligned with the crystallographic direction x; the origin of the coordinate system is placed in the center of a potassium ion.

The units of the x and y axes are values xO and yO connected with the lattice constant a; the unit of the z axis is the lattice constant c. Additional constant values in the algebraic expression are: the bond length sulfur–oxygen in SO_4^{2-} ions (SO); the distance between a hydroxyl group (treated as one group) and the nearest oxygen of the SO_4^{2-} ion (b_3), and the angle

TABLE 1

Coordinates x, y, z: space lattice of alunite [9]

Hydroxyl of plane 6–1		
$4nx\mathrm{O}$	$(6m+4)y\mathrm{O}+b_3\cos\alpha$	$kc+(2/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$4nx\mathrm{O}+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+4)y\mathrm{O}-(1/2)b_3\cos\alpha$	$kc+(2/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$(4n+2)x\mathrm{O}-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+1)y\mathrm{O}-(1/2)b_3\cos\alpha$	$kc+(2/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$(4n+2)x\mathrm{O}$	$(6m+1)y\mathrm{O}+b_3\cos\alpha$	$kc+(2/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$(4n+2)x\mathrm{O}+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+1)y\mathrm{O}-(1/2)b_3\cos\alpha$	$kc+(2/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$4nx\mathrm{O}-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+4)y\mathrm{O}-(1/2)b_3\cos\alpha$	$kc+(2/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$4nx\mathrm{O}$	$(6m+4)y\mathrm{O}-b_3\cos\alpha$	$kc-(2/3)\mathrm{SO}-b_3\sin\alpha$
$4nx\mathrm{O}+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+4)y\mathrm{O}+(1/2)b_3\cos\alpha$	$kc-(2/3)\mathrm{SO}-b_3\sin\alpha$
$(4n+2)x\mathrm{O}-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+1)y\mathrm{O}+(1/2)b_3\cos\alpha$	$kc-(2/3)\mathrm{SO}-b_3\sin\alpha$
$(4n+2)x\mathrm{O}$	$(6m+1)y\mathrm{O}-b_3\cos\alpha$	$kc-(2/3)\mathrm{SO}-b_3\sin\alpha$
$(4n+2)x\mathrm{O}+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+1)y\mathrm{O}+(1/2)b_3\cos\alpha$	$kc-(2/3)\mathrm{SO}-b_3\sin\alpha$
$4nx\mathrm{O}-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+4)+(1/2)b_3\cos\alpha$	$kc-(2/3)\mathrm{SO}-b_3\sin\alpha$
Aluminum of plane 6–1		
$4nx\mathrm{O}$	$(6m+1)y\mathrm{O}$	$kc+(5/6)c$
$(4n+1)x\mathrm{O}$	$(3m+2.5)y\mathrm{O}$	$kc+(5/6)c$
$(4n+2)x\mathrm{O}$	$(6m+4)y\mathrm{O}$	$kc+(5/6)c$
$(4n+3)x\mathrm{O}$	$(3m+2.5)y\mathrm{O}$	$kc+(5/6)c$
Oxygen of plane 6		
$4nx\mathrm{O}$	$(6m+4)y\mathrm{O}$	$kc+(2/3)c+(2/3)\mathrm{SO}$
$4nx\mathrm{O}$	$6my\mathrm{O}+(2/\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c+(2/3)\mathrm{SO}$
$4nx\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$6my\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c+(2/3)\mathrm{SO}$
$4nx\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$6my\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c+(2/3\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+1)y\mathrm{O}$	$kc+(2/3)c+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+3)y\mathrm{O}+(2\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$(6m+3)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$(6m+3)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c+(2/3)\mathrm{SO}$
Potassium of plane 5–6		
$4nx\mathrm{O}$	$(6m+2)y\mathrm{O}$	$kc+(2/3)c$
$(4n+2)x\mathrm{O}$	$(6m+5)y\mathrm{O}$	$kc+(2/3)c$
Sulfur of plane 5–6		
$4nx\mathrm{O}$	$6my\mathrm{O}$	$kc+(2/3)c(1/3)\mathrm{SO}$
$4nx\mathrm{O}$	$(6m+4)y\mathrm{O}$	$kc+(2/3)c-(1/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+1)y\mathrm{O}$	$kc+(2/3)c-(1/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+3)y\mathrm{O}$	$kc+(2/3)c+(1/3)\mathrm{SO}$

Oxygen of plane 5		
$4nx\mathrm{O}$	$6my\mathrm{O}$	$kc+(2/3)\mathrm{SO}$
$4nx\mathrm{O}$	$(6m+4)y\mathrm{O}-(2\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c-(2/3)\mathrm{SO}$
$4nx\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$(6m+4)y\mathrm{O}+(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c-(2/3)\mathrm{SO}$
$4nx\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$(6m+4)y\mathrm{O}+(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c-(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+3)y\mathrm{O}$	$kc+(2/3)c-(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+1)y\mathrm{O}-(2\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c-(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$(6m+1)y\mathrm{O}+(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c-(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$(6m+1)y\mathrm{O}+(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)c-(2/3)\mathrm{SO}$
Hydroxyl of plane 4–5		
$4nx\mathrm{O}$	$6my\mathrm{O}+b_3\cos\alpha$	$kc+(1/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$(4n+2)x\mathrm{O}-(\sqrt{3}/2)b_3\cos\alpha$	$6my\mathrm{O}-(1/2)b_3\cos\alpha$	$kc+(1/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$(4n+2)x\mathrm{O}-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+3)y\mathrm{O}-(1/2)b_3\cos\alpha$	$kc+(1/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$(4n+2)x\mathrm{O}$	$(6m+3)y\mathrm{O}+b_3\cos\alpha$	$kc+(1/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$(4n+2)x\mathrm{O}+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+3)y\mathrm{O}-(1/2)b_3\cos\alpha$	$kc+(1/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$4nx\mathrm{O}-(\sqrt{3}/2)b_3\cos\alpha$	$6my\mathrm{O}-(1/2)b_3\cos\alpha$	$kc+(1/3)c+(2/3)\mathrm{SO}+b_3\sin\alpha$
$4nx\mathrm{O}$	$6my\mathrm{O}-b_3\cos\alpha$	$kc+(2/3)c-(2/3)\mathrm{SO}-b_3\sin\alpha$
$4nx\mathrm{O}+(\sqrt{3}/2)b_3\cos\alpha$	$6my\mathrm{O}+(1/2)b_3\cos\alpha$	$kc+(2/3)c-(2/3)\mathrm{SO}-b_3\sin\alpha$
$(4n+2)x\mathrm{O}-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+3)y\mathrm{O}+(1/2)b_3\cos\alpha$	$kc+(2/3)c-(2/3)\mathrm{SO}-b_3\sin\alpha$
$(4n+2)x\mathrm{O}$	$(6m+3)y\mathrm{O}-b_3\cos\alpha$	$kc+(2/3)c-(2/3)\mathrm{SO}-b_3\sin\alpha$
$(4n+2)x\mathrm{O}+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+3)y\mathrm{O}+(1/2)b_3\cos\alpha$	$kc+(2/3)c-(2/3)\mathrm{SO}-b_3\sin\alpha$
$4nx\mathrm{O}-(\sqrt{3}/2)b_3\cos\alpha$	$6m+(1/2)b_3\cos\alpha$	$kc+(2/3)c-(2/3)\mathrm{SO}-b_3\sin\alpha$
Aluminum of plane 4–5		
$4nx\mathrm{O}$	$(6m+3)y\mathrm{O}$	$kc+(1/2)c$
$(4n+1)x\mathrm{O}$	$(3m+0.5)y\mathrm{O}$	$kc+(1/2)c$
$(4n+2)x\mathrm{O}$	$6my\mathrm{O}$	$kc+(1/2)c$
$(4n+3)x\mathrm{O}$	$(3m+0.5)y\mathrm{O}$	$kc+(1/2)c$
Oxygen of plane 4		
$4nx\mathrm{O}$	$6my\mathrm{O}$	$kc+(2/3)\mathrm{SO}$
$4nx\mathrm{O}$	$(6m+2)y\mathrm{O}+(2\sqrt{2}/3)\mathrm{SO}$	$kc+c/3+(2/3)\mathrm{SO}$
$4nx\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$(6m+2)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+c/3+(2/3)\mathrm{SO}$
$4nx\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$(6m+2)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+c/3+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+3)y\mathrm{O}$	$kc+c/3+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+5)y\mathrm{O}+(2\sqrt{2}/3)\mathrm{SO}$	$kc+c/3+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$(6m+5)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+c/3+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$(6m+5)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+c/3+(2/3)\mathrm{SO}$

TABLE 1 (continued)

Potassium of plane 3–4		
$4nxO$	$(6m+4)yO$	$kc+(1/3)c$
$(4n+2)xO$	$(6m+1)yO$	$kc+(1/3)c$
Sulfur of plane 3–4		
$4nxO$	$6myO$	$kc+(1/3)c-(1/3)SO$
$(4n+2)xO$	$(6m+3)yO$	$kc+(1/3)c-(1/3)SO$
$4nxO$	$(6m+2)yO$	$kc+(1/3)c+(1/3)SO$
$(4n+2)xO$	$(6m+5)yO$	$kc+(1/3)c+(1/3)SO$
Oxygen of plane 3		
$4nxO$	$(6m+2)yO$	$kc+c/3-(2/3)SO$
$4nxO$	$6myO-(2\sqrt{2}/3)SO$	$kc+c/3-(2/3)SO$
$4nxO+\sqrt{2/3}\,SO$	$6myO+(\sqrt{2}/3)SO$	$kc+c/3-(2/3)SO$
$4nxO-\sqrt{2/3}\,SO$	$6myO+(\sqrt{2}/3)SO$	$kc+c/3-(2/3)SO$
$(4n+2)xO$	$(6m+5)yO$	$kc+c/3-(2/3)SO$
$(4n+2)xO$	$(6m+3)yO-(2\sqrt{2}/3)SO$	$kc+c/3-(2/3)SO$
$(4n+2)xO+\sqrt{2/3}\,SO$	$(6m+3)yO+(\sqrt{2}/3)SO$	$kc+c/3-(2/3)SO$
$(4n+2)xO-\sqrt{2/3}\,SO$	$(6m+3)yO+(\sqrt{2}/3)SO$	$kc+c/3-(2/3)SO$
Hydroxyl of plane 2–3		
$4nxO$	$(6m+2)yO-b_3\cos\alpha$	$kc+(1/3)c-(2/3)SO-b_3\sin\alpha$
$4nxO+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+2)yO+(1/2)b_3\cos\alpha$	$kc+(1/3)c-(2/3)SO-b_3\sin\alpha$
$(4n+2)xO-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+5)yO+(1/2)b_3\cos\alpha$	$kc+(1/3)c-(2/3)SO-b_3\sin\alpha$
$(4n+2)xO$	$(6m+5)yO-b_3\cos\alpha$	$kc+(1/3)c-(2/3)SO-b_3\sin\alpha$
$(4n+2)xO+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+5)yO+(1/2)b_3\cos\alpha$	$kc+(1/3)c-(2/3)SO-b_3\sin\alpha$
$4nxO-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+2)yO+(1/2)b_3\cos\alpha$	$kc+(1/3)c-(2/3)SO-b_3\sin\alpha$
$4nxO$	$(6m+2)yO+b_3\cos\alpha$	$kc+(2/3)SO+b_3\sin\alpha$
$4nxO+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+2)yO-(1/2)b_3\cos\alpha$	$kc+(2/3)SO+b_3\sin\alpha$
$(4n+2)xO-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+5)yO-(1/2)b_3\cos\alpha$	$kc+(2/3)SO+b_3\sin\alpha$
$(4n+2)xO$	$(6m+5)yO+b_3\cos\alpha$	$kc+(2/3)SO+b_3\sin\alpha$
$(4n+2)xO+(\sqrt{3}/2)b_3\cos\alpha$	$(6m+5)yO-(1/2)b_3\cos\alpha$	$kc+(2/3)SO+b_3\sin\alpha$
$4nxO-(\sqrt{3}/2)b_3\cos\alpha$	$(6m+2)yO-(1/2)b_3\cos\alpha$	$kc+(2/3)SO+b_3\sin\alpha$
Aluminum of plane 2–3		
$4nxO$	$(6m+5)yO$	$kc+(1/6)c$
$(4n+1)xO$	$(3m+0.5)yO$	$kc+(1/6)c$
$(4n+2)xO$	$(6m+2)yO$	$kc+(1/6)c$
$(4n+3)xO$	$(3m+0.5)yO$	$kc+(1/6)c$

TABLE 1 (continued)

Oxygen of plane 2		
$4nx\mathrm{O}$	$(6m+2)y\mathrm{O}$	$kc+(2/3)\mathrm{SO}$
$4nx\mathrm{O}$	$(6m+4)y\mathrm{O}+(2\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)\mathrm{SO}$
$4nx\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$(6m+4)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)\mathrm{SO}$
$4nx\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$(6m+4)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+5)y\mathrm{O}$	$kc+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+1)y\mathrm{O}+(2\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$(6m+1)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$(6m+1)y\mathrm{O}-(\sqrt{2}/3)\mathrm{SO}$	$kc+(2/3)\mathrm{SO}$
Potassium of plane 1–2		
$4nx\mathrm{O}$	$6my\mathrm{O}$	kc
$(4n+2)x\mathrm{O}$	$(6m+3)y\mathrm{O}$	kc
Sulfur of plane 1–2		
$4nx\mathrm{O}$	$(6m+2)y\mathrm{O}$	$kc-(1/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+5)y\mathrm{O}$	$kc-(1/3)\mathrm{SO}$
$4nx\mathrm{O}$	$(6m+4)y\mathrm{O}$	$kc+(1/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+1)y\mathrm{O}$	$kc+(1/3)\mathrm{SO}$
Oxygen of plane 1		
$4nx\mathrm{O}$	$(6m+2)y\mathrm{O}-(2\sqrt{2}/3)\mathrm{SO}$	$kc-(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+5)y\mathrm{O}-(2\sqrt{2}/3)\mathrm{SO}$	$kc-(2/3)\mathrm{SO}$
$4nx\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$(6m+2)y\mathrm{O}+(\sqrt{2}/3)\mathrm{SO}$	$kc-(2/3)\mathrm{SO}$
$4nx\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$(6m+2)y\mathrm{O}+(\sqrt{2}/3)\mathrm{SO}$	$kc-(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}+\sqrt{2/3}\,\mathrm{SO}$	$(6m+5)y\mathrm{O}+(\sqrt{2}/3)\mathrm{SO}$	$kc-(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}-\sqrt{2/3}\,\mathrm{SO}$	$(6m+5)y\mathrm{O}+(\sqrt{2}/3)\mathrm{SO}$	$kc-(2/3)\mathrm{SO}$
$4nx\mathrm{O}$	$(6m+4)y\mathrm{O}$	$kc-(2/3)\mathrm{SO}$
$(4n+2)x\mathrm{O}$	$(6m+1)y\mathrm{O}$	$kc-(2/3)\mathrm{SO}$

n, $\ldots -2, -1, 0, +1, +2\ldots$
$m = \ldots -2, -1, 0, +1, +2\ldots$
$k = -2, -1, 0, +1, +2\ldots$
α, angle between the base of tetrahedron SO_4^{2-} and straight line b_3
b_3, 2.52 Å
c, 17.35 Å (lattice constant)
$y\mathrm{O}$, $a\sqrt{3}/6 = 6.96$ Å $\times\sqrt{3}/6$
$x\mathrm{O}$, $a/4 = 6.96$ Å$/4$
SO, 1.51 Å (length of sulfur–oxygen bond)

which is formed by this section (b_3) with the triangle axis of the crystal $(90-\alpha)$.

The accepted value of this angle is $\alpha = 0.497$ rad following an optimizing operation in which the criterion was the best agreement of the calculated distances K–OH and Al–OH with the experimentally determined distances [1], which were respectively equal to 0.285 and 0.204 nm.

In the algebraic expressions of the algorithm formed there occur three independent parameters n, m and k; their combination gives the site of any ion in one of the many elementary cells of the considered section of space. Table 1 shows the set of these expressions with the names of planes used in Fig. 1.

THE PROGRAM "ALUNITE"

The program ALUNITE is written in the language BASIC. In this program the computer takes algebraic expressions and keeps in its memory the coordinates of lattice points of any selected section of the crystal. These points are of the following types: potassium, K^+; aluminum, Al^{3+}; sulfur, S^{6+}; axial oxygen, O^{2-} (when the sulfur–oxygen bond is alongside the triple axis); nonaxial oxygen, O^{2-}; and hydroxyl ion. On the basis of the collection of coordinates the program ALUNITE enables the calculation (in an interactive system) of the distance between a selected central ion and other ions and, because of the minimizing method, the choice of the nearest environment of the central ion.

The program ALUNITE includes 394 lines and its text occupies 7 kbyte in computer memory. The time needed for calculation is short, from a few seconds to a few minutes, but everything depends on the types of ions and the dimensions of the lattice section. The results obtained so far are given in Table 2 and shown in Fig. 2. The agreement of these results with the results of X-ray diffraction studies cited in the literature [1,10] is evidence that the program is correct.

THE PROGRAM "SURFACE"

Mineralogical studies of a natural and a synthetic alunite [11,12] showed that the most probable external planes are the plane with the most con-

TABLE 2

Distances A–B (ångströms) and number of neighbors B from the viewpoint of ion A

Kind of ion	A B:	1	2	3	4	5	6
Potassium	1	6.96×6	3.52×6	4.05×6	4.14×6	2.78×6	2.85×6
Aluminum	2	3.52×2	3.48×4	3.12×2	3.96×4	1.97×2	2.04×4
Sulfur	3	4.05×3	3.12×3	6.96×6	1.51×1	1.51×3	3.50×3
Axial oxygen	4	4.14×3	3.96×6	1.51×1	3.77×1	2.47×3	2.52×3
Nonaxial oxygen	5	2.78×1	1.97×1	1.51×1	2.47×1	2.47×2	2.60×2
Hydroxyl	6	2.85×1	2.04×2	3.50×1	2.52×1	2.60×2	2.60×2

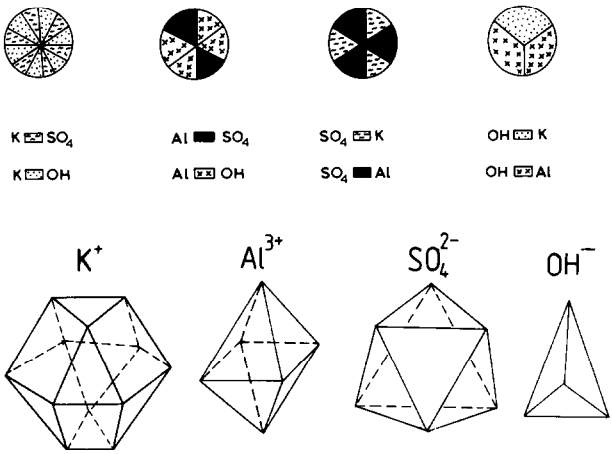


Fig. 2. Coordination polyhedra of ions inside the alunite crystal (quality pattern) and their graphical symbols.

TABLE 3

Qualities and quantities of surface defect ions

Kind of ion	Plane $10\bar{1}1$ [a] (+) surface ions sector 1.278 nm^2	Kind of ion	Plane $10\bar{1}1$ [a] (−) surface ions sector 1.278 nm^2
K^+		K^+	
Al^{3+}		Al^{3+}	
SO_4^{2-}		SO_4^{2-}	
OH^-		OH^-	

[a] Plane equation: $0.818x + 0.472y + 0.328z - 4.2703 = 0$

Kind of ion	Plane 0001 [b] (+) surface ions sector 0.839 nm^2	Kind of ion	Plane 0001 [b] (−) surface ions sector 0.839 nm^2
K^+		K^+	
Al^{3+}		Al^{3+}	
SO_4^{2-}		SO_4^{2-}	
OH^-		OH^-	

[b] Plane equation: $z - 1.8796 = 0$

centrated ions—$10\bar{1}1$—and the cleavage plane—0001. The calculations of a theoretical surface concentration of different types of ions present on the surface and the quantity and the quality of voids in the coordination polyhedra were conducted from these planes. In order to achieve this, the program SURFACE was devised. This program, when Miller coefficients of the external crystal plane are introduced into the computer, deduces the equation of this plane and sites it in the lattice with unchanged directional coordinates in such a way that this plane passes through the specified crystal section. Next, the program enables the calculation of the distance of each ion from the external plane; ions whose distance is smaller than the "radius" of their coordination polyhedra will be found on two lists of surface ions. The first list includes the ions lying on the positive (+) side of the plane and the second list includes the ions lying on the negative (−) side of the plane. These lists describe two different external surfaces of an ideal crystal and they complement one another from the point of view of coordination polyhedra. The next stage of the programme involves analyzing the quality and quantity of voids in coordination polyhedra of the ions.

The programme SURFACE includes 70 BASIC lines and lines of output data. The time needed for execution of this program together with the program ALUNITE is about 8 h. The volume size of 3240 ions (with 490 surface ions included) is limited by the operational capacity of the computer memory; this capacity is enlarged in the new version of the programs, written in Turbo Pascal language. The results obtained so far are given in Table 3.

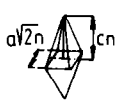
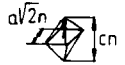
VERIFICATION OF THE METHOD OF SURFACE-STRUCTURAL CALCULATIONS

The procedure discussed above enables us to perform calculations of the surface state of the ideal crystal of titanium dioxide with the anatase structure [14], and results of the calculations are given in Table 4. The assumed shape of the particles (Table 4, column 1) determined the planes (column 2) for which calculations of the concentration of surface ions were carried out (column 3).

Considering, in the description of the particle shape, the parameter n, which is the standard particle size, the particle volume and its surface as a function of this parameter were determined (columns 4 and 5). It was then possible to calculate the quantity of chemisorption centers occurring for 1 mole of TiO_2 included in the particle (column 6). The calculated number of surface centers of water chemisorption agrees with the experimental value (0.34 mole of H_2O to 1 mole of TiO_2) for particles with diameters of ca. 10 nm (column 8), which is typical for the local titanium dioxide produced as a pigment.

TABLE 4

Chemisorptive properties of anatase calculated according to "ANATASE" program [14]. a, c: lattice constants of anatase; n: standard of particle size; x: state of the anatase hydration, $TiO_2 \cdot xH_2O$; $n_{0.34}$: size of particle having $0.34 \times 6.02 \times 10^{23}$ sites for H_2O; $d_{z0.34}$: substitute diameter of particle having this number of surface centers

Particle shape	Kind of surface	Surface concentration of H_2O (per nm^2)	Particle volume	Particle surface	x	$n_{0.34}$	$d_{z0.34}$
1	2	3	4	5	6	7	8
	0 0 1	7.2	$v = a^2cn^3$	$S = (4ac + 2a^2)n^2$			
	0 1 0	5.7			$\frac{6}{n}$	17.65	90 Å
	1 0 0	5.7					
	1 0 1	10.63	$v = \frac{8}{3}a^2cn^3$	$S = 8a\sqrt{a^2 + c^2}\,n^2$			
	0 1 1	10.63			$\frac{3}{n}$	8.82	62 Å
	1 1 1	7.79	$v = \frac{4}{3}a^2cn^2$	$S = 4a\sqrt{2c^2 + a^2}\,n^2$			
					$\frac{3}{n}$	8.82	50 Å
	1 1 2	7.05	$v = \frac{2}{3}a^2cn^3$	$S = a\sqrt{16a^2 + 8c^2}\,n^2$			
					$\frac{3}{n}$	8.82	39 Å

CONCLUSIONS

The base model of the structure of a basic aluminum–potassium sulfate was defined on the basis of literature data.

A set of algebraic expressions which makes up the algorithm of calculation for the coordinates x, y and z of all lattice points of the ideal crystal of alunite in any specified lattice section was worked out.

A program was devised which allows calculation, by means of a computer, of the coordinates of lattice points, and enables analysis of the environment of a selected ion.

A program was written which allows one to count the number of crystal surface ions on the surface, having assumed the Miller coefficients, and to segregate these ions according to the quantity and quality of voids in their coordination polyhedra.

The calculations give results which can be compared with the experimental data for water chemisorption on the anatase surface.

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