Thermochimica Acta, 181 (1991) 35-43
Elsevier Science Publishers B.V., Amsterdam

THE SURFACE OF AN IDEAL CRYSTAL OF ALUNITE IN MATHEMATICAL CLOSE-UP.
Part II. Localization of surface ions and a map of local electrical charges of the surfaces $10\bar{1}1$

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(Received 21 August 1990)

ABSTRACT

By means of computer techniques and on the basis of X-ray diffraction parameters of an ideal crystal of alunite and of coordination regularities resulting from these parameters, determinations were made, pointwise, of the excess electrical charge of the surface $10\bar{1}1$, the equation of which was found by optimization according to criteria of a minimum total charge or to the minimum sum of absolute charge values.

In many transformations involving crystalline substances, such as, for instance, reactions of thermal decomposition, processes of chemisorption and adsorption reactions on solid catalysts etc., the surface state of a solid substance on the molecular scale is of great importance. On this scale the mathematical description of the quality and distribution of surface ions is possible and seems to be reasonable. In the first part of this work [1] we obtained, by means of computer calculations, repeat sets of surface ions of type K^+, Al^{3+}, SO_4^{2-} and OH^- while specifying the qualities and quantities of voids in their coordinating polyhedra for the equation of the plane $10\bar{1}1$, which is the external plane of a model crystal

$$X \cos\alpha + Y \cos\beta + Z \cos\gamma + PE = 0$$

where $\cos\alpha = 0.81806$, $\cos\beta = 0.47231$, $\cos\gamma = 0.32817$ and the distance, PE, of the plane from the origin of the cartesian coordinate system is 42.703 Å. This set is shown in Table 1.

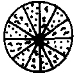
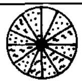
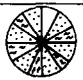
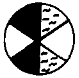
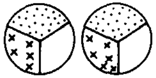
The aim of this work was

to find all possible planes of the family $10\bar{1}1$ (with the same directional coefficient but with different PE values) possessing different sets of surface ions of the type K^+, Al^{3+}, SO_4^{2-} and OH^-

to calculate for each of these planes the set of local electrical charges resulting from incompleteness of coordinating polyhedra of surface ions and, eventually

TABLE 1

Quality and quantity of surface defect ions [1]. PEa sector 0.4261 nm^2

i	Kind of ions	Crystal interior coordination sphere [b]	Plane $10\bar{1}1$ [a] $(+)$ surface ions			Plane $10\bar{1}1$ [a] $(-)$ surface ions		
			Graphic symbol	Algebraic symbol [c]	Distance from the plane (Å)	Graph symbol	Algebraic symbol	Distance from the plane (Å)
1	K^+	12 		$1 \times K\ (1, 0)$	$+2.8468$		$1 \times K\ (1, 0)$	-2.8469
2	Al^{3+}	6 					$1 \times Al\ (1, 2)$	-10^{-6}
3	SO_4^{2-}	6 		$1 \times SO_4\ (1, 1)$	$+1.1141$		$1 \times SO_4\ (1, 0)$	-1.1141
4	OH^-	3 		$2 \times OH\ (0, 1)$	$+1.2708$			

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[a] Plane equation: $Xc\sqrt{3}/\sqrt{4c^2+3a^2} + Yc/\sqrt{4c^2+3a^2} + Za\sqrt{3}/\sqrt{4c^2+3a^2} - ac\sqrt{3}\,n/\sqrt{4c^2+3a^2} = 0$, where $a = 6.96$ Å, $c = 17.35$ Å, $n = 7.5$.

[b] Ion–ion interaction marked as follows:
K–SO interaction marked by tildes and far by x
K–OH interaction marked by dots and far by y
Al–SO interaction marked by solid black and far by z
Al–OH interaction marked by crosses and far by w.

[c] In parentheses (n, m) are given the numbers of voids in succeeding coordinating polyhedra according to the index i of ion vacancy.

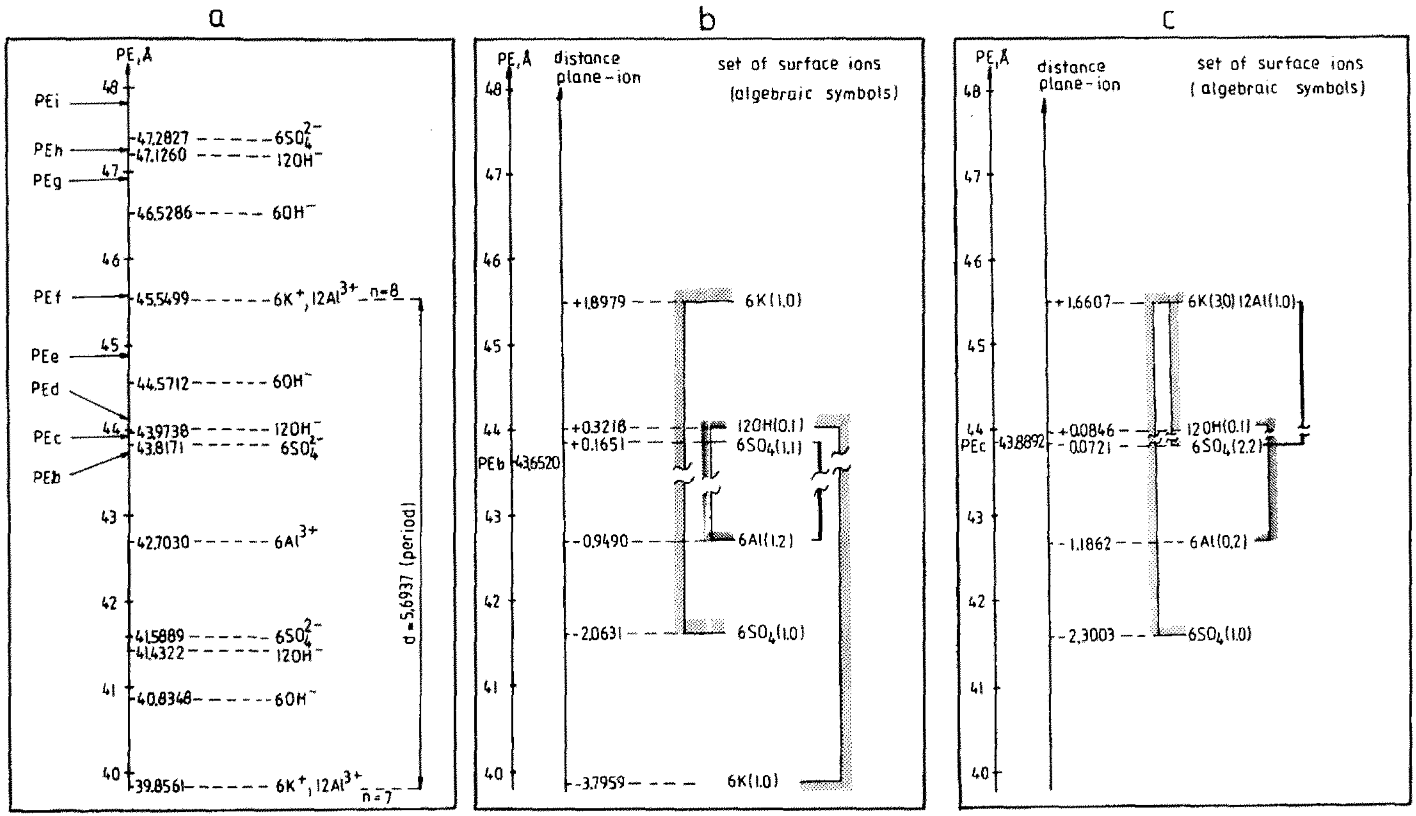

Fig. 1. Sets of $10\bar{1}1$ ions as a function of the parameter PE in the plane equation

$X \cos \alpha + Y \cos \beta + Z \cos \gamma - PE = 0$

Plane sector 2.5566 nm^2.

[a] Set of $10\bar{1}1$ ions as a function of parameter PE (crystal interior).

[b] Set of surface ions, PEb(+) and PEb(−) planes.

[c] Set of surface ions, PEc(+) and PEc(−) planes.

TABLE 2

Quality and quantity of surface defect ions of all $10\bar{1}1$ planes [a]

Distance from $10\bar{1}1$	Surface ions	Electrical charge [b] $24 \times q/e$	Distance from $10\bar{1}1$	Surface ions	Electrical charge [b] $24 \times q/e$
PEb = 43.6520 Å					
+1.8979 Å	6K (1, 0)	$+6\times2 = +12$	−0.9490 Å	6Al (1, 2)	$+6\times(14+22) = +216$
+0.3218 Å	12OH (0, 1)	$-12\times11 = -132$	−2.0630 Å	$6SO_4$ (1, 0)	$-6\times2 = -12$
+0.1651 Å	$6SO_4$ (1, 1)	$-6\times(2+14) = -96$	−3.7959 Å	6K (1, 0)	$+6\times2 = +12$
		$\Sigma q/e = -216/24$			$\Sigma q/e = +216/24$
		$\Sigma\lvert q/e\rvert = 240/24$			$\Sigma\lvert q/e\rvert = 240/24$
PEc = 43.8892 Å					
+1.6607 Å	6K (3, 0)	$+6\times3\times2 = +36$	−0.0721 Å	$6SO_4$ (2, 2)	$-6\times2\times(2+14) = -192$
+1.6607 Å	12Al (1, 0)	$+12\times14 = +168$	−1.1862 Å	6Al (0, 2)	$+6\times2\times11 = +132$
+0.0846 Å	12OH (0, 1)	$-12\times11 = -132$	−2.3003 Å	$6SO_4$ (1, 0)	$-6\times2 = -12$
		$\Sigma q/e = +72/24$			$\Sigma q/e = -72/24$
		$\Sigma\lvert q/e\rvert = 336/24$			$\Sigma\lvert q/e\rvert = 336/24$
PEd = 44.1264 Å					
+1.4235 Å	6K (3, 2)	$+6\times(3\times2+2\times2) = +60$	−0.1526 Å	12OH (1, 1)	$-12\times(2+11) = -156$
+1.4235 Å	12Al (1, 1)	$+12\times25 = +300$	−0.3093 Å	$6SO_4$ (2, 2)	$-6\times2(14+2) = -192$
			−2.5375 Å	$6SO_4$ (1, 0)	$-6\times2 = -12$
		$\Sigma q/e = +360/24$			$\Sigma q/e = -360/24$
		$\Sigma\lvert q/e\rvert = 360/24$			$\Sigma\lvert q/e\rvert = 360/24$
PEe = 44.8381 Å					
+0.7118 Å	6K (3, 3)	$+6\times3\times(2+2) = +72$	−0.2669 Å	6OH (1, 2)	$-6\times(2+2\times11) = -144$
+0.7118 Å	12Al (1, 2)	$+12\times(14+22) = +432$	−0.8643 Å	12OH (1, 1)	$-12\times(2+11) = -156$
			−1.0211 Å	$6SO_4$ (2, 2)	$-6\times2\times(2+14) = -192$
			−3.2492 Å	$6SO_4$ (1, 0)	$-6\times2 = -12$
		$\Sigma q/e = +504/24$			$\Sigma q/e = -504/24$
		$\Sigma\lvert q/e\rvert = 504/24$			$\Sigma\lvert q/e\rvert = 504/24$

PEf = 45.5499 Å					
+3.9610 Å	$6SO_4$ (1, 0)	$-6\times2 = -12$	−0.0000 Å	12Al (1, 2)	$+12\times(14+22) = +432$
+1.7328 Å	$6SO_4$ (2, 2)	$-6\times2\times(2+14) = -192$	−0.0000 Å	6K (3, 3)	$+6\times3\times(2+2) = +72$
+1.5761 Å	12OH (1, 1)	$-12\times(2+11) = -156$			
+0.9787 Å	6OH (1, 2)	$-6\times(2+22) = -144$			
		$\Sigma q/e = -504/24$			$\Sigma q/e = +504/24$
		$\Sigma\lvert q/e\rvert = 504/24$			$\Sigma\lvert q/e\rvert = 504/24$
PEg = 46.9733 Å					
+2.5376 Å	$6SO_4$ (1, 0)	$-6\times2 = -12$	−1.4234 Å	6K (3, 2)	$+6\times(3\times2+2\times2) = +60$
+0.3094 Å	$6SO_4$ (2, 2)	$-6\times2\times(2+14) = -192$	−1.4234 Å	12Al (1, 1)	$+12\times(14+11) = +300$
+0.1527 Å	12OH (1, 1)	$-12\times(2+11) = -156$			
		$\Sigma q/e = -360/24$			$\Sigma q/e = -360/24$
		$\Sigma\lvert q/e\rvert = 360/24$			$\Sigma\lvert q/e\rvert = 360/24$
PEh = 47.2105 Å					
+2.3004 Å	$6SO_4$ (1, 0)	$-6\times2 = -12$	−0.0845 Å	12OH (0, 1)	$-12\times11 = -132$
+1.1863 Å	6Al (0, 2)	$+6\times2\times11 = +132$	−1.6606 Å	6K (3, 0)	$+6\times3\times2 = +36$
+0.0722 Å	$6SO_4$ (2, 2)	$-6\times2\times(2+14) = -192$	−1.6606 Å	12Al (1, 0)	$+12\times14 = +168$
		$\Sigma q/e = -72/24$			$\Sigma q/e = +72/24$
		$\Sigma\lvert q/e\rvert = 336/24$			$\Sigma\lvert q/e\rvert = 336/24$
PEi = 47.9922 Å					
+3.3214 Å	6K (1, 0)	$+6\times2 = +12$	−0.6395 Å	$6SO_4$ (1, 1)	$-6\times(2+14) = -96$
+1.5886 Å	$6SO_4$ (1, 0)	$-6\times2 = -12$	−0.7963 Å	12OH (0, 1)	$-12\times11 = -132$
+0.4745 Å	6Al (1, 2)	$+6\times(14+2\times11) = +216$	−2.3725 Å	6K (1, 0)	$+6\times2 = +12$
		$\Sigma q/e = +216/24$			$\Sigma q/e = -216/24$
		$\Sigma\lvert q/e\rvert = 240/24$			$\Sigma\lvert q/e\rvert = 240/24$

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[a] Plane sector 2.5566 nm^2.

[b] e: electron charge. q: electrical charge of ions.

to choose the plane whose sum of local electrical charges is the smallest.

By means of the program "SURFACE" in conjunction with the program "ALUNITE" [1], eight parallel $10\bar{1}1$ planes with different sets of ions have been found (Fig. 1a). Such configurations are repeated periodically as the values of PE increase (or decrease). For reasons of order, in the programme SURFACE one of the cycles ($7.5d < \mathrm{PE} < 8.5d$) was chosen, where $d = 5.6937$ Å, and calculations were made of the quantities and qualities of voids in the coordinating polyhedra of surface ions, determined with various PE values, of eight sequential parallel $10\bar{1}1$ planes designated PE*b*, PE*c*, PE*d*, PE*e*, PE*f*, PE*g*, PE*h* and PE*i*.

The sign (−) was used to designated the variant in which, from the center of the coordinate system, there occur in turn: volume of crystal, surface $10\bar{1}1$ and lack of solid.

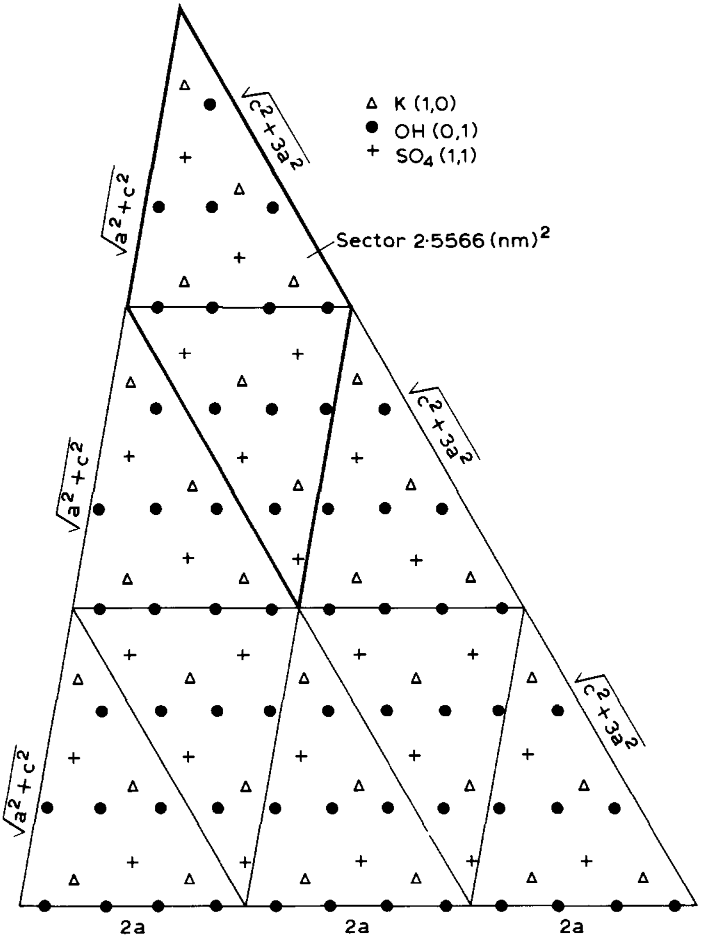

Fig. 2. Localizations of surface ions of PE*b*(+) plane.

The sign (+) designated the variant in which, from the center of the coordinate system, these occur in turn: lack of solid, surface $10\bar{1}1$ and volume of crystal.

Results of calculations are shown in Table 2 and, partly, in Figs. 1b and 1c. Localizations of surface ions are given in Fig. 2.

As the basis of calculations of local charges external to an ideal crystal, the following assumptions were made:

the ionic charge is completely balanced by interaction of the nearest neighbors

only bonds of the same length can correspond with the same formal electrical charges.

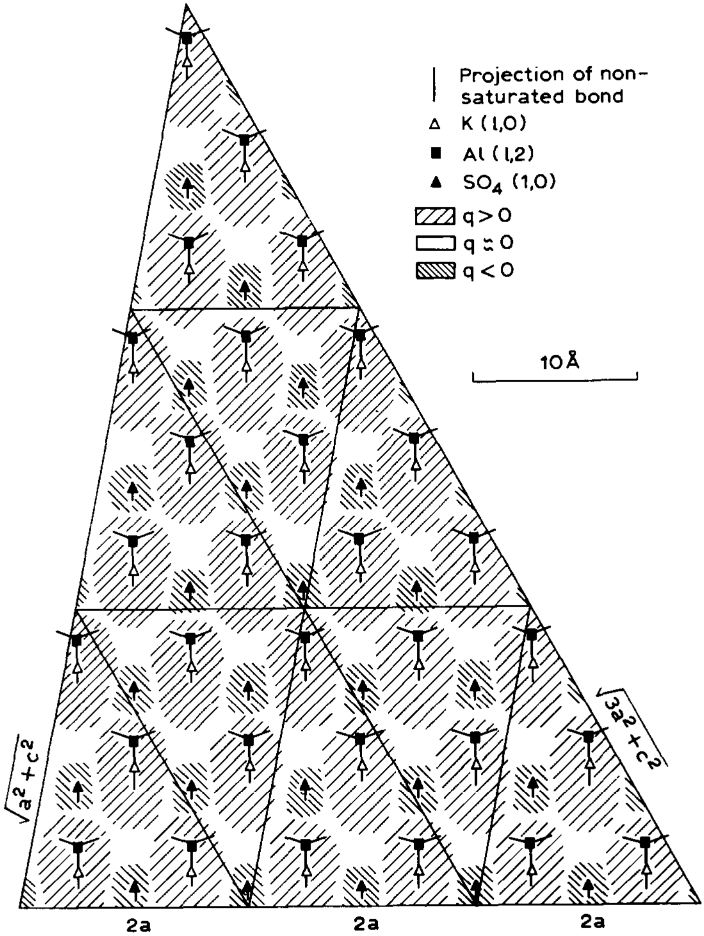

Fig. 3. Maps of local electrical charges of plane PE*b*(−).

For basic aluminum–potassium sulfate with the alunite structure, the above assumptions lead to the equations

for K^+ $\quad 6x + 6y = 1$
for Al^{3+} $\quad 4w + 2z = 3$
for SO_4^{2-} $\quad 3x + 3z = 2$
for OH^- $\quad 2w + y = 1$

in accordance with determinations reported in Table 1.

Solution of the system of equations gives the formal charges dependent on each type of void in the coordinating polyhedra: $x = 2/24$; $y = 2/24$; $z = 14/24$; $w = 11/24$, thereby allowing calculation of the local (q) and total ($\Sigma|q|$ and $|\Sigma q|$) charges of each possible plane $10\bar{1}1$ (Table 2). Comparison of the results leads to the conclusion that, among all 16 possible mathematical $10\bar{1}1$ planes, the planes PE*b*(+), PE*i*(+), PE*b*(−) and PE*i*(−) have the, so-called, most probable sum of absolute values of local charges ($\Sigma|q|$) or—in other words—the least number of non-saturated bonds. Because PE*b*(+) is the same as PE*i*(−), PE*i*(+) is the same as PE*b*(−), and PE*b*(+) is the same as PE*b*(−) but differs in sign, all these four mathematically possible planes signify only one actual situation where, to keep electrical neutrality of the crystal particle, each section, for instance PE*b*(+), can correspond to (on the other side of the particle) the plane PE*b*(−). More non-saturated bonds, although better balances within the plane of local charges, are exhibited by planes PE*c*(+), PE*c*(−), PE*h*(+) and PE*h*(−). The distribution of local charges on the optimal plane PE*b* and the projection of potential non-saturated bonds on this plane are shown in Fig. 3.

CONCLUSIONS

We have calculated the formal charges corresponding to interactions of each pair of neighbor ions in alunite; these charges are: $q(K\text{–}SO_4) = 2e/24$; $q(K\text{–}OH) = 2e/24$; $q(Al\text{–}SO_4) = 14e/24$; $q(Al\text{–}OH) = 11e/24$.

It has been shown that there are 16 mathematically possible $10\bar{1}1$ planes with periodicity defining four different situations, while their optimal plane has the equation

$$0.81806x + 0.47231y + 0.32817z - \mathrm{PE} = 0$$

where $41.5889\ \text{Å} < \mathrm{PE} < 43.8171\ \text{Å}$.

The total amount of non-saturated bonds of the optimal surface $10\bar{1}1$, calculated as the sum of absolute values of local charges, is $10e$ on the surface section of $2.5566\ \mathrm{nm}^2$.

The density of the electrical charge of the optimal surface $10\bar{1}1$, calculated as the sum of local charges, is $9e$ on the surface section of 2.5566 nm^2.

The plane $10\bar{1}1$ with the smallest density of electrical charge, amounting to $3e$ for each 2.5566 nm^2, has the equation

$$0.81806x + 0.47231y + 0.32817z - \mathrm{PE} = 0$$

where $43.8171\ \text{Å} < \mathrm{PE} < 43.9738\ \text{Å}$ or $41.4322\ \text{Å} < \mathrm{PE} < 41.5889\ \text{Å}$; however, the total amount of non-saturated bonds of this plane is up to $14e$ for each 2.5566 nm^2.

Use of the program ALUNITE allows all the above characteristics to be obtained rapidly for any modified lattice constants of alunite and for any Miller indices describing the external planes of the crystal.

REFERENCE

1 B. Andruszkiewicz and J. Pysiak, Thermochim. Acta, 181 (1991) 23.