# Computer Modeling of Radiating Stability of Sulfates of Metals

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Abstract – Based on the theory of functional local density, band spectra, densities of states, distributions of the valence and difference densities in alkali metal sulfates are calculated by the method of pseudopotential in the basis of localized orbitals.

It is established, that atoms of oxygen are in a different charge state and have different force of chemical bonding in anion. Models of photoelectronic spectra and mechanisms of education of chemical bond for interpretation of processes of radiating decomposition and an explanation of various radiating stability of crystals are offered.

## 1. Introduction

Sulfates of alkaline metals M<sub>2</sub>SO<sub>4</sub> (M: Li, Na, K, Rb, Cs), double sulfates MLiSO<sub>4</sub> show under the certain external conditions ferroelectrics, ferroelastic, piezoelectric properties. They are used as elements of various gauges. It demands all-round studying of their physical and chemical properties under usual conditions and their changes at external influences, including radiation.

At irradiation of Li<sub>2</sub>SO<sub>4</sub>, using of a method of xray photoelectronic spectroscopy (XPS), they observe [1] forming of Li<sub>2</sub>SO<sub>3</sub>, Li<sub>2</sub>S, Li<sub>2</sub>O, sulfur and adsorbed oxygen. End-products of reaction are sulphite and oxide of lithium. At  $\gamma$ -irradiated Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> also it was observed  $O_3^-$ . Radiating stability of sulfates approximately is higher two order, than nitrates or chlorates of metals and it essentially differs in line M<sub>2</sub>SO<sub>4</sub>. These experimental results require a theoretical explanation and an establishment of the general laws of processes of radiolysis in sulfates, forecasting of their behavior at other kinds of power influences such as photolysis and thermolysis.

In the present work the general laws of an electronic structure of sulfates of metals  $M_2SO_4$ , double sulfates MLiSO<sub>4</sub>, and also of their products of radiolysis  $M_2SO_3$ ,  $M_2S$ ,  $M_2O$  are considered. On the basis of comparison of spectra of density of state of sulfates, sulfites, sulfides, oxides it is modeled XPS of the irradiated crystals. The analysis of mechanisms of formation of chemical bond is done from maps of distribution of electronic density and the power quantities describing its durability are determined. On this basis probable ways of this or that formation of structure are predicted.

# 2. Crystal structure

Crystal structures of sulfates belongs to three types: monoclinic with space group  $C_{2h}^{5}$  and number of formular units per unite cell Z=4 ( $\beta$ -Li<sub>2</sub>SO<sub>4</sub>); orthorhombic –  $D_{2h}^{16}$ , Z=4 ( $\beta$ -K<sub>2</sub>SO<sub>4</sub>, Rb<sub>2</sub>SO<sub>4</sub>, Cs<sub>2</sub>SO<sub>4</sub>); rhombic –  $D_{2h}^{17}$ , Z=2 ( $\epsilon$ -Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>). Double sulfates MLiSO<sub>4</sub> are characterized by a distorted tridymite-type structure, which can be described by a framework consisting of six-membered rings of alternating SO<sub>4</sub> and LiO<sub>4</sub> tetrahedra. In some interval of temperatures symmetry of these crystals is orthorhombic with space group  $D_{2h}^{16}$  or monoclinic  $C_{2h}^5$ , Z=4 (RbLiSO<sub>4</sub>, CsLiSO<sub>4</sub>).

In researched crystals atoms of oxygen form different number nonequivalent sublattices. In  $Li_2SO_4$  their number is four and lengths of bonds S-O1=1.470, S-O2=1.471, S-O3=1.474, S-O4=1.478 Å [2]; in  $Na_2SO_4$  – two [3] and  $K_2SO_4$  it is three [4]. In monoclinic phase RbLiSO<sub>4</sub> their four sublattices of oxygen: S-O1=1.433, S-O2=1.443, S-O3=1.450, S-O4=1.451 Å [5]. In hexagonal KLiSO<sub>4</sub> – are two: S-O1=1.442, S-O2 (3,4)=1.414 Å.

In Li<sub>2</sub>SO<sub>4</sub> atoms of lithium are in tetrahedral environment from atoms of oxygen, each of which belongs to different sulfate groups. All distances Li-O are various, and for sublattice Li1 they are equal: Li1-O1=1.963, Li1-O3=1.976, Li1-O4=1.914, 1.976 Å, and for Li2: Li2-O1=1.962, Li1-O2=1.928, 1.990, Li1-O3=1.981 Å. Atoms of rubidium in Rb<sub>2</sub>SO<sub>4</sub> are also formed by two sublattices with nonequivalent distances Rb1-S=3.415 Å, Rb2-S=3.544 Å. They have the oxygen environment close to octahedron, with minimal lengths Rb1-O1=2.769 Å and Rb2-O2=2.875 Å. For others isostructural compounds crystallographic data can be found in [4,5].

Sulphites of alkaline metals crystallize mainly in hexagonal lattice.  $Na_2SO_3$  has space group of symmetry  $C_{3i}^1$  and two formular units per unite cell [6]. Thus atoms of sodium take three nonequivalent positions, whereas sulfur and oxygen – on one. The same structure, but with higher symmetry –  $D_{3d}^1$  has and  $K_2SO_3$ .

#### 3. A method of research

Research of electronic structure of sulfates was carried out by methods of computer modeling. The band structures of crystals is calculated within the theory of the local electron density functional using nonlocal BSH-pseudopotentials and a basis of numerical  $sp^3d^5$ pseudoorbitals. These were obtained by solving the Schrodinger equation with the same pseudopotentials. The occupation numbers were varied so as to obtain a diagram of atomic energy levels similar to the experimentally observed one. The details of the numerical implementation of the method were reported in [7].

For studying features of formation of chemical bond the sublattice method [8] was applied. In the sublattice method, the difference density  $\Delta \rho(\mathbf{r})$  is calculated, which is defined as the difference between the crystal valence density and the sublattice density. The sublattices are formed of atoms bonded with each other by the symmetry elements of the space group of the crystal; they are electrically neutral. The structural parameters in all cases are set according to the real geometric structure. It follows from the condition of normalization of electron density to the number of electrons that the integral of the difference density over the unit cell is equal to zero and, therefore, the maps  $\Delta \rho(\mathbf{r})$  contain regions with both positive and negative densities, which visualizes the charge redistribution between the sublattices. Thus, the difference density contains the most important information about the mechanism of the formation of chemical bonds in crystals, determining the role of each sublattice in this process.

## 4. Modeling of photoelectronic spectra

It is known, that solid products of radiating decomposition of crystal compounds are established by XPS methods. As a rule, for such researches use 1s levels of atomic core. However it is possible to apply to these purposes valence bands where energy gaps can be more than core splitting. Such researches, for example for NaNO<sub>3</sub> are executed in [9].

For modeling of photoelectronic spectra of sulfates and products of their radiating decomposition spectra of density of states N(E) are used. The nature of quantum states was determined from calculations partial electronic density from separate energy bands, and also partial density of states. Calculations of band structures of oxides and sulfides of alkaline metals are executed by us earlier in [10], and sulphites in [11].

In Fig. 1 spectra N(E) sulfates, sulphites, oxides and sulfides of lithium, sodium, potassium, rubidium are resulted. For zero of energy last filled states is accepted. Values of density of states are given in arbitrary units. Values of energy are given in eV.

Distribution of partial density of states specifies a small role of quantum states of sulfur in formation of valence bands of sulphites and sulfates of metals. Oxygen character of the bottom valence band of sulfate anions is shown in rather steady energy position of corresponding bands of N(E). The full width of a valence bands increases with growth of ionic radius of cation and radius of anion. The width of separate subbands at transition from Na<sub>2</sub>SO<sub>n</sub> to K<sub>2</sub>SO<sub>n</sub> (*n*=3,4), on the contrary, decreases. It is consequence of reduction of an active polarizing role of an ion of potassium in comparison with sodium.





Group of energy bands with energy -13 eV are constructed from *s*-states of sulfur, and in the field of -10 eV - from *p*-states of atoms anions. The valence band top is formed mainly *p*-states of oxygen. For highest subband and lower subband *p*-orbitals of oxygen have mutually perpendicular character. The uppermost filled crystal orbital (CO) consists of  $\pi$ orbitals of oxygen.

From partial density of states follows, that the contribution of nonequivalent atoms of oxygen to formation of valence bands is various. Presence of two nonequivalent oxygen sublattice results to significant splitting of energy bands in  $Na_2SO_4$  and  $Rb_2SO_4$ . Those widening in comparison with sulphites it is caused by increase in number of oxygen states and strengthening of interaction of them. In N(E) M<sub>2</sub>O (M<sub>2</sub>S) the bottom valence band is formed by *s*-states of oxygen (sulfur), and top valence band – *p*-oxygen (sulfur). Energy of a *s*-states of sulfur makes about -10 *eV* and poorly varies at transition from one compound to another. Energy bottom valence CO in oxides decreases with growth of nuclear number cation.

In RbLiSO<sub>4</sub> and KLiSO<sub>4</sub> in the bottom valence bands allocated three strips N(E) are with significant energy splitting. It the structure of density of states of double sulfates coincides with Rb<sub>2</sub>SO<sub>4</sub> and differs from K<sub>2</sub>SO<sub>4</sub>, Li<sub>2</sub>SO<sub>4</sub>. In the field of connecting S-O states structure N(E) the majority of sulfates differs from each other and it is consequence of a different charging states nonequivalent in crystallographic relation of atoms of oxygen.

Comparison of spectra of density of states of sulfates, sulphites, sulfides and oxides alkaline metals shows, that at energy about  $-30 \ eV N(E)$  considerably differ as on number of maxims, and their energy position. Energy differences exceed errors XPS and consequently can be fixed experimentally. Presence of a band in area from -20 up to -15 eV unequivocally specifies presence at samples subjected to an irradiation oxide of metal as in spectra N(E) all other crystals at such energy the allowed states are absent. In energy area, answering connecting S-O states, also there are differences. They are most typical for double sulfates which radiating stability earlier experimentally was not investigated. Therefore the results received in the framework represent the certain interest not only for interpretation, but also the description of mechanisms of radiolysis. For these purposes rather useful there can be representations about mechanisms of formation of chemical bond in sulfates.

#### 5. Modeling of chemical bond

Influence of high-energy x-ray or  $\gamma$ -ray on oxyanion crystals results to irreversible consequences: they decay with allocation of gaseous and firm products. Mechanisms of thus processes appear for series of salts rather similar [12]. However, radiating stability even within series differs rather essentially. It is known, that decomposition of a crystal begins with destruction its complex anion, and it assumes break of one or several chemical bonds. Therefore on their durability it is possible to judge predisposition of a crystal matrix to such processes. In this connection, is of interest to consider on sublattice method laws of formation of chemical bond in a series of sulfates. In part, these questions were considered by us earlier in [13, 14].

Figure 2 represents the distribution of the difference density  $\Delta\rho(\mathbf{r})$  for Li<sub>2</sub>SO<sub>4</sub>, which characterizes the charge transfer between the sublattices. Values  $\Delta\rho(\mathbf{r})$ are specified in terms of  $e/Å^3$  (e – elementary charge). On inserts distribution of the difference density along the selected lines is resulted. Color specifies areas maximal of the difference density.

Distribution of the difference density specifies that the charge follows from intratomic areas of atoms and accumulates in external areas. For atoms of oxygen they have the dissymmetric form *p*-orbital  $\sigma$ - and  $\pi$ type. The negative area falls at positions of atoms of sulfur (S) that testifies theis positive effective charge. There are maxim  $\Delta \rho(\mathbf{r})$  on lines of bonds S-O. Their sizes for nonequivalent atoms of oxygen (1-4) appear various: they are maximal for bonds S-O1 and S-O2 and less for S-O4. Such distribution  $\Delta \rho(\mathbf{r})$  testifies about covalent character of chemical bond between oxygen and sulfur. The charge follows along line of bond S-O3 and consequently she will be least strong of all others. Thus, various character of an overflow of a charge in atoms of oxygen testifies that they are in a different charging state and have different force of chemical bonding in anion. At external influences break of bonding will required different energy, as causes radiating instability of sulfate of lithium.



Fig. 2. Distribution of the difference density in various planes  $Li_2SO_4$ 

From Fig. 2 follows, that the electronic charge follows from a vicinity of a nucleus of lithium so the effective charge of atom can be counted positive. It is observed small filling of charge on the middle of lines Li-O, except for case Li-O1 where it is great near to a nucleus of oxygen. It testifies to presence of weak bonding Li-O, sufficient for formation of a tetrahedron. As well as for chemical bond S-O interaction Li-O appears various for nonequivalent atoms of oxygen. The strongest is observed for Li2-O2 and it provides coupling anionic groups among themselves. Break of this bond will result in the most effective decomposition of a crystal. In other image business in  $K_2SO_4$  will be. As shown in [15], filling of charge in bonding area differs already for pairs atoms of oxygen O1, O2 and O3 (4). Therefore processes of decomposition in sulfates of lithium and potassium will differ both on intensity, and on character of formed products. Evidently it shows Fig. 3 where distribution of difference density in KLiSO<sub>4</sub> is resulted. Force of chemical bonding S-O2 (3,4) is much less, than for S-O1. Therefore in this connection formation  $O_3^-$ , and also Li<sub>2</sub>SO<sub>3</sub> is possible. In this sense research of products of radiating decomposition of double sulfates represents the certain interest.



Fig. 3. Distribution of the difference density in various planes  $KLiSO_4$ 

Figure 4 represents the distribution of the difference density in anionic plane of RbLiSO<sub>4</sub>. As against sulfate of lithium in bonding area S-O here it is necessary the greater difference charge, therefore force of chemical bonding of atoms of anion in this crystal is stronger.

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Fig. 4. Distribution of the difference density in various planes RbLiSO<sub>4</sub>

The charge accumulates in antibonding area S-O. However crystal structure of RbLiSO<sub>4</sub> is those that this area is simultaneously bonding for Li-O. Therefore and on line Li-O here too it is necessary the greater difference charge. Especially it concerns to area Li-O1. Here, as well as in KLiSO<sub>4</sub>, the greatest is observed filling of charge. As a whole, distribution of the difference density in these compounds has similar character. Thus it is necessary to assume, that radiating stability of double sulfates will be the greater, rather than unary.

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