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Abstract

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STUDY OF E.P.R. SPECTRA OF RADIOACTIVE AND IRRADIATED SAMPLES OF CALCIUM, STRONTIUM, AND BARIUM SULFATES

At the present time there is a fairly considerable amount of experimental material on the influence of radioactive radiation of certain solids, as well as of their external irradiation, on various physicochemical properties of these substances ([1–3]), etc. However, these studies do not reveal those defects of the crystal lattice which determine the changes in properties caused by radiation.

We have applied the method of electron paramagnetic resonance (e.p.r.) to study transformations occurring in the crystal lattice of alkaline-earth element sulfates under the influence of the β-radiation of S^{35}, introduced into the indicated preparations. For comparison, nonradioactive samples of the same salts were irradiated on a γ-installation Co^{60}.

Although primary and more complex radiation disturbances in crystals have long been studied in detail, the information obtained does not shed light on such objects as sulfates of elements of the second group, since most of the published work is devoted to alkali halides ([4–6]).

Radioactive preparations

Nonradioactive sulfates of alkaline-earth elements do not possess paramagnetic properties. Polycrystalline powders of radioactive sulfates of Ca, Sr, and Ba were prepared according to a previously described procedure ([7]). The isotope S^{35} introduced into them is a pure β-emitter with $E(\beta)_{\max} = 0.167$ MeV and a half-life $T = 87.1$ days. Weighed portions of the listed substances were placed in ampoules made of "Luch" glass. First, the e.p.r. signal was recorded at room temperature without preliminary evacuation or heating of the samples. The ampoules were then evacuated at a temperature of 300° to a residual pressure of 10^{-4} mm Hg and sealed. After a control recording of the spectrum (the signal was barely noticeable), the samples were placed in liquid nitrogen for definite intervals of time. This made it possible to follow the accumulation of paramagnetic centers. The integral doses received by the radioactive sulfates of Ca, Sr, and Ba are given in Table 1. The number of paramagnetic centers

Fig. 1

Figure 1: Fig. 1

was determined with the aid of a nomogram by comparison with a standard sample of diphenylpicrylhydrazyl (DPPH). Field calibration was carried out using a benzene solution of DPPH. The spectra were studied on an RE-1301 radiospectrometer.

Fig. 1. E.p.r. spectra of heated radioactive samples of sulfates (50 mCu/g), recorded at −197° after two days' holding in liquid nitrogen: *a* −$CaSO_4$, *b* −$SrSO_4$, *c* −$BaSO_4$. A −ion-radical SO_4^{-*}; B −cation that has captured one electron.

A study of the e.p.r. spectra of radioactive sulfates of Ca, Sr, and Ba, recorded at room temperature, showed that the total concentration of the paramagnetic centers formed is 10^{16}—10^{18} 1/g (Table 1).

Table 1

Number of paramagnetic centers in radioactive samples of Ca, Sr, and Ba sulfates

Substance	Initial radioactivity, mCu/g	Time of aging of the initial sample, t, days	Radioactivity at the moment of measurement, mCu/g	Sample weight, g	M_0—mean ionization power, eV/g · s	P—integral dose*, eV/g	Concentration of paramagnetic centers, g^{-1}	Yield G, particles/100 eV
*$CaSO_4 \cdot 2H_2O$	50.0	123	18.0	4.6	$1 \cdot 10^{13}$	$6.7 \cdot 10^{19}$	$1.3 \cdot 10^{17}$	0.2
*$SrSO_4$	0.8	55	0.5	0.5	$5 \cdot 10^{11}$	$2 \cdot 10^{18}$	$1.5 \cdot 10^{17}$	7.5
*$SrSO_4$	5.0	218	0.9	0.8	$2 \cdot 10^{12}$	$2 \cdot 10^{19}$	$2.9 \cdot 10^{18}$	–
*$SrSO_4$	50.0	49	34.0	1.0	$2 \cdot 10^{13}$	$7 \cdot 10^{19}$	$2.9 \cdot 10^{18}$	–
*$BaSO_4$	50.0	130	18.0	0.1	$1 \cdot 10^{13}$	$7 \cdot 10^{19}$	$3.5 \cdot 10^{17}$	0.5

* $P = M_0 \cdot 1.44\,T\left(1 - e^{-0.693\,t/T}\right)$ (3), T and t are in seconds.

Heated samples of Ca, Sr, and Ba sulfates, after two days of holding at the temperature of liquid nitrogen, gave asymmetric signals (Fig. 1). The spectrum of

Fig. 2. E.p.r. spectra of γ-irradiated $CaSO_4 \cdot 2H_2O$. Second spectrum: $-197°C$, recorded after holding the sample in liquid nitrogen for 1 day after irradiation

Figure 2: Fig. 2. E.p.r. spectra of γ-irradiated $CaSO_4 \cdot 2H_2O$. Second spectrum: $-197°C$, recorded after holding the sample in liquid nitrogen for 1 day after irradiation

calcium sulfate changed in comparison with the unheated sample: its similarity to the signals of Sr and Ba sulfates increased. This is apparently explained by the removal of water of crystallization from the sample. The form of the e.p.r. signal from the $^*SrSO_4$ preparation with an initial radioactivity of 50 mCu/g returned to its original form; however, the concentration of paramagnetic centers was two orders of magnitude lower than the equilibrium value. It may be assumed that in the spectrum of strontium sulfate (Fig. 1b), which consists of two signals, singlet A with a g-factor of ~ 2.004 belongs to the free ion-radical SO_4^-. Then four symmetric peaks with a total extent of 125 Oe may represent the hyperfine interaction of the unpaired electron with S^{33} atoms ($I = 3/2$). A similar splitting on S^{33} atoms was observed in $K_2CH_2(SO_3)_2$ irradiated with γ-quanta (9). In this case SO_3^- ion-radicals are formed. The unpaired electron of paramagnetic center A is localized mainly on the oxygen of the sulfate ion, as also in the case of the SO_2^- ion-radical in a study devoted to the radiolysis of sodium thiosulfate (10). Centers giving signal B with g-factor ~ 2.01 possess axial symmetry of paramagnetic absorption. Possibly they are associated with the cation that has captured one electron. Strontium sulfate with an initial radioactivity of 10 mCu/g, kept at room temperature for 3 years, gave a signal with g-factor ~ 2.004. During this time S^{35} had practically completely decayed into Cl^{35}, present in the form of Cl^{+7} or Cl^- ions, which do not give an e.p.r. signal. The presence of the signal indicates the stability of the paramagnetic center.

Fig. 2. E.p.r. spectra of γ-irradiated $CaSO_4 \cdot 2H_2O$. Second spectrum: $-197°C$, recorded after holding the sample in liquid nitrogen for 1 day after irradiation.

Irradiated Preparations

Powders of nonradioactive Ca, Sr, and Ba sulfates were prepared by the same procedure as the radioactive samples. Ampoules with weighed portions of these substances

were pumped down to a residual pressure of 10^{-4} mm Hg at room temperature. Radiation treatment of the sulfates was carried out at liquid-nitrogen temperature in a Co^{60} gamma unit of the Institute of Electrochemistry, Academy of Sciences of the USSR (40,000 g-eq. Ra), for 1 hour. The EPR spectra were also recorded at $-197°$ immediately after irradiation. The kinetics of the decay of the paramagnetic centers were then measured. The samples were heated until

Fig. 3. EPR spectra of γ-irradiated $SrSO_4$

Figure 3: Fig. 3. EPR spectra of γ-irradiated $SrSO_4$

the EPR signal disappeared completely. The absorbed dose was determined with a ferrous-sulfate dosimeter.

Fig. 3. EPR spectra of γ-irradiated $SrSO_4$

Investigation of the EPR spectra showed that immediately after irradiation the total concentration of paramagnetic centers reaches values on the order of 10^{17} g^{-1} for $CaSO_4 \cdot 2H_2O$ and 10^{18} g^{-1} for $SrSO_4$ and $BaSO_4$ (Table 2).

The observed spectra are very asymmetric and poorly resolved. As the samples were thawed, the appearance of the spectra changed; recombination of paramagnetic centers occurred (Figs. 2-4). On this basis, it may be concluded that the EPR spectrum of the sulfates studied consists of several signals from paramagnetic centers differing in nature. The spectroscopic splitting factors of the observed signals are greater than the g-factor of a free electron.

For calcium sulfate (Fig. 2), four to five mutually overlapping signals can be distinguished. During thawing, the intensity of signal a decreases rapidly, and already at -100° it disappears completely. At -50°, signal v becomes noticeable and persists up to $+40^\circ$. Doublet c disappears at $+150^\circ$. Singlet d, with a g-factor close to the g-factor of a free electron, decays at room temperature. It may be assumed that the singlet d is due to an electron captured by some crystal defect or vacancy. Judging from the fact that doublet c disappears after removal of the water of crystallization, it may be assigned to a hole localized on oxygen of the sulfate ion, connected with the hydroxyl of water by a hydrogen bond ([12]). Singlet a is as yet difficult to interpret.

The spectra of $SrSO_4$ and $BaSO_4$ (Figs. 3, 4) have much in common. In the spectrum of strontium sulfate (Fig. 3) at room temperature, four signals can be distinguished, one of which, with g-factor ~ 2.004, persists up to a temperature of 350° (A). Such thermal stability indicates that this cannot be an electron captured by a vacancy or defect. Most likely

Table 2

Number of paramagnetic centers in samples of Ca, Sr, and Ba sulfates treated with γ-rays

Fig. 4. EPR spectra of γ-irradiated $BaSO_4$

Figure 4: Fig. 4. EPR spectra of γ-irradiated $BaSO_4$

Substance	Cation radius, Å	Free volume of the unit cell of the crystal per ion SO_4^{2-}, Å^3	Energy of the crystal lattice, kcal/mol	Absorbed dose (γ-quanta), 10^{20} eV/g	Concentration of paramagnetic centers, 10^{18} g^{-1}
$CaSO_4 \cdot 2H_2O$	1.06	—	623	2.0	0.96
$SrSO_4$	1.27	16.9	579	1.9	1.36
$BaSO_4$	1.43	22.1	549	1.8	1.77

this is the stable ion-radical SO_4^-, firmly seated at a site of the crystal lattice and having lost one electron in the process of ionization.

In ionic crystals the bonds between the elements of the lattice are strong, the volume of free interstices is small (Table 2), and this leads to a low probability of displacement of anions from their normal positions into interstices. In the case of a complex oxygen-containing anion, the free radical formed may exist for a long time without having the ability to attract the electron knocked out during ionization. The further fate of the free radical formed depends on its chemical characteristics, the type of structure, and the rigidity of the matrix. In the case of the ion-radical SO_4^- it is difficult to assume its decomposition with detachment of oxygen or, still more, the interaction of similar radicals with one another. Most likely, they will exist until some electron accidentally recombines with them.

The signal B with g-factor ~ 2.01 is retained up to a temperature of $+150^\circ$. It is possible that it corresponds, as in the case of radioactive samples, to a cation that has captured one electron.

Fig. 4. EPR spectra of γ-irradiated $BaSO_4$

A similar picture is also observed in the spectra of barium sulfate (Fig. 4), with the only difference that the residual concentration of paramagnetic centers with g-factor ~ 2.004 after heating the samples to $+200^\circ$ is somewhat lower than in $SrSO_4$. Evidently, in this case as well they correspond to SO_4^- ion-radicals, which are retained up to a temperature of 350°.

Comparison of the EPR spectra of radioactive and irradiated samples of calcium, strontium, and barium sulfates showed that the nature of certain paramagnetic centers (A, B) is the same in both cases. The spectra of γ-irradiated samples of

$CaSO_4 \cdot 2H_2O$, $SrSO_4$, and $BaSO_4$, in contrast to the radioactive preparations, consist of a larger number of paramagnetic centers differing in their nature, since the absorbed dose in the first case is two orders of magnitude greater than in the second. Comparison of the yields of paramagnetic centers of the three substances showed that $CaSO_4 \cdot 2H_2O$ has the greatest radiation resistance, and $SrSO_4$ the least. A corresponding regularity is observed for the heats of formation of these compounds ($CaSO_4 \cdot 2H_2O$ 483.06 kcal/mole, $BaSO_4$ 350.2 kcal/mole, and $SrSO_4$ 345.3 kcal/mole) (13).

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Note: Figure translations are in progress. See original paper for figures.