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Stable Paramagnetic Species in Natural Strontium Sulfate Crystals

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Natural strontium sulfate crystals were found to show complex ESR spectra without any special irradiation. The spectra were classified into three groups, A, B, and C; the thermal and photochemical behavior of each group was distinguished from that of the others. It was proposed that Group B originates from SO_3^- radicals, and Groups A and C were tentatively interpreted as due to lattice defects (F-center and V-center).

γ-Irradiated single crystals of potassium sulfate have been reported to give rise to stable paramagnetic species at room temperature,[1,2] and their physical and chemical nature was the object of interest with regard to the mechanism of electron transfer in the crystal.[3]

Recently we have found that some *natural* strontium sulfate crystals contain stable paramagnetic species even without any special irradiation. In the present paper we shall report the ESR characteristics of these paramagnetic species, with special attention paid to their assignments as well as to their thermal and photochemical behavior.

Experimental

Material. The strontium sulfate samples, produced in the USSR were subjected to ESR investigations, the numbering and the localities of production are shown below.

No	Localities	No	Localities
2	Fergana	5	Central Russia
3	North Caucasus	6	South Caucasus
4	North Fergana	7	Turkmenistan

These $SrSO_4$ samples were seemingly crystalline and transparent to a certain extent, and all gave rise to complex ESR spectra at room temperature. Only the No. 4 sample was subjected to detailed investigations because of its less irregular form. The X-Ray analysis of the No. 4 sample has, in fact, shown that it is a twin crystal. An emmission spectro-chemical analysis of the sample showed that it contains some alkali and alkaline earth metals as impurities: (Mg(+), Ca(+++), Ba(++), Na(−), K(+), and Rb(−)), where (−) indicates the absence of metals and (+), (++) and (+++) the relative abundance.

Apparatus and Procedure. The ESR measurements were made at room temperature with a JEOL–P-10-type spectrometer, using a microwave frequency of the X-band with 100kHz field modulation. The ESR spectra were taken at every 5° rotation around the three principal axes of an orthogonate (X,Y,Z) of the crystal. The *g*-values were calculated by using a standard signal of manganese dispersed in MgO powder, which had previously been calibrated with a DPPH signal.

The effects of annealing and photoirradiation on the paramagnetic species were monitored by means of an ESR spectrum observable at the fixed position of the sample crystal. The sample was heated in an electric furnace for 30 minutes at every 50°C from room temperature up to 350°C. Photoirradiations of the sample were carried out by means of a low-pressure mercury lamp (Ushio Denki Co., 200 W). γ-Irradiations (5×10^5 rad/hr from ^{60}Co) were also performed, and the results were compared qualitatively with the results of the photoirradiations.

The parallel surfaces of the sample used made it possible to measure the UV absorption spectra ranging from 210 to 700 mμ, and also the thermal effects on the UV spectra.

Results and Discussion

A typical ESR spectrum for the *virgin* $SrSO_4$ sample (No. 4) fixed at a certain position in the microwave cavity is shown in Fig. 1. The spectrum appeared to be characterized by a number of resonance lines,

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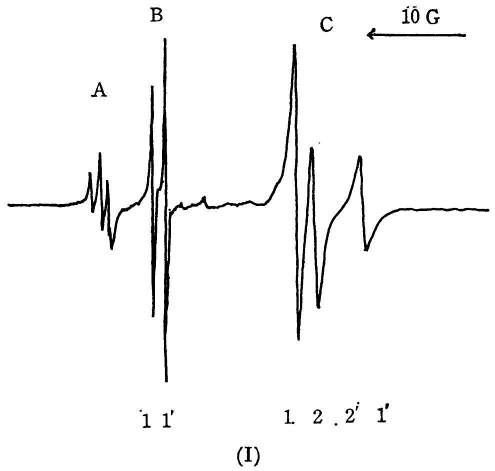


Fig. 1. A typical ESR spectrum of the natural $SrSO_4$ crystal.

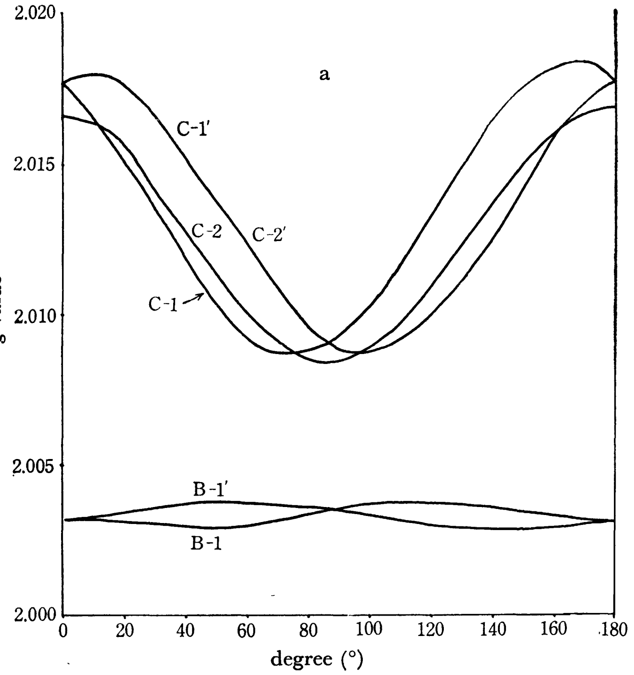
probably due to different paramagnetic species. However, the lines may be classified for convenience into three groups, A, B, and C, from the higher to the lower magnetic field respectively as is illustrated in Fig. 1.

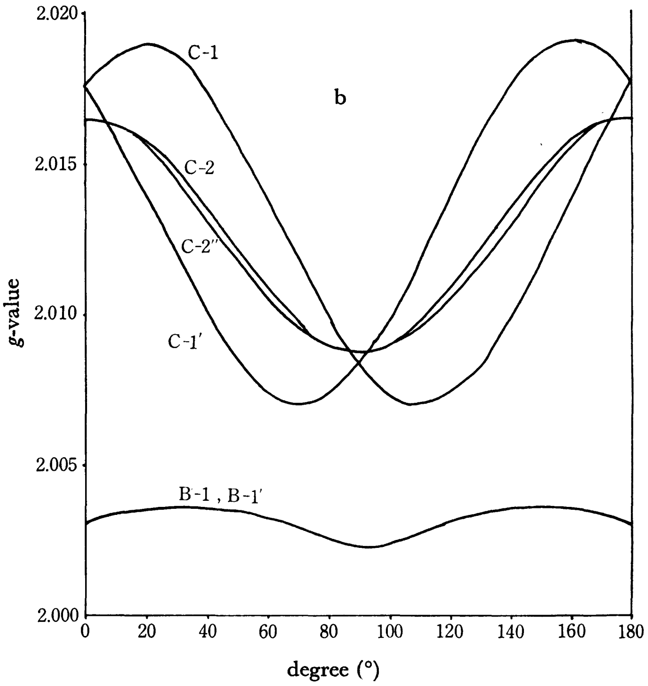
Group A was usually a minor one in the spectrum. Group B consisted of two resonance lines of a similar shape (designated as B-1 and B-1' respectively), and Group C, probably of four lines (C-1 and C-1', C-2 and C-2'). Figures 2a, b, and c show, respectively, the changes in the *g*-factors of these spectral lines when the sample crystal was rotated around its three axes (*X*, *Y*, *Z*). The principal *g*-values, calculated from the *g*-factor dependence, are shown in Table 1.

As is shown in Table 1, the principal *g*-values of the *paired* lines, such as B-1 and B-1', C-1 and C-1', and C-2 and C-2', nearly coincided with each other, suggesting that the pair of signals is due to a common paramagnetic species and that the signals differ in their direction in the crystal in harmony with their twin characters, as revealed by X-ray analysis. The angular variation of the *g*-factor for Group A, consisting of several resonance lines, appeared to be rather complicated and did not permit us to derive any general trend. However, their *g*-values were all less than that

TABLE 1

Signal	g_1	g_2	g_3
A		1.9965—2.0018	
B-1	2.0041	2.0033	2.0021
B-1'	2.0041	2.0033	2.0021
C-1	2.0194	2.0094	2.0064
C-1'	2.0192	2.0091	2.0069
C-2	2.0167	2.0090	2.0082
C-2'	2.0166	2.0090	2.0082





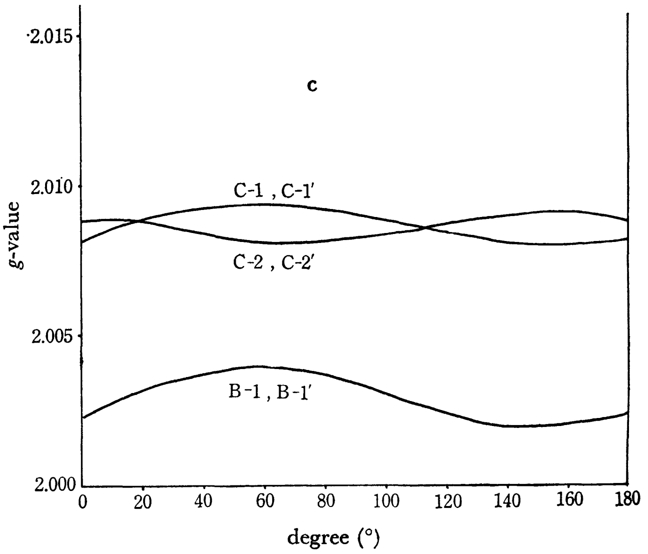


Fig. 2. a. b. c.
Angular dependence of *g*-factors of B and C signals around *X*, *Y*, and *Z* axes.

of a free spin (1.9965—2.0018).

We shall discuss the origin of each Group. First, the fact that the *g*-values of Group A were slightly less than that of a free spin suggests that Group A originates from electrons trapped at anion vacancies of F-centers rather than from hole defects in the $SrSO_4$ crystal; the *g*-values of F-centers in alkali halide crystals have been reported by many workers to be the results of negative *g*-shifts.[4] However, since *g*-values alone are not very informative, it is hard at present to identify the species corresponding to Group A without ambiguity.

The principal *g*-values of B-1 and B-1′ were isotropic and were close to that of a free spin (2.0041, 2.0033, 2.0021). It has already been reported by one of the present authors[1] that the γ-irradiated single crystals of K_2SO_4 give two kinds of ESR spectra; one is highly anisotropic, while the other is characterized by an almost isotropic *g*-tensor, with the principal *g*-values of 2.0033, 2.0033, and 2.0023. Accordingly, the two spectra were assigned to SO_4^- and SO_3^- respectively. Thus, on the basis of that report, the paramagnetic species corresponding to Group B are attributed to SO_3^- radicals rather than SO_4^- radicals.

The formation of O_3^- radicals has also been proposed for γ-irradiated single crystals of K_2SO_4.[5] The reported *g*-values (2.139, 2.0127, and 2.0102) for O_3^- radicals do not seem, however, to correspond to those of any Group. Also, the principal *g*-values for the SO_2^- produced in some ionic crystals have been reported to be 2.012, 2.0082, and 2.0037.[6] The *g*-values for our paramagnetic species are, again, distinguished from those of SO_2^-. Consequently, the origin of Group C seems to be associated with some lattice defects in the crystal rather than with sulfur- or oxygen-containing radicals.

The effects of thermal annealing on our paramagnetic species were investigated in order to support our assignments (Fig. 3). Group B was most stable on heating and did not decay until 350°C. Such a thermal stability has also been reported with SO_3^- in a γ-irradiated K_2SO_4 crystal;[3] this would support our assignment for the B signal.

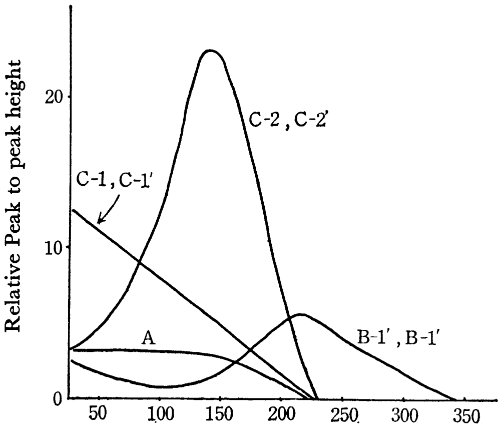


Fig. 3. Effects of thermal annealing on A, B, C signals.

Both the A and C groups were less stable on annealing; they nearly disappeared around the temperature of 200°C. However, it was rather surprising to note that the intensity of C-2 and C-2′ *increased* to a remarkable extent below 150°C, while the C-1 and C-1′ decreased monotonously within the temperature range studied. This phenomenon may suggest that the C-1 species can be distinguished from the C-2 species, even if the two species collapse at almost the same temperature. An inspection of the two annealing curves might lead one to presume that the C-1 paramagnetic center collapses upon heating by reaction with some other defects in the crystal, thus giving rise to another paramagnetic C-2 center.

As has already been mentioned, all the ESR signals (Fig. 1) disappeared completely when the crystal was heated to 350°C. However, some signals were restored upon UV irradiation. For example, when a highly-annealed sample, hence one showing no ESR signal, was irradiated with UV light at room temperature for less than 10 min, only the Group C signals were reproduced, while γ-irradiation for five hours showed a full recovery of all the signals, together with some additional signals. Thus, the C signal is considered to be quite sensitive to UV light as well as to heating as compared with the B singal.

UV absorption measurements of the sample crystal have shown that there exist two broad but distinct absorption bands around 250 and 550 mμ. In particular, the absorption band at 250 mμ was found to be unstable to heating; it disappeared completely at 200°C, quite in parallel with the ESR intensity of Group C upon annealing. All the results can be explained naturally if Group C is assumed to be associated with some labile crystal defects.

In recent years many types of color centers have been found, in particular in alkali halide crystals, and explained in terms of a variety of crystal defects. For example, the V- and F-centers in a potassium chloride crystal have been assumed to give two optical absorption bands[7] near the two wavelengths, 250 and 550 mμ, mentioned above with respect to our sample. Thus, the optical absorption at 250 mμ for the sample is likely to be associated with a color center such as a V-center, although further investigations will be required to confirm the assignments.

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