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ESR Studies of Radiation-Damage Centers in Barium Sulfide*

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Single crystals of BaS have been grown and irradiated with neutrons, producing an intense *F*-center spectrum with a spectroscopic splitting factor, $g=1.9637\pm0.0005$. The isotropic part of the hyperfine interaction A is 41.0 ± 0.2 and 36.4 ± 0.2 G for the nearest-neighbor ^{137}Ba and ^{135}Ba nuclei, respectively. The dipolar hyperfine interaction constants B are found to be 4.0 ± 0.1 and 3.8 ± 0.1 G, respectively, for the same nuclei. *F* centers were also observed in samples which had been crushed or γ-irradiated following deformation. Other damage centers were observed with less intensity than the *F* center and are briefly discussed.

INTRODUCTION

STUDIES of radiation-damage centers in the alkaline-earth oxides have been made primarily on magnesium oxide since single crystals have been available for many years. Wertz *et al.*[1] first observed the *F* center produced in MgO by neutron irradiation. Their electron-spin-resonance (ESR) data suggested that the *F* center was one electron trapped in an oxygen vacancy. This was later confirmed by Unruh and Culvahouse,[2] using electron-nuclear double-resonance techniques. In recent years as the oxides of calcium, strontium, and barium became available as single crystals, *F* centers and other electron excess centers have been observed by ESR techniques in these crystals also.[3–5]

Electron excess centers such as the *F* center are produced in the oxides as a result of inelastic collisions between the incident radiation and the lattice ions. Since no evidence has been presented showing interstitial metal ions, it is presumed they do not remain in their displaced positions. Therefore, most of the centers for which models have been proposed from ESR data do not involve a positive-ion vacancy which is caused by the neutron irradiation itself. While most of the irradiations have been carried out in reactors using fast neutrons and sample temperatures up to several hundred degrees centigrade, energetic electrons can also be used to produce *F* centers, and a greater degree of control over the sample temperature is usually possible with this method.

Only a few irradiation-produced ESR centers have been investigated in powders of the alkaline-earth sulfides.[6] Since these sulfides have the same crystalline structure as the alkaline-earth oxides, studies of similar centers give information about the relative extent of the interactions of the radiation-damage centers with neighboring ions in the host lattice, and should also be able to clarify some of the processes by which the radiation damage occurs in these crystals.

This investigation is concerned with some of the ESR properties of radiation-damage centers in single crystals of barium sulfide. The most intense ESR spectrum produced by neutron irradiation of these crystals can be identified as the *F* center by means of its hyperfine structure and symmetry properties. The other centers which were observed will be briefly described.

EXPERIMENTAL PROCEDURE

The single crystals were grown in a carbon arc furnace operating in an argon-gas atmosphere to prevent the spontaneous conversion of the BaS starting powder to $BaSO_4$. Most of the melt in which single crystals were formed was very dark, and a close investigation of thin plates showed that the dark portions were homogeneously colored dark gray. Extensive chemical analyses have been made to determine the source of this coloration, which at first was thought to be due to the inclusion into the melt of minute carbon particles from the electrodes. Spectroscopic, flame photometry, and x-ray microprobe techniques were used for the analyses. Although most of the melt was made up of dark crystals, small portions were found where clear crystals $1\times2\times2$ mm in size could be obtained. Other crystals were also found of this size which were yellow in color. X-ray powder patterns of both the dark and light crystals showed only those lines characteristic of barium monosulfide, and no significant deviation from the accepted lattice parameter was observed.

Spectroscopic analyses of both the clear and the dark crystals showed that the ions of the iron transition group were not present within the concentration sensi-

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[2] W. P. Unruh and J. W. Culvahouse, Phys. Rev. **154**, 861 (1967).

[3] D. H. Tanimoto, W. M. Ziniker, and J. O. Kemp, Phys. Rev. Letters **14**, 645 (1965).

[4] J. W. Culvahouse, L. V. Holroyd, and J. L. Kolopus, Phys. Rev. **140**, A1181 (1965).

[5] K. E. Mann (private communication).

[6] J. E. Wertz, J. W. Orton, and P. Auzins, Discussions Faraday Soc. **31**, 140 (1961).

tivity of the analysis ($\sim$5 ppm by weight), and did not vary significantly between the two types of crystals. A more precise analysis for the alkali and alkaline-earth ions was also made on these crystals; the results are given in Table I. The test for carbon was made by wet-chemistry techniques, while the test for free barium involved a reaction with HCl and a subsequent analysis of the products of the reaction. An attempt to analyze for free sulfur in the crystals, which was known to be present in the starting powder, was unsuccessful. Supporting the results of the chemical analyses concerning the low concentration of impurity ions were ESR measurements taken at temperatures down to 1.5°K. No resonance lines were seen in the clear as-grown crystals —a feature which is in marked contrast to the alkaline-earth oxides where the iron transition group impurity ions are always detected in concentrations of a few ppm or more.

An x-band superheterodyne spectrometer capable of operating at 1.5°K, a K_a-band spectrometer (35 GHz) operating at room temperature, and an x-band homodyne spectrometer using 100-kHz modulation and operating from 500 to 90°K were used for these measurements. Most of the data were taken with the 100-kHz spectrometer at a temperature of about 100°K. An NMR proton probe in conjunction with a Hewlett-Packard model 524C frequency counter was used to measure the magnetic field positions of the resonance lines.

The crystals were γ-irradiated using ^{60}Co and ^{137}Cs γ rays with doses up to 2×10^7 R at room temperature, and 1.5×10^6 R at 77°K. Neither of these treatments produced any detectable ESR signals in the crystals. Electron bombardment by 1.7-MeV electrons from a Van de Graaff at 77°K without a subsequent warm-up to room temperature, produced two resonance signals—one a broad isotropic ($\Delta H\sim20$ G) line near $g=2$, which will be discussed later, and a second sharper line about 4 G wide at a slightly higher magnetic field. This latter line is the central isotropic line of the F center, but its intensity was low and no hyperfine structure could be seen. Subsequent irradiations were made using fast neutrons with total irradiation doses of 10^{17}, 3×10^{17}, and 4×10^{18} neutron/cm^2 in the Oak Ridge Research Reactor (ORR) at an ambient temperature of about 330°K, and also at a temperature of 150°K with a total dose of 8.4×10^{16} neutron/cm^2 in the Bulk Shielding Reactor at the Oak Ridge National Laboratory. After these irradiations, the crystals had a dark blue-green color. They showed similar damage centers although in different concentrations to those observed in the electron-irradiated crystals. The most intense center in the higher-dose samples could be identified as the F center, and its properties will be described first and in more detail than those of the other centers.

TABLE I. Impurity analysis of BaS.

Element	Clear crystals (μg/g)	Dark crystals (μg/g)	Technique
Li	88	43	Flame photometry
Na	31	64	Flame photometry
K	70	29	Flame photometry
Rb	<10	<10	Flame photometry
Cs	<20	< 20	Flame photometry
Mg	<100	<100	Flame photometry
Ca	68	86	Flame photometry
Free Ba	750	300	HCl reaction
Cr, Mn, Fe	<5	<5	Spectroscopic
Ni, Cu	<3	<3	Spectroscopic
	Percent	Percent	
Sr	1.37	1.40	Flame photometry
Carbon	0.007	0.016	Wet chemistry

RESULTS

F Center

The observed ESR spectrum of the F center in BaS is similar to the F-center spectra seen in the alkaline-earth oxides.[1,4] In BaS there are two isotopes of barium, both with nuclear spin $I=\frac{3}{2}$, ^{135}Ba—6.6% abundant, and ^{137}Ba—11.3% abundant. The magnetic moments of these nuclei differ by about 10%. The probability that an F center which is formed at a sulfur-ion vacancy will have 0, 1, 2,$\cdots$, nearest neighbors with a nuclear spin is found to be:

nn with $I=\frac{3}{2}$	0	1	2	3	4, 5, or 6
Fraction of F centers	0.306	0.401	0.218	0.063	0.012

Therefore, more centers are situated in sites with one magnetic nucleus, which may be either ^{135}Ba or ^{137}Ba, as a nearest neighbor. The individual lines arising from this spectrum are much less intense than the single isotropic centerline because the total intensity is, in general, divided among many lines. For the same reason, the multiplicity of lines in the spectra due to centers with three or more magnetic neighbors is not seen, since the individual lines of these spectra are weak. It is assumed that the production of centers is random with respect to the spin of the nuclei, and that interactions with nuclei of S^{33} in the next-nearest-neighbor positions can be neglected because of the low natural abundance (0.74%) of this isotope.

The nn positions lie along $\langle100\rangle$ crystalline directions with respect to the F center and the ESR spectrum with the magnetic field along a $\langle111\rangle$ axis is most easily understood because all of the axes of the centers make equal angles with the magnetic field. Figure 1 shows the spectrum for this orientation with the positions of the hyperfine lines arising from each of the two magnetic barium nuclei indicated below. Less intense lines between these hyperfine lines can be seen which are due to F centers with two nearest neighbors with spin $\frac{3}{2}$.

The ratio of the magnetic moments of the two magnetic barium nuclei is $^{135}\text{Ba}/^{137}\text{Ba}=0.894$. The same ratio as calculated from the hyperfine splittings of the sets of lines due to the two types of nuclei is 0.896. The intensity of the outer pair of lines also agrees well with the relative isotopic abundance of the ^{135}Ba and ^{137}Ba nuclei, as well as with their total intensity compared to that of the central isotropic line. The extra line marked with an arrow is due to an axial center whose principal axis lies along a [100] direction. It will be discussed later.

Figure 2 shows the spectra which arise with the magnetic field along a [100] and a [110] axis, respectively. For the first case, two of the ⟨100⟩-type axes make angles of $\theta = 0°$ with respect to the magnetic field, and four make angles of $\theta = 90°$. The corresponding case for the [110] spectrum is that two axes make angles of $\theta = 90°$, while four make angles of $\theta = 45°$, where θ is always measured as the angle between the principal hyperfine axis (a ⟨100⟩ direction) and the magnetic field. The intensities of the hyperfine lines reflect this angular degeneracy and are indicated below the spectra in Fig. 2. The weaker set of lines due to the interactions with two spin neighbors cannot, in general, be resolved because of the multiplicity of lines for these directions.

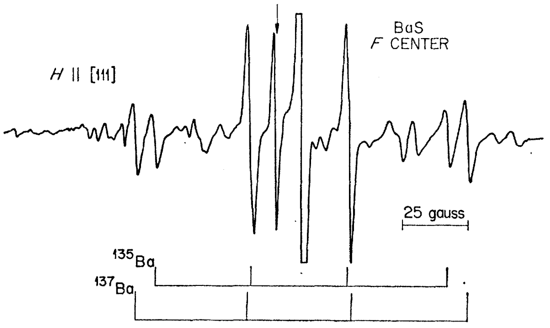

FIG. 1. The ESR spectrum of F centers in BaS with the magnetic field H in the [111] direction is shown. The positions of the hyperfine lines resulting from the two barium nuclei with $I = \frac{3}{2}$ are indicated below. The line indicated by an arrow is due to an axial center with its principal axis along a ⟨100⟩ direction.

No difference between the F-center spectrum observed at 35 and 9 GHz could be detected, and a spin Hamiltonian which adequately describes the observed spectrum can be written

$$\mathrm{H} = g\beta \mathbf{H}\cdot\mathbf{S} + \mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}.$$

Other terms, such as the nuclear quadrupole term, were not necessary to fit the line positions in gauss to the order of $1/H$ in the second-order perturbation treatment of the above Hamiltonian. The line positions for axial hyperfine splitting are thus given by the expression[7]

$$H = H_0 - Km_I - [A_\perp^2(A_z^2 + K^2)/4H_0K^2] \times [I(I+1) - m_I^2],$$

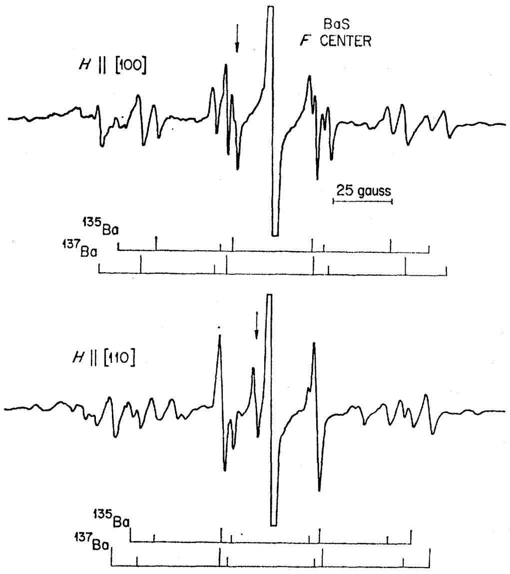

FIG. 2. The F-center spectrum with H in the [100] direction (top) and [110] direction (bottom) is shown. The positions of the hyperfine lines are marked with lines proportional to their relative intensities expected on the basis of multiplicity of sites. The arrows indicate the $\theta = 0°$ and $\theta = 45°$ positions, respectively, of the ⟨100⟩ axial center.

where

$$H_0 = \frac{h\nu}{g\beta} \quad \text{and} \quad K^2 = A_z^2 \cos^2\theta + A_\perp^2 \sin^2\theta.$$

The experimental values for the above parameters measured at 9 GHz and 100°K are as follows:

$$g = 1.9637 \pm 0.0005,$$

$$A_z(137) = 49.0 \pm 0.2 \text{ G}, \quad A_\perp(137) = 37.0 \pm 0.2 \text{ G},$$

$$A_z(135) = 44.0 \pm 0.2 \text{ G}, \quad A_\perp(135) = 32.6 \pm 0.2 \text{ G}.$$

An alternative form of the spin Hamiltonian can be written as[4]

$$\mathrm{H} = g\beta\mathbf{H}\cdot\mathbf{S} + A\mathbf{I}\cdot\mathbf{S} - B[\mathbf{I}\cdot\mathbf{S} - 3(\mathbf{I}\cdot\mathbf{e})(\mathbf{S}\cdot\mathbf{e})],$$

where the unit vector $\mathbf{e}$ is directed from the F center to the nn position. The first-order hyperfine interval is then $A' = A + B(3\cos^2\theta - 1)$, where the constants A and B are related to A_z and $A_\perp$ by the expressions

$$A = \tfrac{1}{3}(A_z + 2A_\perp), \quad B = \tfrac{1}{3}(A_z - A_\perp),$$

and have the following values:

$$A(137) = 41.0 \pm 0.2 \text{ G}, \quad B(137) = 4.0 \pm 0.1 \text{ G},$$

$$A(135) = 36.4 \pm 0.2 \text{ G}, \quad B(135) = 3.8 \pm 0.1 \text{ G}.$$

A determination of the concentration of F centers produced by the neutron irradiations in the ORR at about 60°C showed that $n_F = 3.0 \times 10^{16}$ cm^{-3} for a dose of 1.1×10^{17} n/cm^2, and $n_F = 1.2 \times 10^{18}$ cm^{-3} for a dose of 4.3×10^{18} n/cm^2, where the neutron flux is measured for energies ≥ 1 MeV.

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[7] B. Bleaney, Phil. Mag. 42, 441 (1951).

Several single crystals which initially showed no ESR spectra were selected for deformation and/or crushing in order to determine whether F centers could be generated by these means, as is the case for MgO.[6,8] One crystal which was inelastically deformed about 5% showed no signals before or after deformation. However, a ^{60}Co γ irradiation of about 5×10^5 R at room temperature produced an F-center resonance corresponding to a concentration of about 5×10^{15} centers cm^{-3}. When the original crystals were crushed to a powder, the F-center signal, although weak, could be detected without further treatment. A subsequent γ dose of about 10^5 R at room temperature doubled the intensity of the F-center resonance. This latter effect is probably due to the fact that as a result of the crushing process, not all of the anion vacancies created by the dislocations are populated with single electrons. The empty anion vacancies are then populated by electrons excited by the ionizing radiation.

A thermal anneal using isochronal pulses 3 min long at 20°C intervals (starting from room temperature) was carried out on one of the more heavily neutron-irradiated samples. A 10% increase in the number of F centers was observed up to a temperature of 400°K, where rapid decay began. The greatest decay rate was observed at 475°K, and by 570°K no F centers remained. Furthermore, they could not be recovered by a γ irradiation, indicating that the sulfur-ion vacancies had presumably been filled with interstitial sulfur ions and the centers destroyed.

Other Centers

Four other paramagnetic centers which were weaker than the F-center resonance were observed in the neutron-irradiated crystals. Two of these centers had axial symmetry with the principal axis lying along a $\langle 100\rangle$ direction. Both had $g_\perp=1.9638\pm0.0010$, which is the same as the isotropic g value of the F center itself, and these lines could not be resolved from the F-center central line even at K_a band. The axial center which occurred in the low dose sample (1.1×10^{17} n/cm^2) had $g_\parallel=1.9554\pm0.0005$. The analogous center observed in the higher dose sample (4.3×10^{18} n/cm^2) had $g_\parallel=1.9737\pm0.0005$, and in each case only the one axial center was present. The latter center was present in the crystal which was used for the annealing of the F center, and its decay paralleled that of the F center exactly. Based on the evidence of the growth and decay as well as the $g_\perp$ values, it is probable that these axial centers are due to F centers whose symmetry is perturbed by additional defects lying along $\langle 100\rangle$ axes. It is possible that the center in the heavier-irradiated sample could be the F_2 center for which, in MgO, Wertz has proposed the model of an F center associated with a positive-ion vacancy.[6] No other center was observed which might be the analog of the V_1 center in MgO.[9]

Another weak spectrum which could be seen in the higher-neutron-dose samples was composed of four anisotropic lines centered at a g value equal to 2.0082, which overlapped some of the low-field hyperfine lines of the F center. It could not be seen in any of the crystals subjected to the γ irradiations and, therefore, it probably does not arise from the high γ flux which accompanies the neturon irradiations. With the decay of the F center at 475°K, the intensity of this center increased, and it finally decayed near 620°K. Further work is necessary to describe its behavior in detail, and no model can yet be proposed for this center.

The last center which was observed in the electron-irradiated samples had a single isotropic line with a width of about 20 G and a g value of 2.007. Its intensity was weak and varied considerably from crystal to crystal. Since no hyperfine lines could be found which were associated with it, and its intensity was generally low, no model is proposed for this center.

CONCLUSIONS

A possible cause of the dark color of most of the BaS single crystals may be an excess of barium in these crystals. Under the conditions in which the crystals were grown, this is quite possible, and a similar problem with barium sulfide crystals grown in a graphite sleeve furnace has also been attributed to excess barium.[10] The analytical test for free barium present in the metallic form as a precipitate in the crystal, indicated a larger amount in the clear samples than in the dark samples. The optical absorption curves of the 2 types of samples show that the dark crystals have, in general, a considerably higher background absorption, uniform throughout the visible region. A scattering process rather than resonant absorption would produce such a high background. The beginning of the absorption edge in both cases was near 340 nm and no bands at longer wavelengths were observed in either crystal. A strong argument that the excess barium or, equivalently, the sulfur deficiency of these crystals is not due to sulfur-ion vacancies can be made on the basis that no F centers were detected in the dark as-grown crystals before or after the γ irradiations of these crystals. If there were sulfur-ion vacancies, such irradiations would almost certainly produce a detectable number of F centers.

The wet-chemistry analysis shows that the concentration of carbon in the darker crystals is higher. However, within the accuracy of this analysis and at the levels reported, it does not seem reasonable to explain the difference in the nonresonant microwave loss properties, which at 9 GHz were considerably higher in the

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[8] M. J. Klein and W. B. Gager, J. Appl. Phys. **37**, 4112 (1966).

[9] J. E. Wertz, P. Auzins, J. H. E. Griffiths, and J. W. Orton, Discussions Faraday Soc. **28**, 136 (1959). (The V_1 center was labeled H_1 in this work.)

[10] D. Warschauer and M. Lichtensteiger, Aerospace Research Laboratories Report No. ARL 65-99, 1965 (unpublished).

dark samples relative to the clear ones, or the difference in visible color by the factor-of-2 difference in the carbon content of the two types of crystals. Furthermore, in the case of BaTe single crystals grown in a graphite sleeve furnace, where carbon particles were included in the melt and in the resulting single crystals from the carbon crucible, the particles were easily seen under an optical microscope.[11,12] In the present case no particles could be resolved even under a magnification capable of resolving particles a few microns in diameter. Therefore, until a better characterization of the material is made, we conclude that the dark coloration is probably due to excess barium. However, the possibility that the color is produced by other sources, such as included carbon in very small particles or even excess sulfur, cannot be excluded.

The results on the irradiation damage studies of BaS indicate that the primary damage is done by inelastic collisions with energetic electrons or neutrons and not by ionizing radiation. In this respect, the material is similar to MgO and the other alkaline-earth oxides, as distinguished from the alkali halides where ionizing radiation produces F centers and V-type centers. Moreover, in BaS and the oxides, the F center is the principal ESR defect produced by fast neutron irradiation.

In order to relate the experimental data for the F center in BaS to the existing experimental and theoretical work, we compare the isotropic part, A, of the hyperfine interaction in these compounds. A is proportional to $|\Psi_F(R_1)|^2$, where $\Psi_F(R_1)$ is the F-center wave function at the nearest-neighbor barium nucleus, which is located at a distance R_1 from the F center. A comparison between the value of A for BaO and BaS, since one is now dealing with the same nuclei, gives a direct comparison between the values of $|\Psi_F(R_1)|^2$ for these two compounds. Such a comparison using data taken for the F center in single crystals of BaO[5] shows that for the two isotopes the ratio of $A_{\mathrm{BaS}}/A_{\mathrm{BaO}}$ is

$$^{137}\mathrm{Ba}: A_{\mathrm{BaS}}/A_{\mathrm{BaO}}=41.0/76.4=0.537$$

and

$$^{135}\mathrm{Ba}: A_{\mathrm{BaS}}/A_{\mathrm{BaO}}=36.2/69.0=0.535.$$

According to the expression given by Culvahouse *et al.*[4] and corrected by Tench and Nelson,[13] $|\Psi_F(R_1)|^2$ should be proportional to $1/R_1^3$, and for these compounds the proportionality constant should be very nearly equal to unity. However, for BaS and BaO, the ratio of R_1^3 for these two lattices is $R_1^3(\mathrm{BaS})/R_1^3(\mathrm{BaO})=1.551$, so that the product

$$A_{\mathrm{BaS}}R_1^3(\mathrm{BaS})/A_{\mathrm{BaO}}R_1^3(\mathrm{BaO})=0.833.$$

The derivation of the expression is based on the assumption of a point ion lattice model,[14] and the above and similar disagreements which are found for the heavier oxides and now for barium sulfide indicate that the more covalent bonding of these compounds makes this assumption invalid. A more extensive theoretical treatment of these compounds, which takes into account their covalency, will be necessary to quantitatively explain the experimental data. Until such calculations are made, it does not seem useful to pursue the extrapolation of the existing expressions too far.

The crystals used for the ESR studies were too small to be used conveniently for optical absorption studies. When larger crystals are available, an attempt will be made to locate the F-center absorption band. As single crystals of the other alkaline-earth sulfides become available, the ESR properties of radiation-produced defects, particularly the F center, will be measured. This additional data may then be useful to measure the effect of the increased covalency of the bonding in the sulfides on paramagnetic defect centers and impurity ions, and to stimulate the theoretical calculations which are necessary for an understanding of these effects.

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