ESR investigation of molecular ions in SrO⁺

L. E. Halliburton, C. D. Norman,* and K. Saha Physics Department, Oklahoma State University, Stillwater, Oklahoma 74074

L. A. Kappers

Department of Physics and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268 (Received 11 January 1977)

Electron-spin-resonance spectra from two distinct molecular ion centers have been observed in SrO. The dominant center, after electron irradiation at 77 K, is a $\langle 111 \rangle$ -oriented molecular ion replacing an O²⁻ ion in an otherwise normal lattice. At 140 K, this center thermally decays while the concentration of a second center increases significantly. The second center is a similar molecular ion which is stabilized by an unidentified lattice defect located at a nearest-neighbor cation site. Near 160 K, this perturbed molecular ion center is reorienting rapidly about the perturbation thus causing its ESR spectrum to exhibit axial symmetry instead of the orthorhombic symmetry observed at 77 K. The perturbed center thermally decays at 190 K.

I. INTRODUCTION

In recent years, the formation of molecular ions in alkaline-earth oxides as a result of irradiation has become a subject of growing interest. Initially, Rius *et al.*^{1,2} observed an OF^{2-} molecular ion in MgO. This was followed by the observation of an OH^{2-} ion in CaO by McGeehin *et al.*³ Also of interest is the report of an O_2^{-} molecule in CaO by Hall.⁴

With the hope of eventually understanding more completely the behavior of oxide materials during irradiation, we have extended the study of radiation-induced molecular ions to strontium oxide. In the present paper, we describe two paramagnetic defects produced in SrO by ionizing radiation at low temperatures. One of these centers is a (111)oriented molecular ion which is assumed to replace an $O^{2^{-}}$ ion in an otherwise normal lattice. The other center is a similar molecular ion that is strongly perturbed by an unidentified defect located at a nearest-neighbor cation site. Spin-Hamiltonian parameters, thermal-anneal behavior, optical-bleaching characteristics, and motionalaveraging effects are reported for these molecular ion centers in SrO.

II. EXPERIMENTAL PROCEDURE

The single crystals of SrO used in this study were purchased from W. and C. Spicer, Ltd. Defect production was accomplished by irradiation with electrons from a Van de Graaff accelerator (1.5 MeV and 5-10 μ A) or with x rays. All irradiations were done while maintaining the sample temperature at 77 K.

The ESR spectrometer was an X band (9.21 GHz) homodyne system with 100-kHz magnetic field modulation and a 6-in. current-regulated magnet.

Spectra were obtained at 77 K by using a small finger Dewar in conjunction with a Varian Model 4531 rectangular cavity, while a Varian variabletemperature system provided the thermal-anneal data. A nuclear-magnetic-resonance proton probe was used to measure the magnetic field positions of all lines. Small corrections for the difference in magnetic field at the sample and probe positions were obtained using the Cr^{3^+} signal (g=1.9800) in MgO. The unfiltered output of a 100-W low-pressure Hg lamp was used for optical bleaching at 77 K.

III. RESULTS AND ANALYSIS

A. (111)-oriented center

The ESR spectrum of a previously observed^{5,6} defect has been investigated in single crystals of SrO following electron irradiation at liquid-nitrogen temperature. When the magnetic field is along the [100] direction, the spectrum consists of two equally intense lines separated by 142.9 G. In the [110] direction, the spectrum contains four equally intense lines; and for the [111] direction, it again consists of four lines but one pair is three times more intense than the other pair. The [111] spectrum is shown in Fig. 1 and the complete angular dependence for rotation of the magnetic field in the (110) plane is shown in Fig. 2.

From the angular data, it is evident that a 100%abundant nuclear spin with $I = \frac{1}{2}$ is interacting with a single unpaired electron. The defect exhibits $\langle 111 \rangle$ symmetry and all four distinguishable $\langle 111 \rangle$ directions in the crystal are equally populated. Because of the relatively large hyperfine splitting, we tentatively assign this spectrum to a $\langle 111 \rangle$ oriented molecular ion. The participating nucleus may be either hydrogen or fluorine and both OH²⁻ and OF²⁻ ions could be reasonably expected to

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FIG. 1. Experimental ESR spectrum of the $\langle 111 \rangle$ -oriented center in SrO taken at 77 K with the magnetic field along the [111] direction.

exist in SrO. However, arguments are presented in the following section favoring the OH^{2^-} assignment.

The concentration of these molecular ions does not readily saturate with increasing radiation dose. In the samples studied, the V_{OH} centers⁷ reached their maximum concentration after only 30 sec of electron irradiation, whereas the $\langle 111 \rangle$ -oriented centers were still growing after 30 min of similar irradiation. For nonquenched samples, these longer irradiations would produce up to 50 times more molecular ion centers than V_{OH} centers.

The $\langle 111 \rangle$ -oriented centers are not affected by an unfiltered ultraviolet bleach, either polarized or unpolarized. The results of a pulse-anneal study are presented in Fig. 3. As the $\langle 111 \rangle$ -oriented molecular ions thermally decay near 140 K, a second spectrum is observed to increase significantly in intensity. This new spectrum is described in Sec. II B.

The following spin Hamiltonian was used to characterize the ESR spectrum of the $\langle 111 \rangle$ -oriented



FIG. 2. Angular dependence of the $\langle 111\rangle$ -oriented center for rotation of the magnetic field in the $(1\bar{1}0)$ plane.



FIG. 3. Thermal stability of the $\langle 111 \rangle$ -oriented and the perturbed centers in SrO. The duration of the annealing pulses was 3 min and the monitoring temperature was 80 K.

centers in SrO:

$$\frac{H}{g_0\mu_B} = \vec{\mathbf{S}} \cdot \frac{\vec{\mathbf{g}}}{g_0} \cdot \vec{\mathbf{H}} + \vec{\mathbf{I}} \cdot \vec{\mathbf{A}} \cdot \vec{\mathbf{S}} - \frac{g_N\mu_N}{g_0\mu_B} \vec{\mathbf{I}} \cdot \vec{\mathbf{H}} \quad . \tag{1}$$

The \vec{g} and \vec{A} tensors are coincident; the x, y, and z axes being along the $[1\vec{10}]$, $[11\vec{2}]$, and [111] directions, respectively. After expressing the Hamiltonian in a common coordinate system having the z direction parallel to the magnetic field, the basis set $|M_s, m_l\rangle$ was used to rewrite the Hamiltonian in the form of a 4×4 matrix. A computer was used for diagonalizing this matrix. All of the lines in the [100], [110], and [111] spectra were used in an iterative procedure to determine the "best" set of parameter values. These parameters for the $\langle 111 \rangle$ -oriented molecular ions are listed in Table I.

B. Perturbed center

When the $\langle 111 \rangle$ -oriented centers thermally decay, a second spectrum increases in intensity. From examination of the data in Fig. 3, there is little doubt that a correlation exists between the two centers and this is reinforced by considering the second spectrum in detail. Figure 4 shows the

TABLE I. Spin-Hamiltonian parameters measured at 77 K for the (111)-oriented molecular ion in SrO.



FIG. 4. Experimental ESR spectrum of the perturbedmolecular-ion center in SrO taken at 77 K with the magnetic field along the [100] direction.

spectrum obtained from the more stable center when the magnetic field is along the [100] direction. As illustrated in the accompanying "stick" diagram, the spectrum consists of three pairs of lines for this orientation. A complete angular dependence for rotation of the magnetic field in the (001) plane is shown in Fig. 5, thus confirming that this second center is an $S = \frac{1}{2}$, $I = \frac{1}{2}$ defect.

This more stable center in SrO is also identified as a molecular ion and presumably, the identity of the participating nucleus is the same as for the $\langle 111 \rangle$ -oriented center. However, the magnitude of the hyperfine interaction is considerably smaller



FIG. 5. Angular dependence of the perturbed-molecular-ion center at 77 K for rotation of the magnetic field in the (001) plane.

than for the $\langle 111 \rangle$ -oriented center described in Sec. IIA. As discussed in Sec. IV, the reduced hyperfine interaction indicates that this more stable center in SrO has a nearest-neighbor imperfection which provides a stabilizing influence on the defect. The directions of the principal axes of the g tensor and hyperfine tensor also suggest a nearest-neighbor perturbation. From the angular dependence shown in Fig. 5, it is evident that one of the principal axes for each tensor must lie along the [001] direction and that the other two axes for each tensor must lie in the (001) plane; but the axes of the two tensors need not be coincident. The spin Hamiltonian given by Eq. (1) was used to describe the ESR spectrum of the perturbed center. The principal axes of the two tensors are illustrated in Fig. 6 and the "best" set of parameters obtained from the computer fitting procedure are given in Table II. It proved impossible to find a set of parameters which described the [100] and [110] data to within experimental error $(\pm 0.3 \text{ G} \text{ for each line})$ if the two tensors were assumed to be coincident. Thus a separate angle for each tensor was introduced to characterize the deviation of the z axis from the unique (100) axis (angles θ_{g} and θ_{A} in Fig. 6).



FIG. 6. Proposed model for the perturbed-molecularion center illustrating the directions of the principal axes for the g tensor and hyperfine tensor.

TABLE II. Spin-Hamiltonian parameters for the perturbed molecular ion in SrO. The principal axes are illustrated in Fig. 6 for the measurement at 77 K, whereas the principal axes are the $\langle 100 \rangle$ directions for the measurement at 162 K.

| At 77 K | |
|---|---|
| gx gy gz θg Ax Ay Az θa | 2.0067 \pm 0.0002 2.0111 \pm 0.0002 2.0041 \pm 0.0002 45.3° \pm 0.5° 23.3 \pm 0.5 G 19.8 \pm 0.5 G 45.3 \pm 0.5 G 38.0° \pm 0.5° |
| At 162 K | |
| $\begin{array}{c} g_{\perp} \\ g_{\parallel} \\ A_{\perp} \\ A_{\parallel} \end{array}$ | $\begin{array}{c} 2.0078 \pm 0.0005 \\ 2.0080 \pm 0.0005 \\ 35.4 \pm 1.0 \text{ G} \\ 48.5 \pm 1.0 \text{ G} \end{array}$ |

Additional information that further demonstrates the correlation between the $\langle 111 \rangle$ -oriented and the perturbed centers is obtained from ultravioletbleaching experiments. A sample initially electron irradiated at 77 K and then annealed at a temperature between 140 and 190 K will contain a significant number of the perturbed centers. Subsequent optical bleaching of such a sample at 77 K with the unfiltered output of a Hg lamp destroys the perturbed centers and causes the $\langle 111 \rangle$ oriented centers to reappear. The conversion from perturbed back to $\langle 111 \rangle$ -oriented centers as a result of bleaching is only about 30% efficient.



FIG. 7. (a) Schematic representation of the perturbedmolecular-ion spectrum at 77 and 162 K with the intervening averaging behavior shown by the dashed lines. (b) Experimental ESR spectrum of the perturbed center taken at 162 K with the magnetic field along the [100] direction.

The ESR spectrum from the perturbed center in SrO changes over to axial symmetry as the temperature is increased thus indicating rapid motion about the perturbation. This behavior is very similar to that found by McGeehin $et \ al.^3$ for the OH^{2-} center in CaO. Figure 7(a) is a schematic representation of the perturbed spectrum in SrO at 77 and at 162 K for the case when the magnetic field is along the [100] direction. As the temperature increases above 77 K, the most widely split pair of lines continuously broadens. The two inner pairs of lines broaden at a faster rate as the temperature is raised and actually become unobservable in the 100-130 K range. Above these temperatures, they reappear as a single averaged pair of lines and then sharpen as the temperature approaches the 160-K region. Figure 7(b) shows the perturbed spectrum observed at 162 K with the magnetic field along the [100] direction. The parameters describing the averaged perturbed spectrum at 162 K were obtained by using the same spin Hamiltonian and fitting procedure previously described. They are presented in Table II along with the unaveraged parameters.

IV. DISCUSSION

Since ENDOR results are not yet available, we are unable to make an absolute identification of the nucleus involved in the two molecular ion centers observed in SrO. The requirement that it be a 100%-abundant $I = \frac{1}{2}$ nucleus narrows the choice to either hydrogen or fluorine; other possibilities are phosphorus, yttrium, rhodium, and thulium. but their presence in SrO in a significant concentration is considered very unlikely. At this point, the situation cannot be clarified by using previously reported results as a guide. The (111)-oriented center in SrO has a hyperfine interaction comparable to the OF^{2-} center reported by Rius *et al.*,^{1,2} while the perturbed center in SrO has a hyperfine interaction and angular dependence very similar to the OH²⁻ center reported by McGeehin *et al.*³ It should be noted, however, that neither of these two previous investigations used the ENDOR technique to verify the nuclear identity. To further confuse the question, both hydrogen and fluorine are present in the SrO samples used in our investigation as evidenced by the appearance of the V_{OH} - and $V_{\rm F}$ - center^{6,7} ESR lines upon irradiation at low temperatures. This precludes simply eliminating one of the two candidates and forces any final choice based on the data presently available to be speculative.

Despite the lack of finality, we feel there is sufficient evidence to draw substantial conclusions as to whether the molecular ion is OF^{2^-} or OH^{2^-} .

Most important is the difference in the production requirements for the OF^{2-} center in MgO and the molecular-ion centers in SrO. Rius et al.² report that ionizing radiation does not produce the OF²⁻ defect in MgO, whereas x rays are sufficient to produce the observed molecular-ion centers in SrO. These earlier investigators concluded that a "knock-on" damage process in MgO most likely produced oxygen interstitials which then became stabilized by substitutional fluorine ions to form the OF^{2^-} ions. This is a quite reasonable explanation of their results in MgO, but a similar phenomenon cannot be happening in SrO because of the ease with which x rays can create the observed molecular ions. This suggests that we should not try to make any analogy between the reported OF^{2-} center in MgO and the molecular ions in SrO. Since ionizing radiation could not produce an OF² center in MgO where considerable fluorine was known to be present, one could argue that ionizing radiation would not produce an OF²⁻ center in SrO. For this reason, we tentatively identify the observed molecular ions in SrO as OH²⁻ centers.

Recently, considerable interest has arisen because of the role played by hydrogen in the formation of V^- centers in alkaline-earth oxides.^{8,9} In MgO at least, the hydrogen exists primarily in the form of $Mg(OH)_{2}$ precipitates¹⁰ and vacancy-associated substitutional OH⁻ molecules. Chen et al.^{9,11} have shown in MgO that ionizing radiation can dissociate the OH⁻ molecules located next to cation vacancies thus leaving V^- centers (O⁻ ions next to the cation vacancies) and widely separated hydrogen. Much of this displaced hydrogen is accounted for in MgO by growth of the Mg(OH), precipitates. Any remaining displaced hydrogen is assumed to be stabilized by forming molecular complexes with oxygen or other impurities or is trapped by large scale imperfections such as dislocations or voids in the crystal.

If hydrogen ions or atoms are being displaced in the alkaline-earth oxides by ionizing radiation, and there is little doubt of this as a result of the excellent work of Abraham, Chen, Unruh, and coworkers, one would expect OH molecules to be created in a variety of local environments and charge states if the temperature is sufficiently low.

The general behavior of the two molecular ion centers in SrO suggests a direct analogy to interstitial halide atoms in the alkali halides and perovskite halides. In KCl and KMgF₃, for example, both intrinsic and perturbed interstitial halide atoms (*H* and H_A centers) have been observed to form X_2^- -type molecular ions by combining with a neighboring halide ion.¹²⁻¹⁵ In our present case, we could visualize an interstitial hydrogen atom combining with an O^{2^-} ion thus forming OH^{2^-} molecules. The hydrogen atom could possibly be produced by a dissociation of OH molecules in a manner similar to the well-known radiolysis process in the alkali halides¹⁶ where dissociation of $X_2^{2^{-*}}$ molecules (self-trapped excitons) leads to the creation of halide interstitial atoms. A significant difference between the *H* centers and the OH^{2^-} centers being, of course, that in one case it is an intrinsic interstitial while in the other case it is an impurity interstitial.

There are many experimental similarities between the halide interstitial centers and the molecular ion centers in SrO. In particular, the achievable concentration of *H*-type centers in the halides is oftentimes higher than for defects such as V_{μ} centers which are created by only a single ionization and thus depend directly on the concentration of electron traps. As noted in Sec. III, the (111)-oriented centers in SrO continue to grow long after the $V_{\rm OH}$ centers have saturated. This suggests that the production mechanism for the molecular-ion centers in SrO does not involve simply a single ionization step. In addition, the intrinsic H centers in the halides, as well as the $\langle 111 \rangle$ -oriented centers in SrO, are not significantly affected by an optical bleach. However, the H_{A} centers and the perturbed-molecular-ion centers in SrO are both converted back to their unperturbed (intrinsic) configurations quite easily as a result of optical bleaching. Also, both the H_{\perp} centers and the perturbed centers in SrO exhibit pronounced motional effects.^{14,15}

The observed hyperfine interactions provide considerable information about the structure of the molecular-ion centers in SrO. The most prominent difference between the two centers is the large change in the Fermi-contact parameter. Experimentally, one sees that the unpaired electron resides much more on the oxygen ion in the perturbed center than in the $\langle 111 \rangle$ -oriented center. A GAUSSIAN-70 molecular-orbital calculation¹⁷ for a "free" OH²⁻ molecule gave a Fermi-contact interaction with the hydrogen nucleus of 150 G for a bond length of 1.40 Å. This value agrees favorably with the experimental results for the $\langle 111 \rangle$ oriented center, and the 1.40-Å bond length is not unreasonable for the SrO lattice. As expected, these computer calculations also showed that as the OH^{2⁻} molecular-ion bond length increases. separate O⁻ and H⁻ ions begin to evolve with the unpaired electron residing on the oxygen ion.

Since OH^{2^-} is not a stable free molecule; the only reason it would be observed in SrO is because of the potential well created by the surrounding lattice. At sufficiently low temperature (in this case, below 140 K), this potential well would

stabilize the OH^{2^-} molecule in the otherwise perfect lattice. Above 140 K, the hydrogen would probably diffuse through the lattice in a "hopping" mode while maintaining its OH^{2^-} character. This hopping mode could be viewed basically as a sequence of randomly alternating hydrogen interstitial and oxygen hole jumps. When the diffusing hydrogen encountered a perturbation in the lattice that provides "extra" room, the OH^{2^-} molecularion would become thermally restabilized. As a result of the "extra" room, the bond length of the molecular ion would be greater and the Fermicontact term correspondingly smaller. In fact, as indicated by the smallness of the Fermi-contact interaction, the perturbed OH^{2^-} center could

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- *Present address: Georgia Southwestern College, Americus, Ga., 31709.
- ¹G. Rius and R. T. Cox, Phys. Lett. A <u>27</u>, 76 (1968).
- ²G. Rius, R. T. Cox, P. Freund, and J. Owen, J. Phys. C <u>7</u>, 581 (1974).
- ³P. McGeehin, B. Henderson, J. F. Boas, and T. P. P. Hall, J. Phys. C 8, 1718 (1975).
- ⁴T. P. P. Hall, J. Phys. C <u>8</u>, 1921 (1975).
- ⁵M. M. Abraham, Y. Chen, J. T. Lewis, and F. A. Modine, Phys. Rev. B <u>7</u>, 2732 (1973).
- ⁶M. M. Abraham, Y. Chen, and J. Rubio O., Phys. Rev. B <u>14</u>, 2603 (1976); J. Rubio O., H. T. Tohver, Y. Chen, and M. M. Abraham *ibid.* <u>14</u>, 5466 (1976).
- ⁷W. B. J. Blake, H. A. Gitelson, and J. E. Wertz, J. Phys. C <u>4</u>, 1261 (1971).
- ⁸M. M. Abraham, Y. Chen, and W. P. Unruh, Phys. Rev. B 9, 1842 (1974).
- ⁹Y. Chen, M. M. Abraham, L. C. Templeton, and W. P.

easily be considered, at least in first order, as a substitutional paramagnetic O⁻ ion and a neighboring interstitial H⁻ ion.

In summary, we have observed two radiationinduced molecular ions, one intrinsic and the other perturbed, in SrO. These are either OH^{2^-} or OF^{2^-} centers although considerable evidence favors the OH^{2^-} assignment. However, an absolute identification cannot be made until ENDOR results are available.

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Unruh, Phys. Rev. B 11, 881 (1975).

- ¹⁰B. Henderson and W. A. Sibley, J. Chem. Phys. <u>55</u>, 1276 (1971).
- ¹¹Y. Chen, M. M. Abraham, and L. C. Templeton, J. Am. Ceramic Soc. <u>60</u>, 101 (1977).
- ¹²W. Kanzig and T. O. Woodruff, J. Phys. Chem. Solids <u>9</u>, 70 (1958).
- ¹³B. H. Rose, J. E. Rhoads, and L. E. Halliburton, Phys. Rev. B <u>14</u>, 3583 (1976).
- ¹⁴C. J. Delbecq, E. Hutchinson, D. Schoemaker, E. L. Yasaitis, and P. H. Yuster, Phys. Rev. <u>187</u>, 1103 (1969).
- ¹⁵J. E. Rhoads, B. H. Rose, and L. E. Halliburton, Phys. Rev. B 11, 5115 (1975).
- ¹⁶E. Sonder and W. A. Sibley, in *Point Defects in Solids*, edited by J. H. Crawford, Jr., and L. M. Slifkin (Plenum, New York, 1972), Vol. 1.
- ¹⁷W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University (unpublished).