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Radiation-Induced $[K]^0$ Center in CaO and SrO†

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Substitutional monovalent potassium ions in CaO and SrO trap holes when the crystals are exposed to ionizing radiation at 77 K. The resulting neutral, but paramagnetic, $[K]^0$ centers have ⟨100⟩ axial symmetry and their spin-Hamiltonian parameters are reported. Unlike the $[Li]^0$ and $[Na]^0$ centers in these hosts, the hyperfine structures of the $[K]^0$ centers are best resolved when the axis of the defect is aligned with the magnetic field, suggesting that the isotropic and anisotropic parts of the hyperfine tensor have the same sign and are roughly equal in value. Optical-absorption bands for these centers are tentatively assigned at approximately 1.6 and 1.5 eV for CaO and SrO, respectively.

I. INTRODUCTION

Previous investigations in the alkaline-earth oxides have identified paramagnetic color centers which are formed by the trapping of holes by cation vacancies.[1-4] These centers are formed when the oxide crystals are exposed to ionizing irradiation at low temperature. The paramagnetic trapped-hole center, since it is negatively charged with respect to the neutral lattice, has been designated as the V^- center.[5] If either a monovalent lithium or sodium is present as a substitutional impurity at a cation site, a similar paramagnetic hole center is produced whose net charge is zero and is designated as the $[Li]^0$ or $[Na]^0$ center, respectively. These centers have recently been studied in detail.[2-4] However, there are still questions as to their nature and the validity of the models proposed for them. We have, therefore, incorporated potassium into these crystals as an extension of the previous work. In this paper, we report the observation of $[K]^0$ centers in both CaO and SrO, and present optical, magnetic, and thermal properties of these centers.

II. EXPERIMENTAL PROCEDURE

Potassium ions were incorporated into CaO and SrO during crystal growth in an arc furnace with starting materials of 10 mol% K_2CO_3 mixed with $CaCO_3$ or $SrCO_3$, respectively, by techniques which were described previously.[6] The single crystals were irradiated at 77 K with ^{60}Co γ rays or 2-MeV electrons and subsequent optical and magnetic measurements were performed without any intervening warmup. A Cary-14R spectrophotometer was used for the optical-absorption measurements and electron-paramagnetic-resonance (EPR) measurements were performed in two different *X*-band spectrometers; one utilizing a Varian V-4531 rectangular cavity and the other utilizing a homemade cylindrical cavity operating in the TE_{011} mode. In both of these cavities, there was a sample entry hole present, allowing a swift change of sample to be made at low temperatures, a step made necessary because of the low thermal stability of the centers.

III. RESULTS

Figures 1 and 2 show the EPR spectra of the irradiated SrO:K and CaO:K single crystals observed at 4.2 K. The hyperfine structure due to the 93% abundant $^{39}K(I=\frac{3}{2})$ readily verifies that the holes have been trapped by potassium ions, while the angular variation of the spectra reveals the characteristic ⟨100⟩ axial symmetry of such hole centers. The appropriate spin Hamiltonian has the form

$$\mathcal{H} = \mu_B \vec{H}\cdot\overleftrightarrow{g}\cdot\vec{S} + \vec{I}\cdot\overleftrightarrow{A}\cdot\vec{S} + \vec{I}\cdot\overleftrightarrow{P}\cdot\vec{I} - g_N \mu_N \vec{H}\cdot\vec{I}. \quad (1)$$

The hyperfine is clearly resolved with the magnetic field parallel to the axis. For SrO, it cannot be resolved at all along the perpendicular orientation where the linewidth is approximately the same as the total width of the parallel set. The hyperfine splitting in CaO is larger than in SrO such that the additional four hyperfine lines due to the 7% naturally abundant ^{41}K $(I=\frac{3}{2})$ can be resolved in CaO. When the field is not in the parallel direction, the selection rules break down due to the combined effect of the hyperfine, nuclear quadrupole, and nuclear Zeeman interactions. This effect produces a rather complicated spectrum and a further study does not seem feasible at this time, especially in view of the small hyperfine values. Since we do not have values for the perpendicular components of the hyperfine tensors, we cannot extract the isotropic and anisotropic parts. Results are tabulated in Table I.

The thermal stability of the $[K]^0$ centers and two other paramagnetic centers in SrO, which have ⟨111⟩ axial symmetry, was studied. These latter ⟨111⟩ centers were also formed by irradiation and are probably aggregates of potassium ions. The $[K]^0$ centers show the thermal instability which is

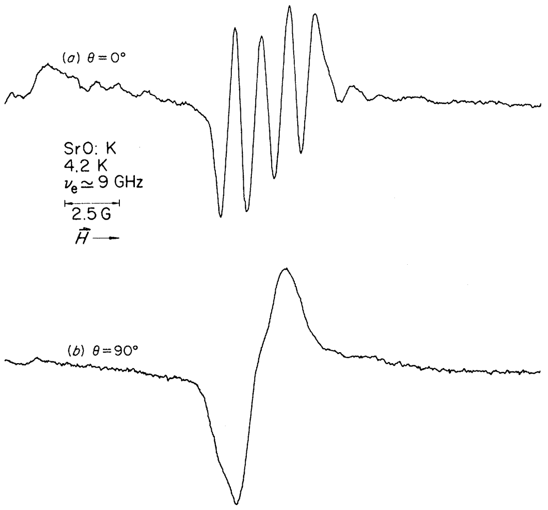

FIG. 1. EPR spectrum of the $[K]^0$ center in SrO with the magnetic field parallel ($\theta=0$) and perpendicular ($\theta=90°$) to the axis of the center. The unequal intensity of the ^{39}K hyperfine lines is unaffected by the traverse direction of the magnetic field.

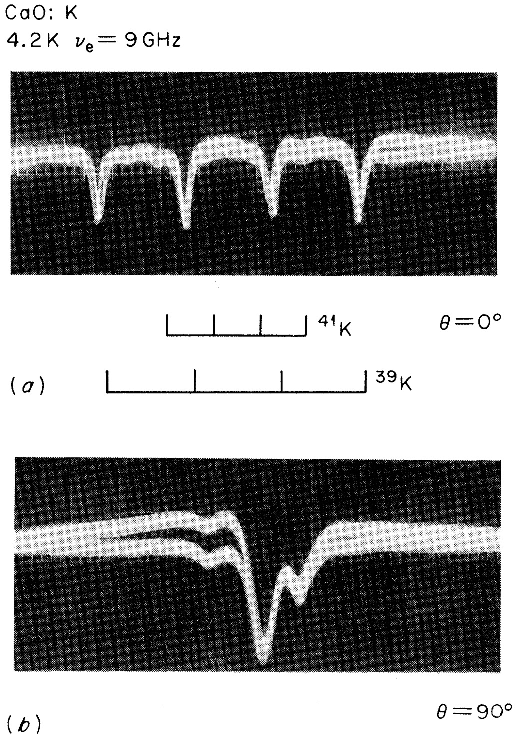

FIG. 2. EPR spectrum of the $[K]^0$ center in CaO with the magnetic field parallel ($\theta=0$) and perpendicular ($\theta=90°$) to the axis of the center. The total spread of the ^{39}K hyperfine lines in (a) is approximately 10 G and the magnetic field scale for both (a) and (b) is equal.

characteristic of hole-trap centers. Figure 3 shows the EPR spectra at 77 K observed before and after warming an irradiated SrO:K sample to room temperature. After a short (on the order of minutes) anneal at 295 K, the $[K]^0$ center and the two ⟨111⟩ centers disappeared, leaving only the structured isotropic line shown on an expanded scale. An isochronal annealing experiment showed that these lines vanished at different temperatures, indicating that two different ⟨111⟩ centers are involved.

Since the hole-trap centers are unstable at higher temperature, isochronal annealing experiments can be used to correlate the EPR and optical-absorption spectra. The radiation-induced optical spectra are shown in Fig. 4. Band peaks at approximately 1.5 and 1.6 eV for the SrO:K and CaO:K crystals, respectively, are observed. The annealing temperatures of the $[K]^0$ centers, taken to be that at which the concentration of the centers decreased to half of its initial value, were found to occur at 170 and > 200 K in SrO and CaO, respectively. The 170-K annealing correlates well with that of the 1.5-eV band in the SrO:K crystal, but in the case of CaO:K, the optical-absorption coefficient of the 1.6-eV band was too low to permit an accurate comparison with the EPR annealing curve. Although the initial potassium dopant was roughly the same for both CaO and SrO, the potassium ion is less readily accepted in the CaO matrix because of the greater discrepancy in size between the K^+ ion and the Ca^{++} ion that it replaces. This conjecture is supported by chemical analyses of the crystals and the relatively large EPR signals of $[K]^0$ and K-aggregate centers observed in the SrO crystals.

TABLE I. Spin-Hamiltonian parameters.

	Temp. (K)	$g_\parallel$	$g_\perp$	$A(^{39}K)$ (MHz)	$A(^{41}K)$ (MHz)
CaO : $[K]^0$	77	2.0018 ± 0.0010	2.0726 ± 0.0010	•••	•••
	4.2	2.0006 ± 0.0005	2.0962 ± 0.0005	8.99 ± 0.15	4.95 ± 0.15
SrO : $[K]^0$	77	Obscured	2.1348 ± 0.0010	•••	•••
	4.2	1.9966 ± 0.0005	2.1356 ± 0.0005	3.39 ± 0.15	•••

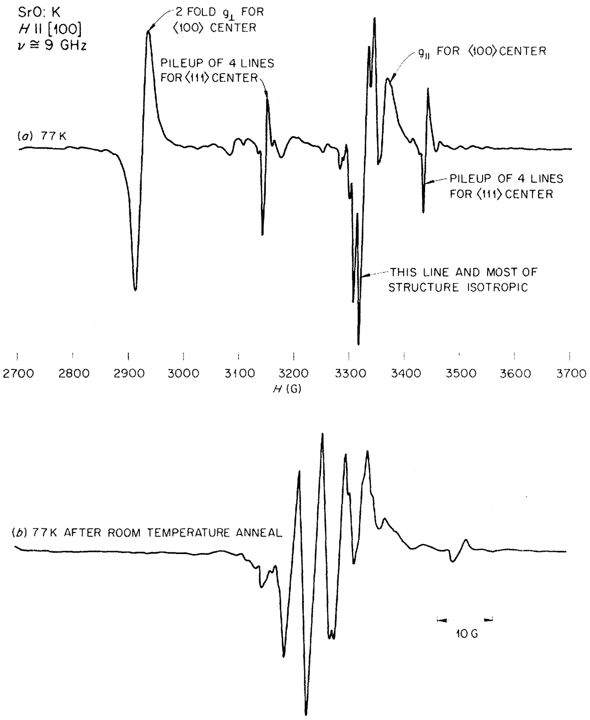

FIG. 3. EPR spectrum of SrO : K crystal at 77 K. The top trace shows the spectrum obtained immediately following γ irradiation at 77 K. The bottom trace illustrates on an expanded scale the remaining almost isotropic structured spectrum after a room-temperature anneal.

TABLE II. Summary of data on trapped-hole parameters.

	$\Delta g_\parallel$	$\Delta g_\perp$	Ref.	Δ(eV)	Ref.	Annealing temperature (K)	Ref.
V^-							
MgO	+0.0009	+0.0362	a	2.3	b	>295	b, c
CaO	−0.0012	+0.0687	d	1.85	e	⋯	
SrO	−0.0013	+0.0680	f				
$[\mathrm{Li}]^0$							
MgO	+0.0020	+0.0519	g	⋯		⋯	
CaO	−0.0004	+0.0862	e, g	1.73	e	200	e
SrO	−0.0024	+0.0908	g	⋯		⋯	
$[\mathrm{Na}]^0$							
MgO	+0.0032	+0.0698	h	1.58	h	190	h
CaO	−0.0021	+0.1211	e	1.39	e	165	e
SrO	−0.0066	+0.1431	h	1.34	h	160	h
$[\mathrm{K}]^0$							
CaO	−0.0017	+0.0939	i	1.6	i	>200	i
SrO	−0.0057	+0.1333	i	1.5	i	170	i

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IV. DISCUSSION AND CONCLUSION

Earlier we discussed[3,4] the difficulties in accepting a proposed model[1,7] for these centers based on the localization of the hole on a single oxygen ion. The resulting O^- ion is split by the crystalline field into a singlet p_z ground state and a doublet excited (p_x, p_y) state, separated by the energy Δ, which is assumed to correspond to the optical transition. This model failed to explain all the unusual experimental features of the trapped-hole centers: the

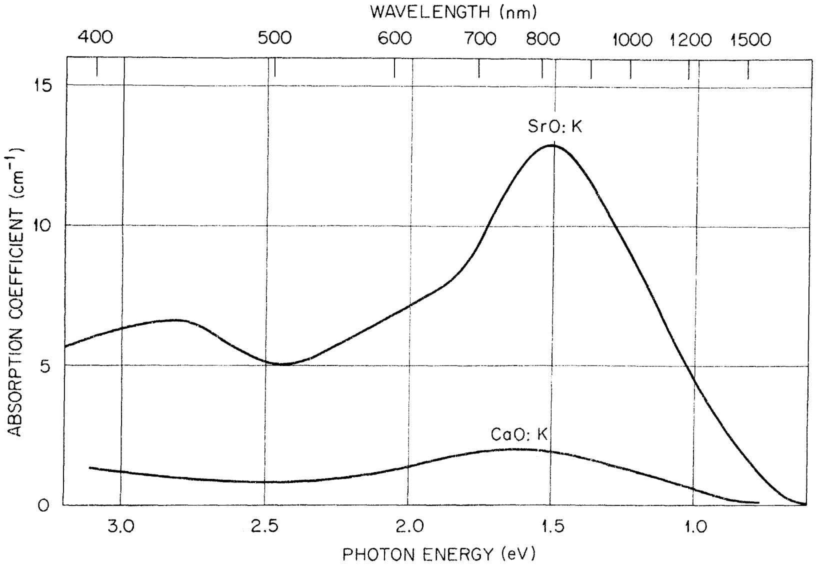

FIG. 4. Radiation-induced optical bands in SrO : K and CaO :K crystals at 77 K.

large g shifts (departures from the free-electron g value) observed, the unusually large oscillator strengths for such forbidden transitions, and the apparently large spin-orbit coupling. These arguments also hold for the [K]^0 centers. One might speculate on other models where the hole is less localized, and indeed some evidence for such delocalization has been noted.[3,4] A satisfactory model should not only explain the large g shifts and oscillator strengths, but also the transition energies, the large half-widths of the optical bands, and the low thermal stability of the centers.

In addition, the model should be able to account for transitional changes in the properties of the centers due to changes in either the ionic size of the impurity or the host lattice. An examination of the properties of the trapped-hole centers upon such changes was an objective of the present study. Our results and that of previous workers are summarized in Table II. There appears to be a correlation between the optical-absorption energy, the annealing temperature, and the g shifts for the centers. As the host crystals are changed, regular trends are observed. Host crystals with heavier cations give centers which are less stable and have lower optical-absorption energy and larger g shifts. Thus, one can conclude that the depth of the potential well for the centers is decreasing in a more or less regular manner with the host lattice, but no single-parameter model has been found.

There are some unexpected features arising from the [K]^0 centers. Potassium is expected to behave differently than lithium or sodium because of its larger ionic size. Indeed, it is surprising that it fits at all into the oxide lattice. The properties of the [K]^0 centers do not fit into a progression corresponding to the ionic size of the monovalent alkali-metal ions. Rather, the optical-absorption energy, g shifts, and annealing temperatures of the [K]^0 centers in CaO and SrO are intermediate between those of the [Li]^0 and [Na]^0 centers in these same hosts.[3,4] Hence, as one proceeds down the series of alkali substitutional ions in the same host, no simple trend exists. Another rather unusual result is that, whereas in the case of the [Li]^0 and [Na]^0 centers[2-4] the hyperfine structures are more clearly resolved when the magnetic field is perpendicular to the axis of the center rather than parallel, the reverse is true for [K]^0 centers. This suggests that for the [K]^0 centers, unlike the [Li]^0 or [Na]^0 centers, the isotropic and anisotropic parts of the hyperfine tensor a and b, respectively, have the same sign and are roughly equal in value.

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Thermo- and Elasto-optic Parameters of NaF and Their Implications for Light Scattering from Second Sound

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The intensity of light scattered from second sound is estimated for the case of NaF, the only dielectric crystal in which second sound is presently known. For this purpose we have measured the thermo-optic coefficient $(\partial n/\partial T)_p$ of NaF between 300 and 10 °K as well as the elasto-optic tensor at room temperature. The scattered intensity is calculated to be less than the value predicted by the Landau–Placzek ratio, and in fact the Rayleigh component is expected to vanish entirely at one particular temperature (approximately 34 °K).

I. INTRODUCTION

The phenomenon of second sound, i.e., wavelike propagation of entropy fluctuation, has recently attracted considerable theoretical[1] and experimental[2] interest, in part because of its recent detection in a normal dielectric crystal, NaF.[3] Most experimental work up to now has been performed

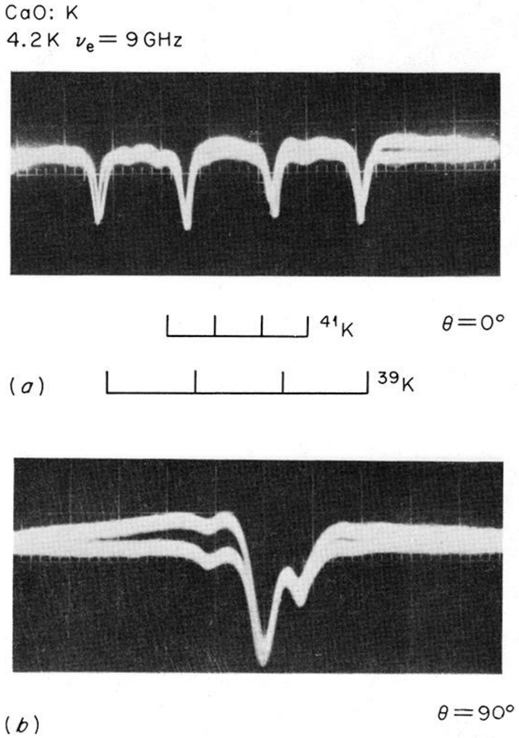

FIG. 2. EPR spectrum of the $[K]^0$ center in CaO with the magnetic field parallel ($\theta = 0$) and perpendicular ($\theta = 90°$) to the axis of the center. The total spread of the ^{39}K hyperfine lines in (a) is approximately 10 G and the magnetic field scale for both (a) and (b) is equal.