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Correlation of EPR and thermoluminescence in crystals of highly colored CaO:Mg: Involvement of a center containing hydrogen ions

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Electron-spin-resonance measurements at ~ 9 and 4 GHz have identified a center with tetragonal symmetry and $S = \frac{1}{2}$, $I = \frac{1}{2}$ [$g_{\parallel} = 1.9998(1)$, $g_{\perp} = 2.0029(1)$, $A_{\parallel} = 0.00203(1)$ cm^{-1}, $A_{\perp} = 0.00134(1)$ cm^{-1}] in crystals of highly colored CaO:Mg. The resonances are produced by illumination at $\lambda < 750$ nm and $T < 200$ K and are associated with the thermoluminescence peak ($\lambda_{max} = 690$ nm) at 180 K. The center involves three lattice sites along $\langle 100 \rangle$ with H$^-$ at an anion-vacancy site next to the cation-vacancy site of a P$^-$ center. The center appears to arise as a result of crystal-growth conditions and is not specifically associated with the Mg dopant.

I. INTRODUCTION

A characteristic feature of highly colored regions of crystals of CaO grown by arc fusion is that they exhibit an intense long-lived phosphorescence at ~ 600 nm at room temperature after excitation with light of wavelength less than 500 nm. It is generally accepted that this emission results from the thermally activated release of an electron from a trap, its subsequent capture by an F^+ center (an anion vacancy containing a single electron) and the radiative decay of the excited state of the resultant F center to the ground state.[1] The thermoluminescence glow curves of crystals from a variety of sources all have their most prominent peaks at around 80 and 330 K and it is this latter peak which is responsible for the room-temperature phosphorescence.[2-4] However, the nature of the metastable traps which give rise to the peaks in the glow curves has not been clearly established.

A recent series of papers by Chen and co-workers[4-8] have given strong evidence that H$^-$ ions (a proton with two electrons) present substitutionally at an anion site act as the electron trap in MgO and CaO. Their model is one in which H$^-$ ions trap electrons photoexcited from the F centers already present in the crystal, producing H^{2-} ions. The trapped electrons are subsequently released by thermal activation. The formation of H^{2-} ions in MgO at temperatures below 50 K after excitation with 400-nm light has been observed using electron paramagnetic resonance (EPR) by Tombrello et al.[9] However they did not report the correlation of the formation and decay of the H^{2-} center as observed by EPR with peaks in the glow curve. Since the thermoluminescence processes involve the transfer of electrons from a metastable trap to F^+ centers, changes in EPR signal intensity may be expected to occur at similar temperatures to the peaks in the glow curve.

As part of a study aimed at elucidating the nature of the trapping centers by correlating EPR spectral changes, thermoluminescence glow curves and optical emission spectra, we examined crystals of CaO doped with a nominal 1 at. % MgO. These crystals have some properties in common with crystals of pure CaO, but also have several unusual features.[10-12] Two of the most striking of these features are the observation in highly colored regions of the melt of an intense glow peak at ~ 180 K[3] and of intense EPR spectral lines produced below 200 K by light of wavelength less than 750 nm.[11] These lines were attributed previously to two centers, each with $S = \frac{1}{2}$.[11] In this paper we show that these EPR lines are related to the glow peak at 180 K. Furthermore, aided by an EPR experiment at around a 4-GHz microwave frequency, we show that they are in fact due to a single center with $S = \frac{1}{2}$ and $I = \frac{1}{2}$. While this suggests the presence of hydrogen, we were unable to find any evidence for H^{2-} ions or other EPR detectable centers which could be correlated with the glow peaks at around 65 and 370 K in these crystals.

II. EXPERIMENTAL

A. Crystals

Crystals of CaO:Mg were grown by arc fusion by W. and C. Spicer Ltd. (Cheltenham, England) and were obtained by courtesy of Hughes (Materials Development Division, Atomic Energy Research Establishment, Harwell, England). Typical analyses are given by Weightman and Hall.[11] The crystals contain two different regions, separated by a sharp boundary. In the highly colored region the main defect appears to be the F center and it is the high concentration of these centers which gives the black appearance of specimens from this region of the melt. The other region has a clear or milky appearance and has fewer anion vacancy centers. The predominant point defects in this region appear to be cation vacancies.

B. EPR measurements

These were made at X band using a Varian Associates E-12 spectrometer (9.1 GHz) and a Bruker ESR-200D-SRC spectrometer (9.5 GHz). Temperatures in the range 100—400 K were obtained using the appropriate nitrogen gas flow systems for these spectrometers. An Oxford Instruments ESR-9 continuous-flow liquid-helium system was used in conjunction with the Varian Associates E-12 spectrometer to obtain temperatures in the range 10—100 K.

The measurements at S band (3.9 GHz) were made using a home-built spectrometer at the Department of Physics, Monash University and the samples were immersed directly in liquid nitrogen.[12,13] All sample cavities allowed *in situ* illumination of the sample, using Oriel Corp. 200-W or 1000-W Xe-Hg arc lamps and either appropriate band-pass filters or a Spex Industries 1670 monochromator.

Isochronal step annealing EPR measurements were performed using the Varian Associates E-12 spectrometer and its associated liquid-nitrogen-based variable temperature system. After cooling to a base temperature of 120 K and subsequent optical excitation at this temperature, the sample was kept in the dark. The temperature controller was then set at the desired temperature, and the sample was allowed 5 min to reach and stabilize at this temperature. The temperature controller was reset to 120 K and 5 min was allowed for the sample temperature to return to and stabilize at this value. The spectrum was recorded and the process repeated at a higher annealing temperature. The measurements at a constant base temperature avoid difficulties due to changes in spectrometer sensitivity and resonance linewidth with temperature.

C. Thermoluminescence and optical emission measurements

These were made at temperatures between 5 and 520 K using an Oxford Instruments CF204 cryostat, with the temperature being controlled by an Oxford Instruments DTC2 temperature controller and SG3 sweep generator. Typical temperature ramp rates were 1 $K\,min^{-1}$. The thermoluminescence emissions were detected either directly or via a Spex Industries 1670 monochromator (grating blazed at 500 nm) using either a RCA 4832 photomultiplier tube and a Keithley 616 electrometer or a RCA C3103A photomultiplier and a photon-counting system. Both photomultiplier tubes have an extended S-20 response. The emission spectra were not corrected for the wavelength response of the monochromator or photomultiplier. Optical illuminations were performed using Oriel Corp. 1000-W or 200-W Xe-Hg arc lamps and another Spex Industries 1670 monochromator or appropriate band pass and cutoff filters. Thermal cleaning experiments (see, e.g., Kappers and Hensley[14]) were performed by preheating the crystal to a given temperature, cooling it to a temperature below that of the glow peak and then heating at a constant-temperature ramp rate through the peak.
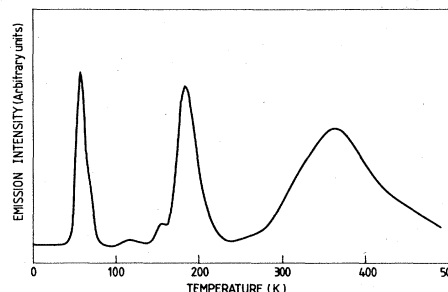

FIG. 1. Thermoluminescence glow curve (total emission intensity) for highly colored CaO:Mg. The measurements were made over two temperature ranges and normalized at 110 K. Heating rate ~ 1 $K\,min^{-1}$. The sample was illuminated for 15 min at ~ 300 nm at 5 and 80 K, respectively for the temperature range required.

III. RESULTS

A. Glow curves and emission spectra

The glow curve of highly colored crystals of CaO:Mg in the temperature range 5 to 520 K after illumination with light of wavelength 300 nm at 5 K is shown in Fig. 1. The main features are the peaks at around 65, 180, and 370 K. A comparison with the glow curve of highly colored non-Mg-doped CaO shows that the peak at 180 K is unique to highly colored CaO:Mg.[3] Thermal-cleaning experiments and the shapes of the glow peaks show that while the peaks at 65 and 370 K are complex and involve more than one type of metastable trap, the peak at 180 K is due to only one type of trap. A trap depth of 0.55 ± 0.05 eV was estimated using the initial rise method of Garlick and Gibson.[15]

The emission spectra recorded during the measurement of the glow curve are shown in Fig. 2, and illustrate the
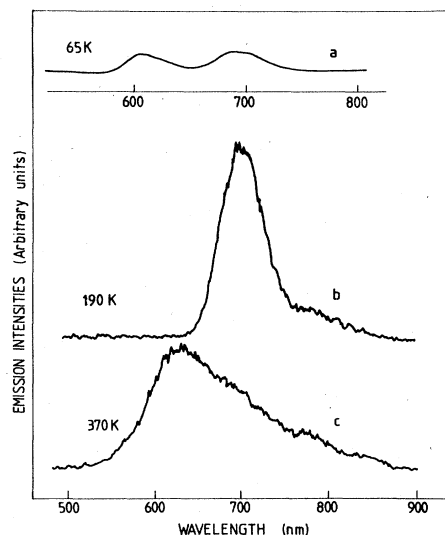

FIG. 2. Emission spectra of highly colored CaO:Mg at 65, 190, and 370 K recorded during the measurement of the glow curve of Fig. 1.

unusual nature of the 180-K peak. While the emissions at 65 and 370 K include a substantial contribution at 610 nm due to the decay of the excited state of the F center, that at 180 K is mainly at 690 nm and is due to the decay of the excited states of the F_A center (an F center where one of the nearest-neighbor calcium cations is replaced by a magnesium ion).[12] The emission at ~785 nm is due to decays from the excited states of the F_{AA} center (an F center where two calcium cations at opposite sides of the oxygen vacancy have been replaced by magnesium ions).[16]

B. EPR spectra of highly colored CaO:Mg

Crystals of highly colored CaO:Mg kept in the dark for some hours and then examined at room temperature showed the intense line at $g = 2.0001$ due to the F^+ center and weaker lines due to the F_A^+ center and to Mn^{2+} and V^{2+} ions.[11,17] No additional resonances of significant intensity were observed in crystals kept in the dark and examined over the temperature range down to 10 K. Illumination of the crystals *in situ* with light of wavelengths less than 750 nm at temperatures below ~200 K produced the A and C lines first observed by Weightman and Hall.[11] Prolonged illumination with ultraviolet light at temperatures around 150 K resulted in these being of similar intensity to the F^+ line. The spectrum at 9.531 GHz in the $g = 2$ region is shown in Fig. 3(a), where the crystal was aligned with the magnetic field along a $\langle 100 \rangle$ direction. No additional signals were observed when the crystals were subjected to combinations of illumination at selected wavelengths in the range 300—750 nm, temperatures of 10, 80, and in the range 120 K to room temperature and microwave powers between 0.1 and 10 mW. It is not clear why we were unable to observe in our crystals signals from the transition-metal ions Ti^+, Cr^+, Cr^{3+}, Fe^+, and Fe^{3+} or from H^{2-} ions, all of which have been suggested as being involved in the thermoluminescence process in the MgO or CaO crystals used by other authors.

Since we were unable to reproduce the g values reported by Weightman and Hall[11] to the expected degree of accuracy using either of the X-band spectrometers, we performed an experiment at S band. The spectrum obtained at this frequency at 77 K and with the magnetic field aligned parallel to $\langle 100 \rangle$ direction is shown in Fig. 3(b). The orientation dependences of the resonances at both X
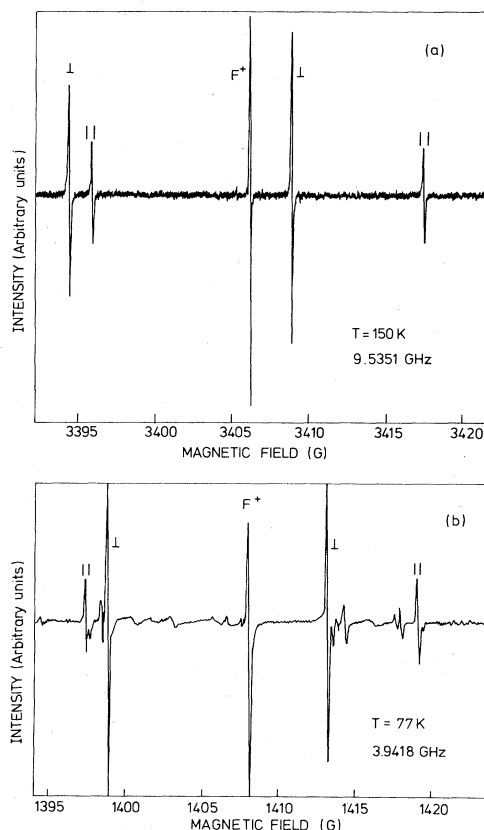

FIG. 3. (a) First derivative EPR spectrum of a single crystal of highly colored CaO:Mg at X band after uv excitation at 150 K. Microwave power 0.2 mW, modulation amplitude 0.08 G at 12.5 kHz, scan rate 11.25 G min^{-1}, recorder time constant 0.01 s. The A and C lines of Weightman and Hall (Ref. 11) are the prominent resonances at high and lower fields respectively than the F^+ line. (b) First derivative EPR spectrum of highly colored CaO:Mg at S band after uv excitation at 77 K. Microwave power reduced to below saturation conditions, modulation amplitude ~0.2 G at 100 KHz, with a scan rate of 10 G min^{-1}, and a recorder time constant of 0.128 s. The crystal used here exhibited some twinning.

and S bands (shown in Fig. 4 for X band for crystal rotations around a $\langle 100 \rangle$ direction with respect to the magnetic field) exhibit tetragonal symmetry, as described by Weightman and Hall.[11] However, a comparison of Figs.

TABLE I. Spin-Hamiltonian parameters of the $(H^- P^-)$ center discussed in this paper and of some related centers.

	$g_{\parallel}$	$g_\perp$	$A_{\parallel}$ (cm^{-1})	$A_\perp$ (cm^{-1})
	(± 0.0001)		(± 0.00001 cm^{-1})	
$(H^- P^-)$: 9.5351 GHz	1.9998	2.0028	0.00203	0.00135
$(H^- P^-)$: 3.9418 GHz	1.9998	2.0030	0.00203	0.00134
F_A^+ (CaO:Mg)[a]	1.9996	2.0006	0.000324	0.000250
P^- (CaO)[b]	1.9995	1.9980		

[a]J. F. Boas, T. P. P. Hall, and A. E. Hughes, J. Phys. C **6**, 1639 (1973). The hyperfine parameters relate to the Mg^{2+} ion.
[b]Errors not quoted. K.-C. To, A. M. Stoneham, and B. Henderson, Phys. Rev. **181**, 1237 (1969).
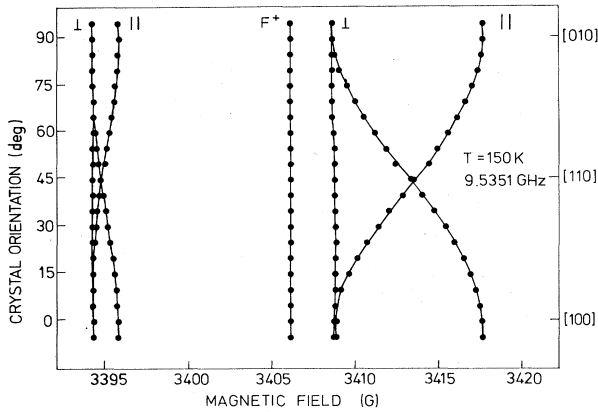
FIG. 4. Angular dependence of the spectrum at 150 K and 9.531 GHz for crystal rotations about a $\langle 100 \rangle$ axis.

3(a) and 3(b) shows that the splittings between the high- and low-field components of both parallel and perpendicular resonances are unaffected by the change in the microwave frequency. Such behavior is characteristic of hyperfine interactions and demonstrates conclusively that the A and C resonances are not due to two distinct centers each with electron spin $S = \frac{1}{2}$ but rather to a single center
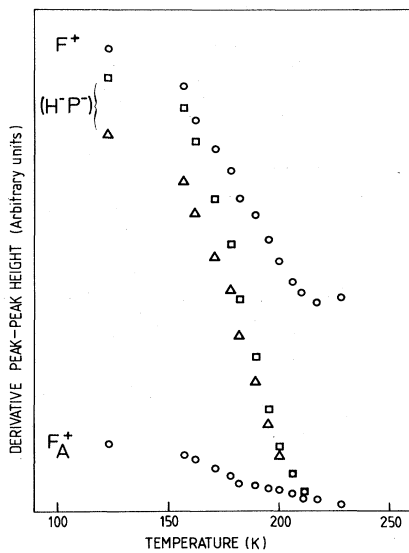

FIG. 5. Dependence of the EPR signal intensity at 9.149 GHz measured as the peak-to-peak derivative height at 120 K, on progressive annealing for 5 min at the temperatures indicated. The intensities due to the high- and low-field perpendicular components of the (H^-P^-) center and the F^+ center were measured at the same spectrometer settings, while that due to the F_A^+ center perpendicular line was measured at 4 times the gain. The difference in the apparent signal intensity of the perpendicular components is due to their different linewidths. However, a comparison of the intensities calculated using the formula intensity = (derivative peak-to-peak height) × (width)^2 shows that the two components have the same intensity to within experimental error. Squares: low-field component; triangles: high-field component.

with $S = \frac{1}{2}$ where the unpaired spin interacts with a nucleus of spin $I = \frac{1}{2}$. Both g and hyperfine interactions are anisotropic. The resonances may be described by the spin Hamiltonian,

$$\mathscr{H} = \beta(g_{||}S_z B_z + g_\perp(S_x B_x + S_y B_y))$$
$$+ A_{||}S_z I_z + A_\perp(S_x I_x + S_y I_y) , \qquad (1)$$

and where the principal axes of both g and A are along the $\langle 100 \rangle$ crystal directions. The spin Hamiltonian parameters are given in Table I.

An examination of the spectra showed that the only resonances whose intensities showed a temperature dependence in the range 120 to 400 K were those due to the F^+, F_A^+, and the $S = \frac{1}{2}$, $I = \frac{1}{2}$ center described above. An isochronal step annealing experiment gave the results shown in Fig. 5, and clearly demonstrates the close relationship between this center and the glow peak at 180 K.

IV. DISCUSSION

A. Thermoluminescence processes in CaO:Mg

The experiments described above link the $S = \frac{1}{2}$, $I = \frac{1}{2}$ center with the glow peak at 180 K in highly colored CaO:Mg. However, there does not appear to be direct association with magnesium ions, as no superhyperfine structure due to ^{25}Mg was observed. Since the lines were less than 0.02 mT wide any magnesium ion must be some distance away. Thus the center appears to be a result of the conditions under which these particular crystals were grown, rather than a specific result of the Mg doping. It is noteworthy that it has not been observed in crystals of "pure" CaO, despite the presence of Mg ions in some of these crystals.[18]

With the nearest Mg ion being some distance from the center, it is surprising that the principal emission at 180 K is at ~690 nm, i.e., from electron capture by F_A^+ centers and the subsequent radiative decay of excited states of the F_A center to the ground state. This is not expected on statistical grounds, and is even more surprising in view of the results of the isochronal step annealing experiment as shown in Fig. 5. This shows that the F^+-center concentration (which was initially some 15 times higher than that of the F_A^+ center) decreases to 50% of its original value and the F_A^+-center concentration decreases to 20% of its initial intensity over the temperature range 150–200 K. However, these results are consistent with those reported by Welch et al.[19] and Welch and Hughes[20] who showed that electrons in the excited states of the F and F_A centers were capable of thermal ionization into the conduction band above temperatures of 70 and 190 K, respectively. Thus while electrons trapped in F centers are readily released back into the conduction band at 180 K, those trapped in F_A centers are not and therefore are more likely to decay radiatively. The experiments of Welch and Hughes[20] and Henderson and McDonagh[21] have shown that tunneling takes place between F_A centers and the ground state of adjacent F^+ centers, where the latter act as the final "sink" for electrons. Thus $F^+ \rightarrow F$

conversion takes place, as shown by the EPR results, without the need for F-band emission at 610 nm. The observation of emission at 785 nm, due to deexcitation of the F_{AA} center presumably takes place through a similar process.

B. Nature of the defect

Possible candidates for the 100% abundant $I = \frac{1}{2}$ nucleus are ^{1}H (i.e., a proton), ^{19}F, ^{31}P, ^{103}Rh, or ^{169}Tm, of which the most likely is the first. Both analysis figures[11] and observations of the presence of hydrogen by other authors make other nuclei unlikely. Although the electron is released from the defect at ~ 180 K, annealing experiments have shown that the intrinsic defect is stable up to approximately 1500 K.[11] Since isolated protons would be expected to diffuse very readily through the lattice, this points to the larger H^- or OH^- ions as providing the $I = \frac{1}{2}$ nucleus. As shown by Gonzalez et al.[8] the H^- ion is stable when substitutionally trapped in anion vacancies in CaO up to at least ~ 1700 K. The observations of Freund et al.[22] indicate that the OH^- ion would not be stable at these temperatures, and this is supported by the observations of McGeehin et al.[23] who were unable to observe OH^{2-} centers in neutron-irradiated CaO after annealing at 473 K for 1 h.

The hyperfine interaction can be decomposed into the isotropic and anisotropic components a and b respectively, where

$$a = \tfrac{1}{3}(A_{||} + 2A_\perp) , \tag{2}$$

$$b = \tfrac{1}{3}(A_{||} - A_\perp) . \tag{3}$$

If $A_{||}$ and $A_\perp$ have the same sign, this gives $a = 0.00158$ cm^{-1} and $b = 0.00023$ cm^{-1}.

If we assume that the anisotropic interaction is due solely to dipole-dipole interactions, we obtain an electron-proton distance of 0.225 nm. While this is slightly smaller than the shortest anion-cation distance in CaO (0.24 nm) indirect bonding and distortions of both the lattice and the electron distribution could make the actual distance somewhat larger. It appears unlikely that an unpaired electron located at a cation site next to an H^- ion at an anion site would be more stable than the H^{2-} ion observed by Tombrello et al.[9] This would be true whether the cation site was occupied by a Ca^{2+} ion (i.e., converted to a Ca^+ ion) or was vacant. Thus the model which emerges is one in which the unpaired electron is trapped at an anion vacancy with an H^- ion present substitutionally at the next anion site in a $\langle 100 \rangle$ direction. For reasons of charge compensation one may also expect the intervening cation site to be vacant, so that the defect is one in which an anion-cation vacancy pair with a single trapped electron (i.e., a P^- center) is located next to and in the $\langle 100 \rangle$ direction from an H^- ion, as shown in Fig. 6. As discussed for the P^- center in MgO, the electron is not expected to be centrally located at the anion site.[24]

Further insight into the electron distribution may be gained by a consideration of the isotropic interaction. In
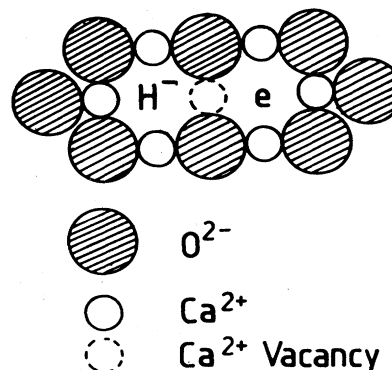

FIG. 6. Model of the (H^-P^-) center in CaO:Mg. The cation site indicated by the open circle is probably vacant, as discussed in the text.

the classical Fermi-Segre form this is related to the square of the wave function of the magnetic electron at the nucleus in question $|\psi(0)|^2$ by

$$a = \tfrac{8}{3}\pi g_e \beta_e g_n \beta_n |\psi(0)|^2 . \tag{4}$$

We obtain $|\psi(0)|^2 = 0.071 \times 10^{24}$ cm^{-3}, which is approximately one third of the value for the H^{2-} ion in MgO.[9] This demonstrates the delocalization of the magnetic electron and is consistent with the proposed model.

Since the defect involves three electrons (two from the H^- ion and one from the P^- center) distributed over two centers, a theoretical calculation of the g values is not expected to be straightforward. However a comparison of g values found here with those of the F_A^+ and P^- centers in CaO (Table I) shows that while the values of $g_{||}$ are similar, those of $g_\perp$ are substantially different. This is not unexpected in view of the influence on $g_{||}$ of the ions perpendicular to the symmetry axis of the defects,[17] which are calcium in all three cases. However $g_\perp$ is largely influenced by the ions in the plane of the symmetry axis and is thus expected to be different in each case.

V. CONCLUSIONS

A combination of EPR, thermoluminescence glow curve, and optical emission spectral measurements have identified the metastable trap responsible for the glow peak at 180 K in highly colored CaO:Mg. The model of the defect is one in which an electron is metastably trapped in a P center with an H^- ion present substitutionally in the collinear anion site immediately next to the cation vacancy. The presence of this center appears to be a peculiarity of this particular melt arising from the conditions of growth, rather than from the Mg doping. EPR signals were not observed from centers which could be specifically associated with the metastable traps responsible for the glow peaks at ~ 65 and 370 K in the Spicer CaO:Mg crystals used in this work. The nature of these traps in these particular crystals is therefore still unresolved.

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