Stable $[Li]^0$ Defects in MgO Single Crystals*

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The $[Li]^0$ center has been formed in lithium-doped single crystals of MgO by high temperature quenching. In contrast to the $[Li]^0$ center formed by low-temperature γ irradiation, the center formed by quenching is stable at room temperature. A heavy electron irradiation also produces stable $[Li]^0$ centers. Investigations using EPR and electron-nuclear double resonance techniques have established that, in all three cases, the $[Li]^0$ center has the same local configuration. The increased stability has enabled us to observe the motionally averaged $[Li]^0$ spectrum for the first time. Optical absorption data indicate that the center is associated with an absorption band at 1.83 eV.

The electronic properties of the particular class of radiation-induced centers known as "trapped-hole" or V centers have provided valuable information concerning the nature of both intrinsic and impurity-related defects in the alkaline-earth oxides. The trapped-hole centers that have been identified include the following[1-3]: (1) the intrinsic V^- and V^0 defects which are cation vacancies with one and two holes, respectively; (2) V_F, V_{OH}, and V_{Al} centers, which are cation vacancies charge-compensated respectively by fluorine, hydrogen, and aluminum inadvertently present in the crystal; and (3) $[Li]^0$, $[Na]^0$, and $[K]^0$ centers which are due to substitutional alkali ions[4-9] introduced during crystal growth.[10]

All of these alkali centers display a low-temperature EPR spectrum due to three inequivalent sites possessing tetragonal symmetry and with the principal axes lying along $\langle 100 \rangle$ crystallographic directions.[4-9] The alkali centers formed by low-temperature irradiation have been observed to annihilate upon warming to room temperature via hole release. One final characteristic of the alkali-metal-associated centers is the previous observation that the trapped hole is not completely localized even at low temperatures[9,11] and that there is a reorientation of the hole between equivalent nearest-neighbor positions. In particular, a thermal averaging of the spectrum was observed for the $[Li]^0$ center in CaO as the temperature increased[6] but, unfortunately, the thermal decay of the center above 180 K prevented the observation of a resulting isotropic "averaged" spectrum. (Such isotropic spectra have been seen in MgO[12] and CaO[13] for the room-temperature-stable V^- center.)

The present work has a threefold purpose. First, we demonstrate that it is possible to form a stable $[Li]^0$ center in MgO by means of a rapid quench from 1500 K or by high-dose electron irradiations. Second, we establish that the $[Li]^0$ center formed by quenching or electron irradiation has exactly the same local configuration as the unstable center formed by ionizing radiation at low temperatures. Third, the increased stability has enabled us to observe the motionally averaged line in the trapped-hole center EPR spectrum.

The single crystals of MgO used in these experiments were grown by an arc-fusion technique[10] using MgO powder from the Kanto Chemical Co., Tokyo. The starting MgO powder was doped with Li_2CO_3 to a concentration of about 5% by weight, but the actual concentration of lithium in the resulting single crystals was determined to be approximately 0.03 to 0.05 at.%.

The X-band EPR spectra obtained using an MgO crystal which had been doped with lithium as described above are shown in Fig. 1. For the spectrum in Fig. 1(a), the sample had been heated to 1500 K and then slowly cooled to room temperature. Spectral structures due to Mn^{4+} in both cubic and axial symmetry sites,[14] and to Fe^{3+} and Cr^{3+} in cubic sites are clearly in evidence. No

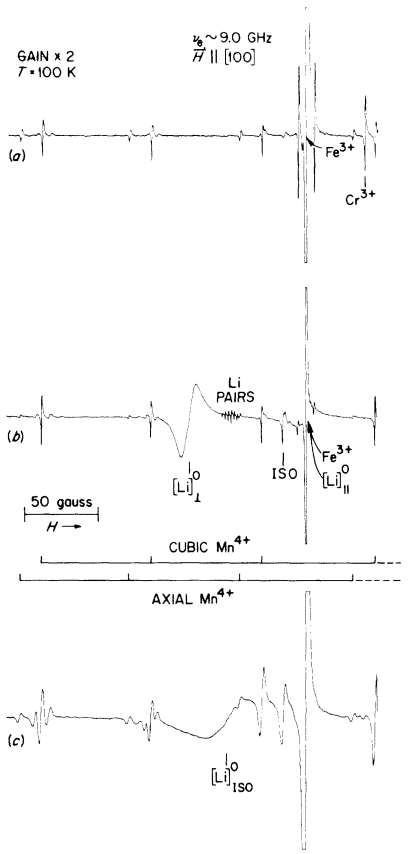

FIG. 1. EPR absorption spectra of MgO:Li crystal. (a) Spectrum at 100 K of annealed crystal with gain multiplied by 2; (b) spectrum at 100 K after quenching from 1500 K; (c) spectrum of quenched crystal at 180 K with modulation increased by 10.

spectral structure due to the $[Li]^0$ center is present, however. For the spectrum in Fig. 1(b) the crystal had been heated to 1500 K and then rapidly quenched to 77 K by immersion in a liquid-nitrogen bath. The impurity-ion spectra present are similar to those shown in Fig. 1(a) with the following exceptions: The Cr^{3+} signal has almost disappeared following the quenching. All of the quenched samples were characterized by a reduction in the cubic Fe^{3+} concentration by a factor of between 3 and 10 and by smaller changes in the intensity of the Mn^{4+} spectral structures. Extra lines are present in the spectrum shown in Fig. 1(b) which are apparently due to lithium pairs ($2I+1=7$), but these were not investigated in detail. A single isotropic line at $g=2.014(1)$ also appears in the spectrum following quenching. This line has a width of about 0.5 G at 77 K. An attempt was made to find possible Li ENDOR signals associated with this line, but none was found; and the origin of this signal is, as yet, undetermined. For

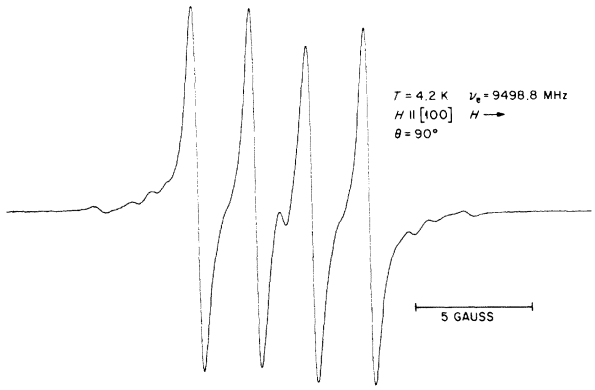

FIG. 2. EPR absorption spectrum of the $[Li]^0$ center in a quenched MgO crystal with the magnetic field perpendicular to the defect axis.

the purposes of the present work, the significant difference between Figs. 1(a) and 1(b) is the appearance of the $[Li]^0$ spectrum in Fig. 1(b) following the rapid quench. The g values determined for this axial spectrum at 77 K are in exact agreement with those determined previously for the trapped-hole $[Li]^0$ center produced by low-temperature irradiation of lithium-doped MgO crystals.[9] In contrast to the $[Li]^0$ center produced by ionizing radiation, the $[Li]^0$ trapped-hole center resulting from quenching is stable indefinitely at room temperature.

The component of the $[Li]^0$ spectrum denoted by $[Li]_\perp^0$ in Fig. 1(b) has a width of about 10 G for a sample temperature of 100 K; but on cooling to 4.2 K, this line clearly resolves into four hyperfine lines whose linewidths are approximately 0.7 G (Fig. 2). These lines are due to the $I=\frac{3}{2}$ nuclear spin of the 93%-abundant ^7Li isotope. It is also possible to observe lines due to ^{25}Mg neighbors and the 7%-abundant ^6Li isotope which has $I=1$ when very high gain settings are employed. The ^7Li hyperfine lines for the $g_\parallel$ component (i.e., for the sites whose principal symmetry axis is parallel to the applied magnetic field) remain unresolved even at 4.2 K because of the small value of the magnetic hyperfine interaction appropriate to this direction.

As the quenched crystal is warmed, the $[Li]_\perp^0$ EPR line corresponding to the orientation of the applied magnetic field perpendicular to the principal symmetry axis is observed to broaden and to move towards higher magnetic field values. As shown in Fig. 1(c), at 180 K the spectrum for the $[Li]^0$ center consists of a single isotropic line with a width of about 30 G. The g value of 2.039 experimentally determined for this line compares favorably with the average value $g_{av}=(g_\parallel+2g_\perp)/3$

$=2.0380$, where $g_{\parallel}$ and $g_{\perp}$ are the components of the tensor describing the axial low-temperature spectrum. The onset of this averaging with increasing temperature has been observed previously for the $[Li]^0$ spectrum when the trapped-hole center was formed by irradiation at low temperatures,[6] and the reorientation at the temperature of liquid helium has been investigated in some detail by Rius and Hervé[11,15] and Rius *et al.*[16] for both the radiation-induced $[Li]^0$ center and the V^- center in MgO. They determined that the reorientation rate for the $[Li]^0$ center was somewhat faster than that of the V^- center. Upon the application of uniaxial stress, they also noted that the defects tended to orient perpendicular to the stress axis for the $[Li]^0$ center and parallel to the stress axis for the V^- center.

The stable $[Li]^0$ center may be destroyed by slowly cooling the MgO crystal from 1500 K and regenerated by reheating the sample and repeating the quenching process. The reversible formation and annihilation of the $[Li]^0$ trapped-hole center has been repeated numerous times for a number of samples and identical results were obtained in each case.

An ENDOR investigation of the stable $[Li]^0$ center formed by rapid quenching of the sample was performed at a temperature of 4.2 K. The ENDOR spectra observed appeared to be exactly the same as those obtained for the radiation-induced defect. By use of the parameters determined previously for the radiation-induced $[Li]^0$ center,[9] the ENDOR spectra for the stable center were described within experimental error by a Hamiltonian given by the expression:

$$H=\mu_B[g_{\parallel}H_zS_z+g_{\perp}(H_xS_x+H_yS_y)]+AI_zS_z +B(I_xS_x+I_yS_y)+P[I_z^2-I(I+1)/3], \quad (1)$$

where all the symbols have their usual significance. The parameters and their values are $g_{\parallel}=2.0049(1)$, $g_{\perp}=2.0545(1)$, $A=+0.087(1)$ MHz, $B=-6.912(1)$ MHz, and $P=-0.014(1)$ MHz. This result establishes that the local configurations are the same for the $[Li]^0$ centers produced by the two different methods.

In addition to the stable $[Li]^0$ center in MgO which has been produced by quenching, we have also produced a room-temperature-stable $[Li]^0$ center by means of a heavy dose of electrons ($\sim 5\times10^{18}$ electrons/cm^2). Measurements using the ENDOR technique at 4.2 and 1.5 K confirm that this center is also identical to the center formed in the unirradiated quenched samples and to the unstable $[Li]^0$ center formed in the γ-irradiated samples at low temperature.

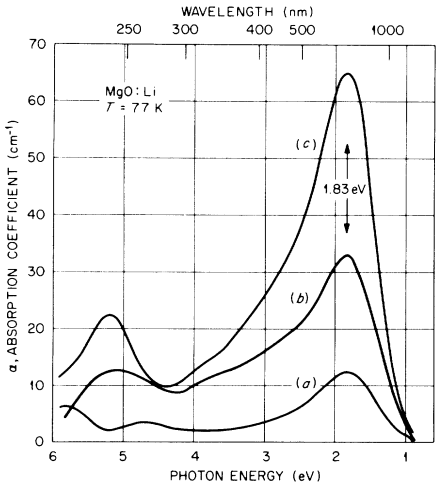

FIG. 3. Optical spectra of Li-doped MgO crystals: Curve *a*, irradiated with a short ionizing dose of electrons at 80 K; curve *b*, irradiated to 5×10^{18} electrons/cm^2 at 295 K; and curve *c*, quenched from 1500 K.

The optical absorption spectra corresponding to the three ways of generating $[Li]^0$ centers are illustrated in Fig. 3. In all instances, the spectra represent the differences in absorption coefficients before and after the irradiation or thermal treatment. Optical bands, the most pronounced of which occurs at 1.83 eV, were created as a result of a short ionizing electron irradiation at ~80 K, shown in spectrum *a*. These bands were unstable at room temperature. The same crystal, quenched from 1500 K, resulted in a more intense 1.83-eV band, spectrum *c*, which is stable even at $T\gg295$ K. Another MgO:Li crystal, irradiated to a dose of 5×10^{18} e/cm^2 at room temperature yielded spectrum *b*. Again a stable band is observed at 1.83 eV. The effect of quenching from high temperature or irradiation to large electron doses is reproducible in other MgO:Li crystals. It is expected that the 1.83-eV band is due to the optical transition of the $[Li]^0$ center by virtue of the large absorbtion half-width and peak wavelength expected of monovalent alkali trapped-hole centers.[6] This is confirmed by the parallel behavior of the band and the EPR $[Li]^0$ signal in the three situations indicated in this figure. Additionally, Modine has unequivocally established this correlation using a Magnetic-Circular-Dichroism–EPR double resonance technique.[17]

Before a definitive model for the different processes involved in the formation of the stable and unstable $[Li]^0$ centers can be formulated, addi-

tional investigations are necessary. Recently Chen and Abraham[18] have found that the addition of lithium to MgO results in a significant suppression of radiation damage in this material, and in view of the interest in using MgO as an electrical insulator in high-radiation environments, the problem of understanding the solid state processes in the lithium magnesium oxide system assumes new importance.

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[1]For a recent review of the properties of trapped-hole centers in MgO see Y. Chen and M. M. Abraham, New Phys. (Korean Phys. Soc.) 15, 47 (1975).

[2]A. E. Hughes and B. Henderson, *Defects in Crystalline Solids*, edited by J. H. Crawford, Jr., and L. M. Slifkin (Plenum, New York, 1972).

[3]B. Henderson and J. E. Wertz, Adv. Phys. 17, 749 (1968).

[4]G. Rius, R. Cox, R. Picard, and C. Santier, C. R. Acad. Sci. 271, 724 (1970).

[5]O. F. Schirmer, J. Phys. Chem. Solids 32, 499 (1971).

[6]H. T. Tohver, B. Henderson, Y. Chen, and M. M. Abraham, Phys. Rev. B 5, 3276 (1972).

[7]M. M. Abraham, Y. Chen, J. L. Kolopus, and H. T. Tohver, Phys. Rev. B 5, 4945 (1972).

[8]M. M. Abraham, Y. Chen, J. T. Lewis, and F. A. Modine, Phys. Rev. B 7, 2732 (1972).

[9]M. M. Abraham, W. P. Unruh, and Y. Chen, Phys. Rev. B 10, 3540 (1974).

[10]M. M. Abraham, C. T. Butler, and Y. Chen, J. Chem. Phys. 55, 3752 (1971).

[11]G. Rius and A. Hervé, Solid State Commun. 15, 399 (1974).

[12]L. E. Halliburton, L. A. Kappers, D. W. Cowan, F. Dravniekds, and J. E. Wertz, Phys. Rev. Lett. 30, 607 (1973).

[13]M. M. Abraham, Y. Chen, L. A. Boatner, and R. W. Reynolds, Solid State Commun. 16, 1209 (1975), and references therein.

[14]J. Rubio, Y. Chen, and M. M. Abraham, J. Chem. Phys. 64, 4804 (1976).

[15]G. Rius and A. Hervé, Solid State Commun. 15, 421 (1974).

[16]G. Rius, A. Hervé, R. Picard, and C. Santier, J. Phys. (Paris) 37, 129 (1976).

[17]F. A. Modine, to be published.

[18]Y. Chen and M. M. Abraham, J. Am. Ceram. Soc. 59, 101 (1976).

Phonon Echoes in Glass

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Phonon echoes, the acoustic analog of spin and photon echoes, are observed in fused silica glass at ultralow temperatures. From the phonon echo decay, we infer a homogeneous transverse lifetime of 14×10^{-6} sec and a longitudinal relaxation time of 200×10^{-6} sec for tunneling states at 0.68 GHz at a temperature of 20 mK. The coupling between the two-level systems and phonons is estimated to be 1.6 eV.

We have observed for the first time the existence of coherent phonon echoes in a structurally disordered solid, fused silica glass. This echo phenomenon shares many features in common with magnetic spin echoes,[1] photon echoes,[2,3] and ultrasonic spin echoes,[4] because in a phonon echo an intense pulse of acoustic energy is observed following the preparation of a resonant system by two appropriately dimensioned acoustic pulses. Unlike the nuclear spin[1] or the electronic spin[2] systems in which echoes have been observed previously, the resonant "spin" system in glass is the broadly distributed two-level atomic tunneling-state system which is believed to be an intrinsic feature of the amorphous phase.[5] The observation of a coherent resonance phenomenon arising from the inherent disorder of a solid is unique and provides a powerful method for detailed study of the decay processes of the glass tunneling states.

Photographs of oscilloscope traces of the phonon echoes appearing in Suprasil W glass at a temperature of ~20 mK are shown in Fig. 1. The first trace shows the decay of a single excitation pulse, R_{10}, at time $t=0$, followed by two acoustic reflections R_{11} and R_{12} separated by $t_d=2.2$ μsec, the round trip delay time, $v_l/2L$, of the 0.68-GHz, 100-nsec duration, longitudinal acoustic pulse. If two excitation pulses, R_{10} and R_{20}, are now applied separated by a time τ_s, in addition to