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## LETTER TO THE EDITOR

### EPR of hydrogen in lithium oxide

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**Abstract.** The EPR spectrum of interstitial  $H^0$  has been observed in x-irradiated  $Li_2O$ . Transferred hyperfine structure for  ${}^7Li$  nuclei shows that at 4 K  $H^0$  is strongly coupled to four equivalent  ${}^7Li$  neighbours, whereas at 300 K it is coupled to eight  ${}^7Li$  neighbours. It is suggested that in the low-temperature site,  $H^0$  is displaced from the centre of a cube formed by eight  $Li^+$  ions towards the centre of one face, and that temperature-induced tunnelling between the six such sites produces the high-temperature site.

As part of a programme of investigation of EPR of defects in lithium oxide, we have found a novel form of spectrum of atomic hydrogen in one batch of  $Li_2O$  crystals. This spectrum is not exhibited by all of our  $Li_2O$  crystals.

Single crystals of nominally pure  $Li_2O$  were irradiated at room temperature for 12 hours with 50 kV x-rays from a Siemens tube running at 40 mA. This produced a black coloration of the crystal which decayed with a time constant of a few hours at room temperature.

Immediately after irradiation the crystals exhibited a strong EPR spectrum comprising two lines separated by about 50 mT, centred near  $g = 2$ , and having an extensive transferred hyperfine structure (THFS). This spectrum is shown in figure 1: the lines at the centre of the spectrum arise from other defect centres. The two-line spectrum decays at room temperature at the same rate as the black colouration.

The spectrum is similar to that arising from atomic hydrogen,  $H^0$ , produced by x-irradiation in alkaline-earth fluorides, such as  $CaF_2$  (for a summary see Hayes and Stoneham 1974), and alkali halides (for a summary see Spaeth and Koschnick 1991). The separation of the two lines confirms that the spectrum we observe arises from  $H^0$ ; the separation in free atomic hydrogen is 50.7 mT. The transferred hyperfine interaction with  ${}^7Li$ —essentially the only nucleus in the material with a magnetic moment, as  ${}^{17}O$  and  ${}^6Li$  are of too low abundance to be observable—gives an indication of the nature of the site occupied by the  $H^0$  atom. The nuclear spin of  ${}^7Li$  is  $\frac{3}{2}$ , and the relative intensities of the lines of the THFS pattern observed at 300 K, equally spaced by 1.28 mT, indicate that the unpaired electron interacts with eight equivalent nuclei with  $I = \frac{3}{2}$ . All 25 lines of the symmetrical THFS pattern, of relative intensity from the outside to the centre (1:8:36:120:322:728:1426:2464:3805:5292:6674:7660:8016:7660: . . .), are not observed because the outermost are too weak, but the relative intensities of the observed 19 lines are an unambiguous indication of the eight equivalent neighbours.

$Li_2O$  has the same structure as  $CaF_2$  with anions and cations interchanged, so it has been called the anti-fluorite structure. This comprises a simple cubic array of  $Li^+$  atoms

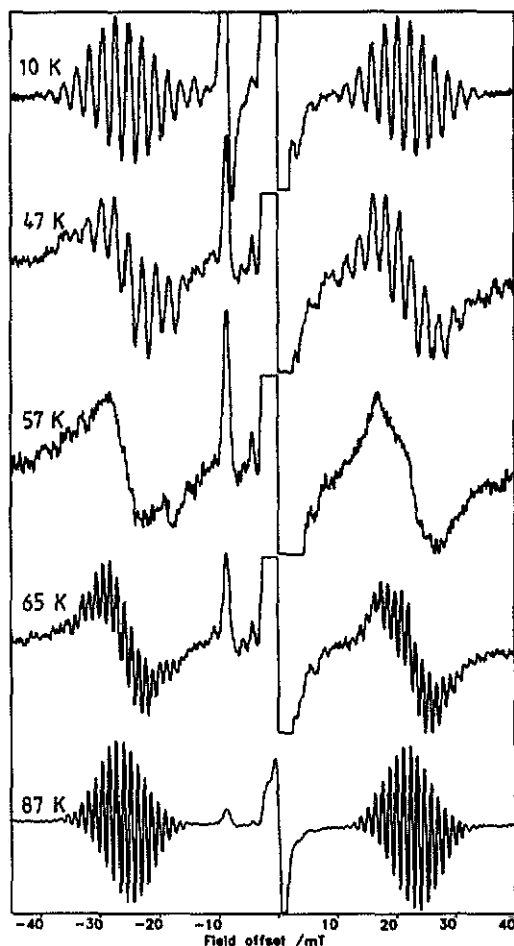


Figure 1. EPR spectra at various temperatures for the same orientation of applied magnetic field.

of which alternate body centres are occupied by  $O^{2-}$ , and alternate body centres are empty. Hence, the likely site for  $H^0$  with eight equivalent  $Li^+$  neighbours is either  $O^{2-}$  vacancy or an interstitial at an empty body-centre site, the latter being more likely for a neutral atom.

At 4 K the THFS comprises fewer equally spaced lines with separation 2.45 mT. Its form suggests that the unpaired electron interacts with four equivalent  $^7Li$  nuclei. For some directions of the applied field  $B$ , all 13 lines are observed with relative intensities of approximately (1:4:10:20:31:40:44:40:...). The overall separation of the two hyperfine lines of  $H^0$  is similar at 4 K to that at 300 K.

Figure 1 shows the spectrum at several temperatures between 4 K and 300 K. Around 55 K the THFS is unresolved.

This suggests that at low temperatures  $H^0$  is in a site displaced from the centre of the cube of eight  $Li^+$  ions along a  $\langle 100 \rangle$  direction towards the centre of one of its faces. Hence it interacts more strongly with the four equivalent nearest  $^7Li$  nuclei and less strongly

with the four more distant  ${}^7\text{Li}$  nuclei. There would presumably be six such sites corresponding to displacement along equivalent  $\langle 100 \rangle$  directions. As the temperature is raised from 4 K,  $\text{H}^0$  tunnels between these possible sites, the tunnelling rate increasing with temperature. Increasing the tunnelling rate broadens the lines until they become unresolved around 55 K. At higher temperatures the tunnelling becomes rapid enough that the nuclei experience only the averaged hyperfine field of all the sites, so the lines become narrow again, and the average hyperfine separation is the mean of the hyperfine separations for the two sets of neighbours at 4 K. So far as we are aware, no such spectrum with motionally averaged extensive THFS has previously been observed in a solid.

At 300 K the EPR spectrum appears to exhibit no anisotropy as the direction of the magnetic field  $\mathbf{B}$  is varied in the crystal. Hence the spectrum can be described by the spin Hamiltonian

$$H = g\mu_B \mathbf{B} \cdot \mathbf{S} + AS \cdot \mathbf{I} + A'_s \mathbf{S} \cdot \sum_{n=1}^N \mathbf{I}_n \quad (1)$$

where  $S = \frac{1}{2}$ ,  $I = \frac{1}{2}$  (proton), and  $I_n = \frac{3}{2}$  for each of the  $N$   ${}^7\text{Li}$  ligands. The prime is used to differentiate the hyperfine parameters for ligands from that of the proton. The measured spin Hamiltonian parameters are as follows:

$$N = 8 \quad A/h = 1462(14) \text{ MHz} \quad A'_s/h = 35.8(8) \text{ MHz} \quad g = 2.003(1).$$

For the cubic site at 300 K, the isotropy of  $g$  and  $A$  are not unexpected, although one would expect an anisotropic contribution to the ligand hyperfine matrix  $\mathbf{A}'$  at least from magnetic dipole-dipole interaction. This dipolar contribution for the known crystal structure is calculated to be  $A'_d = 3.8$  MHz. The spin Hamiltonian for the hyperfine interaction with each  ${}^7\text{Li}$  nucleus allowed by the symmetry, expressed in terms of the bond direction for the  $n$ th ligand, is

$$\mathbf{SA}'\mathbf{I}_n = A'_s \mathbf{S} \cdot \mathbf{I}_n + (A'_p + A'_d)(S_z I_{nz} - \frac{1}{3} \mathbf{S} \cdot \mathbf{I}_n). \quad (2)$$

A reconstruction of the spectrum expected for eight  ${}^7\text{Li}$  ligands, using the experimentally observed line width (18 MHz peak to peak of the derivative), showed that for  $A'_p + A'_d$  up to 10% of  $A'_s$  one would not be able to resolve the effects of the anisotropic term. This contrasts with  $\text{H}^0$  in  $\text{CaF}_2$ , where it was possible to resolve the effects of the anisotropic terms, both because the value of  $A'_s/h$  (104.1 MHz) is larger and because the line width is smaller ( $\approx 12$  MHz peak to peak of the derivative) (Hall and Schumacher 1962). The relative magnitudes of the line widths in  $\text{CaF}_2$  and  $\text{Li}_2\text{O}$  is close to that calculated for purely dipolar interaction with distant nuclei, using the formula of van Vleck (1948), although for both materials the measured values are about three times larger than calculated for purely dipolar interaction. Some of this discrepancy in  $\text{CaF}_2$  is accounted for by contact interaction with more distant nuclei, and some by zero-point motion of the  $\text{H}^0$ . In  $\text{Li}_2\text{O}$ , there is also a contribution from sites containing  ${}^6\text{Li}$ , and there may be a residual contribution from tunnelling between sites. In principle, a large quadrupole interaction could affect the THFS pattern through forbidden transitions, but by comparison with F centres in alkali halides (Holton and Blum 1962) the quadrupole interaction is expected to be too small. The upper limit our measurements allow us to place on the anisotropic term indicates that the anisotropy is not as large as for  $\text{H}^0$  in  $\text{CaF}_2$ , where  $A'_p + A'_d$  is 34% of  $A'_s$ . This is because there is a large contribution from 2p electrons on  $\text{F}^-$ , whereas the 2p electron contribution for  $\text{Li}^+$  is expected to be very small (Zorita and Casas-Gonzales 1990).

The value of  $A'_s$  gives an indication of the value of  $|\varphi(L)|^2$ , the density of the unpaired electron wavefunction at the site of the ligand  $L$ . Our value of  $A'_s$  indicates for  $\text{Li}_2\text{O}$  a value of  $125 \times 10^{21} \text{ cm}^{-3}$  at the  $\text{Li}^+$  ligand 0.200 nm from  $\text{H}^0$ , compared with a value for  $\text{CaF}_2$  of  $166 \times 10^{21} \text{ cm}^{-3}$  for the  $\text{F}^-$  ligand 0.237 nm from  $\text{H}^0$ . This value for  $\text{Li}^+$  is almost identical to that for the F centre (an electron trapped at a  $\text{F}^-$  vacancy) in  $\text{LiF}$  for an almost identical distance from the centre (Holton and Blum 1962).

The spectrum observed at 4 K, to a first approximation, can be described by spin Hamiltonian (1) with the parameters

$$N = 4 \quad A/h = 1410(30) \text{ MHz} \quad A'(1)_s/h = 69(3) \text{ MHz} \quad g = 2.003(1).$$

The  $\text{Li}^+$  ligands have been labelled (1) to distinguish them from the other four  $\text{Li}^+$  ligands, hereafter labelled (2), whose THFS is not resolved.

This site might be expected to be anisotropic, because the interaction with only four  ${}^7\text{Li}$  suggests a site of  $C_{4v}$  symmetry displaced along  $\langle 100 \rangle$  towards the centre of cube face. The symmetry of such a site would allow  $\mathbf{g}$  and  $\mathbf{A}$  to be anisotropic as well as  $\mathbf{A}'(1)$ . Such anisotropy could be visualized as being produced by an admixture into the  $1s$  state of  $\text{H}^0$  of an electron in an antibonding orbital of a rather elongated  $\text{OH}^{2-}$  radical formed between the displaced  $\text{H}^0$  and the adjacent  $\text{O}^{2-}$ , or as a small admixture of a  $2p_z$  orbital on  $\text{H}^0$  caused by the interaction with the environment. The anisotropies of the  $g$ -factor and hyperfine matrix  $\mathbf{A}$  are likely to be very small. The effects of anisotropy in  $\mathbf{A}'(1)$  would be more complicated than for the cubic site because there are three differently oriented tetragonal sites, or 12 differently oriented H-Li bonds (rather than four in the cubic site).

At 4 K, the spectrum does show anisotropy in some features. For all directions of  $\mathbf{B}$  there is a well resolved THFS for which separations between the lines do not vary over the spectrum, or as a function of direction, by more than a few per cent. What does vary a little with the direction of  $\mathbf{B}$  is the number of lines observed, their relative intensity, the shape of their envelope and the position of the strongest line. It is the interpretation of these changes that makes the value of  $A/h$  somewhat uncertain. That the THFS remains well resolved for all directions of  $\mathbf{B}$ , for a potentially complicated pattern of lines, suggests that the anisotropy in the ligand interaction is less than 10% of the isotropic component. That there is near symmetry about the centre of the spectrum shows that  $g$  is isotropic. The line width ( $\approx 36$  MHz peak to peak of the derivative) prevents the resolution of any structure arising from anisotropic effects. The changing shape of the THFS patterns suggests anisotropy in  $\mathbf{A}/h$  of up to 30 MHz, so THFS patterns for differently oriented sites have small relative shifts. There are too many variables in the spin Hamiltonian for it to be possible to make deductions from simulated spectra. For comparison,  $\text{H}^0$  has been observed in three other types of non-cubic site: (a) in  $\text{H}^0\text{-Sr}^{2+}$  and  $\text{H}^0\text{-Ca}^{2+}$  substituting for two cations in  $\text{KCl}$  and  $\text{RbCl}$  (Hoentzsch and Spaeth 1978, Studzinski *et al* 1980), where no evidence was given of anisotropy in  $\mathbf{g}$  or  $\mathbf{A}$ ; (b) in beta alumina, where  $g_{\parallel} - g_{\perp} = 0.0009$  and  $A_{\parallel} - A_{\perp} = 2.8 \pm 5.6$  MHz (Ueda *et al* 1983); (c) in alpha quartz, where  $g_{\text{max}} - g_{\text{min}} = 0.00017$  and  $A_{\text{max}} - A_{\text{min}} = 7.11$  MHz (Perlson and Weil 1974).

The greater line width in the tetragonal site presumably arises from unresolved transferred hyperfine interaction  $\mathbf{A}'(2)$  with the other four  ${}^7\text{Li}$  more distant ligands of  $\text{H}^0$ . If  $A'_s$  is a motional average of  $A'_s(1)$  and  $A'_s(2)$ , we can estimate that  $A'_s(2)$  is 3.6 (3.6) MHz. Depending upon the amount by which  $\text{H}^0$  is displaced from the centre of the interstitial site,  $A'_d(2)$  would be between 3.8 and 1.3 MHz.

A comparison of the EPR signal strength of  $H^0$  with a calibrated sample indicates that our sample contains approximately  $5 \times 10^{15}$   $H^0$  atoms per  $\text{mm}^3$ , or one  $H^0$  atom per 3000 Li atoms. It seems probable that the crystal as grown had incorporated some hydrogen in the form of  $\text{OH}^-$  on a  $\text{O}^{2-}$  site, as it is both difficult to dehydrate completely the starting material,  $\text{LiCO}_3$ , from which the  $\text{Li}_2\text{O}$  was made, and also to eliminate all hydrolysis of the finely divided  $\text{Li}_2\text{O}$  before crystallization. Such  $\text{OH}^-$  may be incorporated substitutionally for  $\text{O}^{2-}$ , either simply or in association with an adjacent  $\text{Li}^+$  vacancy for charge compensation; the latter situation is not much different from  $H^+$  substituting for  $\text{Li}^+$ . As in  $\text{CaF}_2$ , where  $H^-$  is incorporated substitutionally into as-grown crystals, x-irradiation both creates electrons and holes and also displaces H into a position sufficiently far removed from its starting site to produce an interstitial site with cubic symmetry. That it takes several hours at room temperature for H to return to its initial site suggests that it is not just a matter of  $H^0$  capturing a hole and becoming attached to the adjacent  $\text{O}^{2-}$  to form a substitutional  $\text{OH}^-$ .

Because of the large line width, it is unlikely that a careful analysis of the hyperfine structure of the EPR will give more information about this centre. A  $^7\text{Li}$  ENDOR investigation will be undertaken to establish the anisotropic contribution to  $\mathbf{A}'(1)$  in the tetragonal site, and also to measure  $\mathbf{A}'(2)$  and  $\mathbf{A}'$  for more distant sites. From the latter, if non-dipolar anisotropic contributions are not too large, it should be possible to identify the exact site of  $H^0$ . If ENDOR could be measured above 60 K the anisotropic contribution to  $\mathbf{A}'$  in the cubic site could be measured. Also a proton ENDOR investigation of the site at 4 K will establish the magnitude of the anisotropic contribution to the hyperfine interaction with the proton.

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