

Evidence of Molecular-Oxygen Inclusions in Electron-Irradiated Li_2O Crystals through Magnetization Measurements

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We have measured the temperature-dependent magnetization of electron-irradiated Li_2O crystals exhibiting metallic lithium colloids as determined by conduction-electron spin resonance. While diamagnetic before irradiation, the sample is paramagnetic afterwards, with an antiferromagnetic ordering transition at 38 K. The magnetism is attributed to ≤ 1 mol% of molecular oxygen produced together with the Li colloids. It is supposed to be contained in relatively incompressible cavities and to form a solid under “negative” pressure when freezing.

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It has been shown recently that lithium oxide irradiated with energetic electrons near room temperature exhibited metallic Li colloids, which could be observed by conduction-electron spin resonance (CESR), dielectric constant measurements, optical microscopy, and nuclear magnetic resonance (NMR) Knight shift [1–4]. In particular, it appeared that, in monocrystalline specimens, two types of colloid sizes were present after irradiation ($\ll 1 \mu\text{m}$ and $> 1 \mu\text{m}$) giving rise to different CESR signals and to a splitting of the Knight-shifted NMR line. Also, they exhibited quite distinct recovery behavior during thermal annealing.

On the other hand, there was very little evidence for the fate of the complementary radiolysis product to metallic lithium, namely, molecular oxygen. In fact, the Li colloids are formed as a result of a complex mechanism implying ionization, displacement, and diffusion processes, initiated by the creation of charged oxygen vacancies or F^+ centers. The latter are expected to interact with each other forming cavities as a final result. The oxygen ions, pushed out of their sites during the primary collision process, would then migrate through the lattice agglomerating to neutral O_2 molecules for charge conservation reasons. These molecules will either stay inside the sample in bubble form or leave the specimen through the surface. Since we had shown earlier [2,3] that a typical irradiation of Li_2O resulted in concentrations of up to 10^{-2}Li° atoms per formula unit, a corresponding mass loss should be easily detectable in our experimental conditions (specimen weight of the order of 10 mg). As the latter was not the case, we started looking for signs of oxygen presence inside the crystals, especially since optical micrographs had revealed [4,5] that the big Li colloids were attached to large transparent disklike cavities oriented along the $\{111\}$ planes of the fcc Li_2O host lattice. Suspecting the presence of O_2 gas within these cavities, we had undertaken to detect it by measuring the magnetization of the

sample at low temperatures hoping for the observation of possible magnetic manifestations. As shown below, there are not only strong indications for the presence of paramagnetic oxygen gas but also for the paramagnetic-antiferromagnetic (AF) transition of the solid oxygen.

$\sim 3 \times 4 \text{ mm}^2$, 500–600 μm thick specimens were prepared by cleaving Li_2O crystals along (111) and irradiated at 275 K by 1-MeV electrons at the Van de Graaff accelerator of the Laboratoire des Solides Irradiés, to a fluence of the order of $5 \times 10^{19} e^-/\text{cm}^2$. The irradiation temperature was controlled by the beam current, which was of the order of 40 $\mu\text{A}/\text{cm}^2$. The introduced Li colloids were then detected and characterized by CESR (Bruker ER 200D X-band spectrometer). A typical result is shown in Fig. 1, with a temperature-independent narrow Lorentzian line due to small colloids ($\sim 10^2 \text{ nm}$ size)

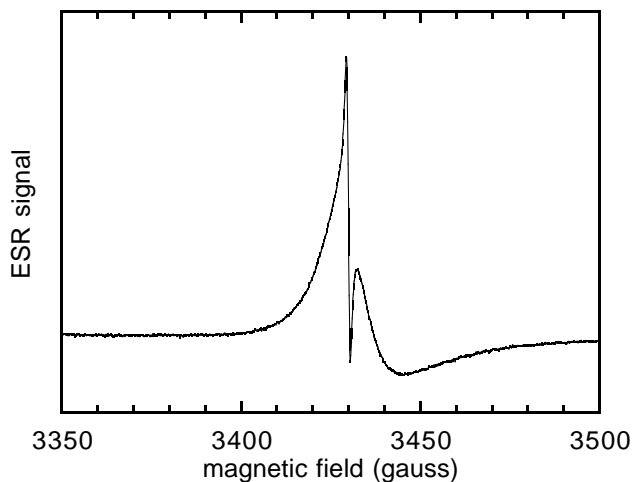


FIG. 1. Room-temperature EPR spectrum of a Li_2O crystal irradiated at 275 K, presenting a Lorentzian line superimposed upon a Dysonian one, due to various types of Li colloids. The narrow line is saturated and overmodulated.

superimposed upon a broader Dysonian line caused by colloids of $>1 \mu\text{m}$, both centered at $g = 2.0023$. The intensity of the former corresponds to a Li-metal concentration of 3×10^{-5} , the latter to that of 8×10^{-4} , probably underestimating the real value because of the skin effect [2,3]. Magnetization measurements were then performed between 1.8 and 300 K, generally in the warming regime, using a SQUID susceptometer (Quantum Design MPMS-5), with an applied external field of 4.7 T, the sample being placed at zero field in the instrument.

Figure 2 shows the susceptibilities of a nonirradiated and an irradiated Li_2O crystal as a function of temperature. As expected, the virgin crystal is weakly diamagnetic, with a susceptibility of -1.4×10^{-6} emu/g, the slight upturn at low temperatures possibly due to paramagnetic impurities (we had ~ 30 at ppm of Mg and Al each, and 0.9 at ppm Fe in our crystal). After irradiation, the sample has turned paramagnetic and exhibits an ordering transition at 38 K. A fit of the high- T part by a form $\chi = A + B/(T - \Theta)$ gives the constants $A = -5.0 \times 10^{-7}$ and $B = 3.25 \times 10^{-4}$ K, with a paramagnetic Curie temperature $\Theta = -58$ K, establishing the transition at $T_N = 38$ K as AF and clearly relating it to the β - γ transformation of solid oxygen. Furthermore, a closer look at the region around T_N (Fig. 3) shows a break at 50 K which is close to the melting point of bulk oxygen, $T_m = 54.4$ K, such as seen in susceptibility measurements [6].

Following the above quantitative and qualitative arguments, it seems reasonable to consider the molecular oxygen to be responsible for the magnetic transformation of Li_2O by irradiation. Assuming a value for the susceptibility of solid γ - O_2 at 50 K of $\chi(\text{O}_2) = 3 \times 10^{-4}$ emu/g (e.g., Ref. [6] or [7]), we can estimate the concentration of molecular oxygen in the irradiated Li_2O sample as 0.8–0.9 at %. This is an order of magnitude more than the Li-colloid concentration estimated from the CESR sig-

nals in Fig. 1 but probably close to the true value, in view of the skin effect mentioned above. In fact, we had noted recently [8] an analogous underestimate of the Li-colloid concentration in an irradiated Li_2O crystal when comparing the CESR intensities with the results obtained from differential scanning calorimetry of Li metal melting: 2.3×10^{-3} and 10.2×10^{-3} respectively, supporting this suggestion. We have also tried to check for an eventual dose dependence of the sample magnetization. The qualitative comparison was satisfactory considering the demagnetization factors due to the different crystal shapes. The transition temperatures did not vary, suggesting a relatively constant cavity size (in agreement with earlier optical observations [4,5])—essentially the result of a coalescence process.

When assigning the break at 50 K to the melting point and the transition at 38 K to the β - γ transformation of solid oxygen, one has to remember that bulk oxygen exhibits (e.g., Ref. [7] or [9]) a $T_m = 54.4$ K and a $T_N = 43.8$ K, some 5–6 degrees Kelvin above our measured values. This difference could be attributed to the fact that, in our case, oxygen is contained in bubble form in a host lattice, with possibly unusual environmental, for example, pressure conditions. Now, Meier *et al.* [9] had observed that, in bulk oxygen, T_N shifted under pressure towards higher values by about 6 K per 10^8 Pa; and the melting curve of oxygen indicates [10] a corresponding shift of T_m by ~ 10 K per 10^8 Pa. Our negative T shifts would, therefore, mean negative pressures. Such a situation could be envisaged for cases where a liquid was filling a cavity surrounded by material with a much lower expansion coefficient than the liquid in its solid phase. This is just what is encountered here: γ oxygen, with a volume expansion coefficient at 50 K of $2.3 \times 10^{-3} \text{ K}^{-1}$ —sometimes called “plastic phase” [11]—contracts 30 times more than the surrounding Li_2O crystal, with a $d/dT(\Delta V/V) \approx 8 \times 10^{-5} \text{ K}^{-1}$ as extrapolated from room-temperature data [12]. Since, at

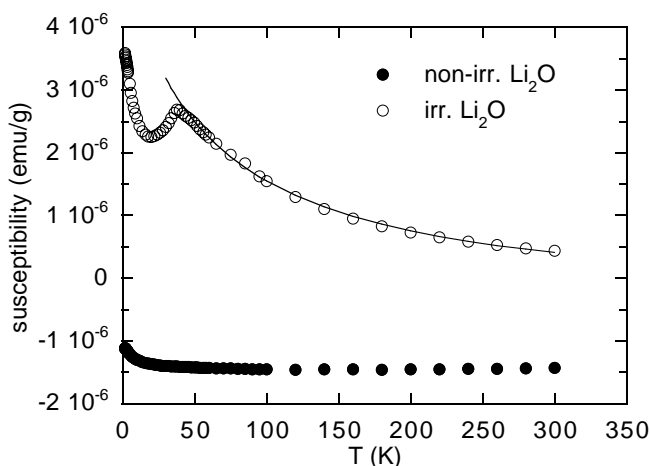


FIG. 2. Temperature dependence of the susceptibilities for an unirradiated (diamagnetic) Li_2O crystal and for the irradiated crystal of Fig. 1, showing a Curie-Weiss fit at higher temperatures, with a paramagnetic $\Theta = -58$ K for the latter.

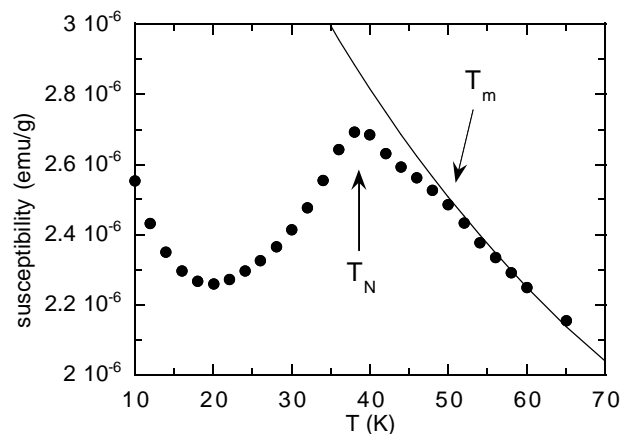


FIG. 3. Enlarged view of the region around T_N , indicating a break at the melting point of solid oxygen.

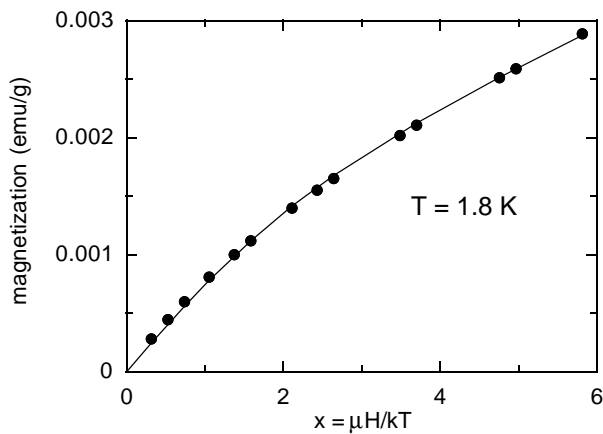


FIG. 4. Field dependence (in reduced units) of the magnetization at $T = 1.8$ K, for the irradiated Li_2O crystal, and its fit by a Langevin-type function $M = ax + b[1/\tanh(x) - 1/x]$, with $\mu = 2.83\mu_B$ as the oxygen magnetic moment.

the same time, the oxygen compressibility in the γ phase is also nearly 2 orders of magnitude higher [13] than that of Li_2O , we are tempted to consider the possibility of negative pressures existing inside the cavities. A rapid estimate using the bulk modulus for γ -oxygen [13], $B(\gamma\text{-O}_2) = V \cdot \Delta P / \Delta V = 2.2$ GPa, gives, with a $\Delta V/V \sim 3\% - 4\%$ for the contraction at the melting point [11,14], a negative pressure $\Delta P \sim 0.08$ GPa when assuming an incompressible Li_2O surrounding [in view of a $B(\text{Li}_2\text{O}) = 82$ GPa [12]]. This negative ΔP would lead to a negative T_m shift of ~ 8 K, in surprisingly good agreement with the measured ΔT_m . The same is true, to an even higher degree because of an additional thermal contraction between T_m and T_N , for the γ - β transformation. It is also worth mentioning, in this context, that micron-size gas bubbles were observed in neutron-irradiated Li_2O and assigned to helium originating from the lithium burnup in the aftermath of the ${}^6\text{Li}(n, \alpha){}^3\text{H}$ reaction [15]. Though the irradiation conditions and products in the two cases are quite dissimilar, it is satisfying to note that large gas bubbles can be formed in this material. Earlier manifestations of gaseous inclusions in ionic oxide crystals after irradiation are, for example, reported in Ref. [16] concerning the observation, in neutron-irradiated MgO , of cavities filled with the transmutation products He and Ne.

As to the missing α - β transition (at 24 K in bulk oxygen under normal pressure) and the upturn below 20 K instead (Fig. 3), it could—following the discussion in Ref. [7]—be related to the presence of two-dimensional layers, either amorphous as suggested by measurements on adsorbed oxygen by Gregory [17] or as the metastable $m\text{-O}_2$ phase measured by Jones *et al.* [18], coexisting with the α phase or blocking it. The stabilizing role of impurities suggested in Ref. [18] could, in our case, be

taken over by the unusual situation given by the cavity environment. The field dependence of the magnetization measured at 1.8 K between 0.3 and 5.5 T showed, for the irradiated crystal, a deviation from linearity, which could be fitted by a Langevin-type function (Fig. 4). This might be an indication for superparamagnetic behavior—another possibility envisaged in Ref. [17] for thin oxygen layers.

Concluding, we have observed the presence of molecular oxygen in electron-irradiated Li_2O crystals, which seems to be trapped within large cavities. It not only renders the initially diamagnetic specimen paramagnetic, but also exhibits the γ - β transition towards the antiferromagnetic state. The negative shift of the transformation temperatures is explained by a negative pressure on the solid oxygen existing in the practically incompressible cavities upon freezing.

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