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Reassessment of Li colloid production and characterization in irradiated Li_2O

P. Vajda *, F. Beuneu

Laboratoire des Solides Irradiés, CNRS–CEA, Ecole Polytechnique, F-91128 Palaiseau, France

Abstract

Poly- and monocrystalline Li_2O samples have been irradiated by 1 and 2.5 MeV electrons at various doses and temperatures and their EPR spectra measured. At low doses, less than 10^{19} e^-/cm^2, and for $T_{irr} < 150$–200 K, the spectra contain a 0.2 mT broad line at $g = 2.0035(3)$, recovering at 650°C, which is due to non-metallic F-center agglomerates and which corresponds to that observed by Noda et al. (Rad. Eff. 97 (1986) 297) in ion- and neutron-irradiated Li_2O. For higher doses and higher T_{irr}, the spectra contain signals at $g = 2.0023(1)$ caused by metallic Li colloids. The latter exist in two sizes, $\ll 1$ μm and $\gg 1$ μm, represented by a Lorentzian and a Dysonian signal, respectively; the former annealing at 300°C, the latter near 450°C. Optical microscopy on semi-transparent crystals indicates that the large colloids are disk-shaped and oriented along {1 1 1}.

1. Introduction

Li_2O is not only a potential tritium breeding material for fusion-reactor application but also a very promising model system for fundamental defect studies. Hence, radiation damage induced by energetic neutrons and ions in Li_2O has been extensively studied during the past decade, in particular by the group of Noda and coworkers at JAERI. Thus, using optical and electron spectroscopy, they identified the F^+-center [1] and attributed an additional EPR-line to metallic lithium [2]. In a recent publication [3], we had argued that the signal described in Ref. [2] was due to non-metallic F-center agglomerates. On the other hand, we succeeded in observing a much narrower temperature-independent line ($\Delta H \sim 10^{-2}$ mT) which emerged in room-temperature electron-irradiated Li_2O [3] at $g = 2.0023$ and was superimposed in single crystals by a wider ($\Delta H \sim 1$ mT) Dysonian signal, also at $g = 2.0023$. Both were clearly originating from metallic Li, as confirmed by NMR and dielectric-constant measurements, and were assigned to colloids of different sizes [4,5].

In this communication, we are further specifying the conditions for colloid creation, as concerns the irradiation dose and temperature, and report also new observations on the anisotropic character of their shape and distribution.

2. Experimental

The specimens were 0.5 to 1 mm thick platelets of irregular form cut from polycrystalline grains (obtained from Cerac) or cleaved from a single crystal grown by a floating-zone method [5] from a sintered rod. The irradiations were performed on a van de Graaff accelerator using 1 and 2.5 MeV electrons. The samples were wrapped in 10 μm Cu-foil and mounted in a liquid-hydrogen cryostat above the liquid bath. The irradiation temperature, T_{irr}, was controlled by the electron beam and measured with a thermocouple soldered to the Cu bag. Typical beam currents were of the order of 40 μA/cm^2, in the interval 150 K $\leqslant T_{irr} \leqslant$ 300 K.

EPR experiments were done with a Bruker ER 200D spectrometer operating at 9.5 GHz, in the 4–300 K range, using a TE_{104} double cavity with a $CuSO_4$ standard at room temperature to check for possible cavity Q-factor variation. Optical microscopy was performed with a polarizing Reichert Polyvar transmission microscope with digital photography. Occasional isothermal annealing treatments (1 h at each temperature) were made in a dynamic vacuum.

* Corresponding author.

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3. Results and discussion

3.1. EPR

In Ref. [3] we had shown that electron irradiation of Li_2O polycrystals at temperatures $T_{irr} \leqslant 200$ K, had induced the creation of F^+-centers which, upon annealing, transformed into F-clusters disappearing above 600°C. For higher T_{irr} and doses close to 10^{20} e^-/cm^2, small ($\sim 10^2$ nm) metallic Li colloids were formed characterized by a narrow Lorentzian EPR line annealing at ~300°C, while single crystals exhibited [4], in addition, a broad Dysonian signal due to big Li colloids (>1 μm). In what follows, we shall present the results of the variation of different irradiation parameters, e.g. dose or T_{irr}, upon the EPR spectra of various types of specimens and their annealing behaviour. (No qualitative difference between 1 and 2.5 MeV irradiations was noted, but there seems to exist a lower threshold for colloid creation at $E_{e^-} = 300$–350 keV. An irradiation at 300 K with $\sim 10^6$ Gy of γ-photons produced by 2.5 MeV electrons impinging upon a thick Cu target did not yield any colloids.)

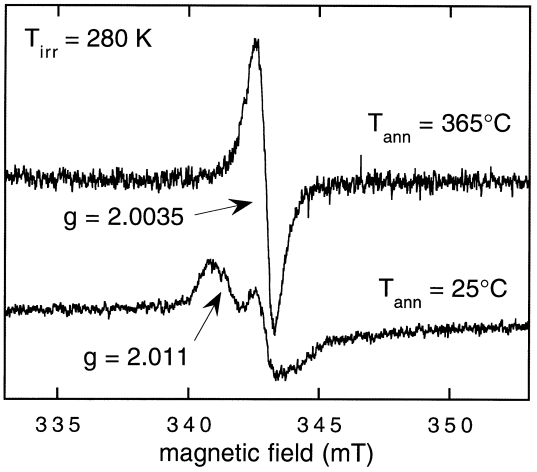

Fig. 1. Room-temperature EPR spectra of polycrystalline Li_2O irradiated at 280 K with 1 MeV electrons to a dose of 0.4×10^{19} e^-/cm^2. Below: after irradiation; above: after an anneal at 365°C. Microwave power $P = 24$ dB (780 μW), modulation $M = 0.2$ mT.

3.1.1. Low-dose irradiation

Fig. 1 shows the spectrum obtained with polycrystalline Li_2O bombarded at room temperature with 0.4×10^{19} e^-/cm^2, an order of magnitude less than the typical doses employed in Refs. [3–5]. Right after irradiation, the spectrum consists of two signals, one centered at $g = 2.0035$, slightly overlapping another at $g = 2.011$. No trace of a colloidal line at $g = 2.0023$ can be found. Upon annealing, the broad line near $g = 2.011$ disappears rapidly while the signal at $g = 2.0035$ grows simultaneously (Fig. 2). The positions and the evolution of these lines correspond to those observed earlier (e.g. Fig. 6 of Ref. [3]) in low-T irradiated Li_2O and attributed to small F-center clusters of various sizes (in accord with Uchida et al. [6]), as well as to the growth of the latter before decomposition. Their size increase in the course of the anneal is also manifest through line narrowing (ΔH diminishing from 0.8 to 0.3 mT) and g-factor decrease (shifting from 2.0042 to 2.0031); it is accompanied by a colour change from khaki to black before final bleaching. The seemingly too strong intensity increase above $T_{ann} = 300$°C could be due to the transformation of otherwise EPR-inactive centers such as F_2, F_4 etc.

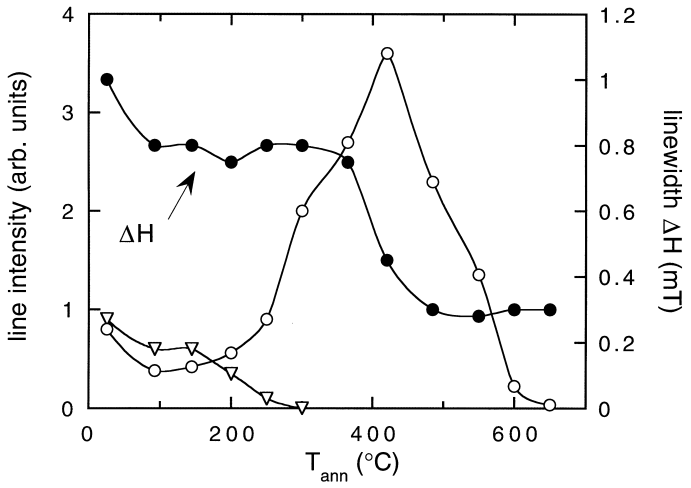

Fig. 2. Isochronal annealing of the EPR lines of Fig. 1, together with the linewidth ΔH of the $g = 2.0035$ signal. o: $g = 2.0035$; ▽: $g = 2.011$.

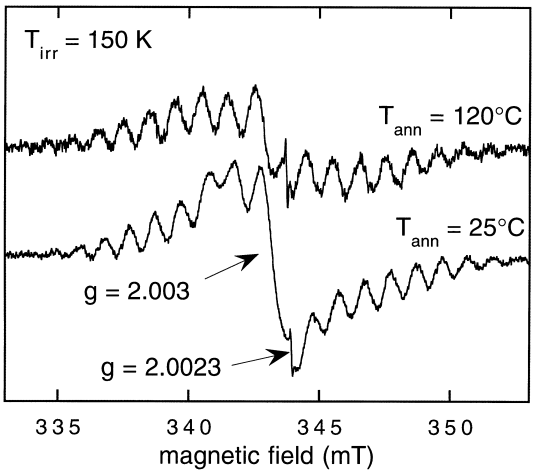

Fig. 3. Room-temperature EPR spectra of a single crystal of Li_2O irradiated at 150 K with 1 MeV electrons to a dose of 4.8×10^{19} e^-/cm^2. Below: after irradiation; above: after an anneal at 120°C. $P = 24$ dB (780 μW), $M = 0.1$ mT.

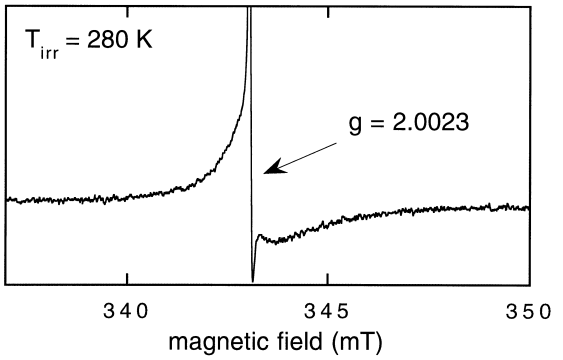

Fig. 4. Same as in Fig. 1 irradiated to a dose of 9.4×10^{19} e^-/cm^2. $P = 0$ dB (200 mW), $M = 0.05$ mT.

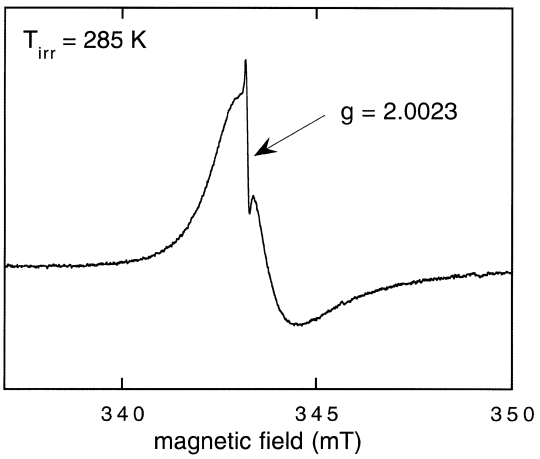

Fig. 5. Room-temperature spectrum of a single crystal of Li_2O irradiated at 285 K with 2.5 MeV electrons to a dose of 5.3×10^{19} e^-/cm^2. $P = 0$ dB (200 mW), $M = 0.1$ mT. Note the Dysonian and the Lorentzian colloid lines at $g = 2.0023$ (the latter saturated and overmodulated).

3.1.2. Low-temperature irradiation

Fig. 3 exhibits the spectra taken on a Li_2O single crystal after irradiation at $T_{irr} = 150$ K with 4.8×10^{19} e^-/cm^2. Note the presence of the $g = 2.003$ line superimposed upon the hyperfine signal of the F^+-center, but also the manifestation of the colloidal line at $g = 2.0023$. (Analogous spectra were obtained for $T_{irr} = 200$ K.) This result has to be compared with the polycrystal irradiations of Ref. [3] where one had to reach a $T_{irr} = 200$ K to observe first signs of the $g = 2.0023$ line, stressing the less favourable growth conditions (more trapping centers) in the latter case.

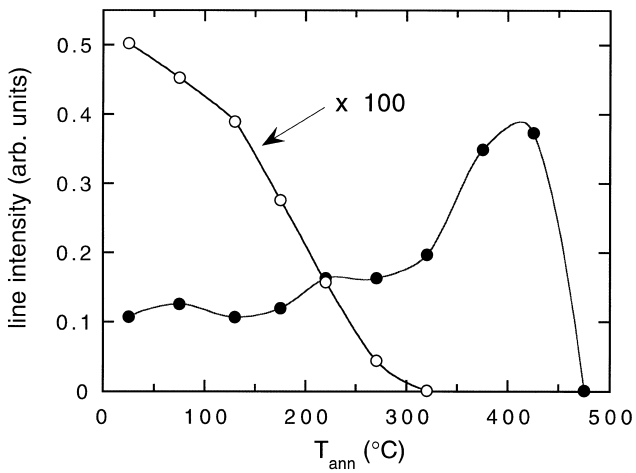

Fig. 6. Isochronal annealing of the two lines of Fig. 5 (○: Lorentzian, ●: Dysonian). The sample begins to bleach at 425°C and decomposes into white powder for $T_{ann} = 475$°C.

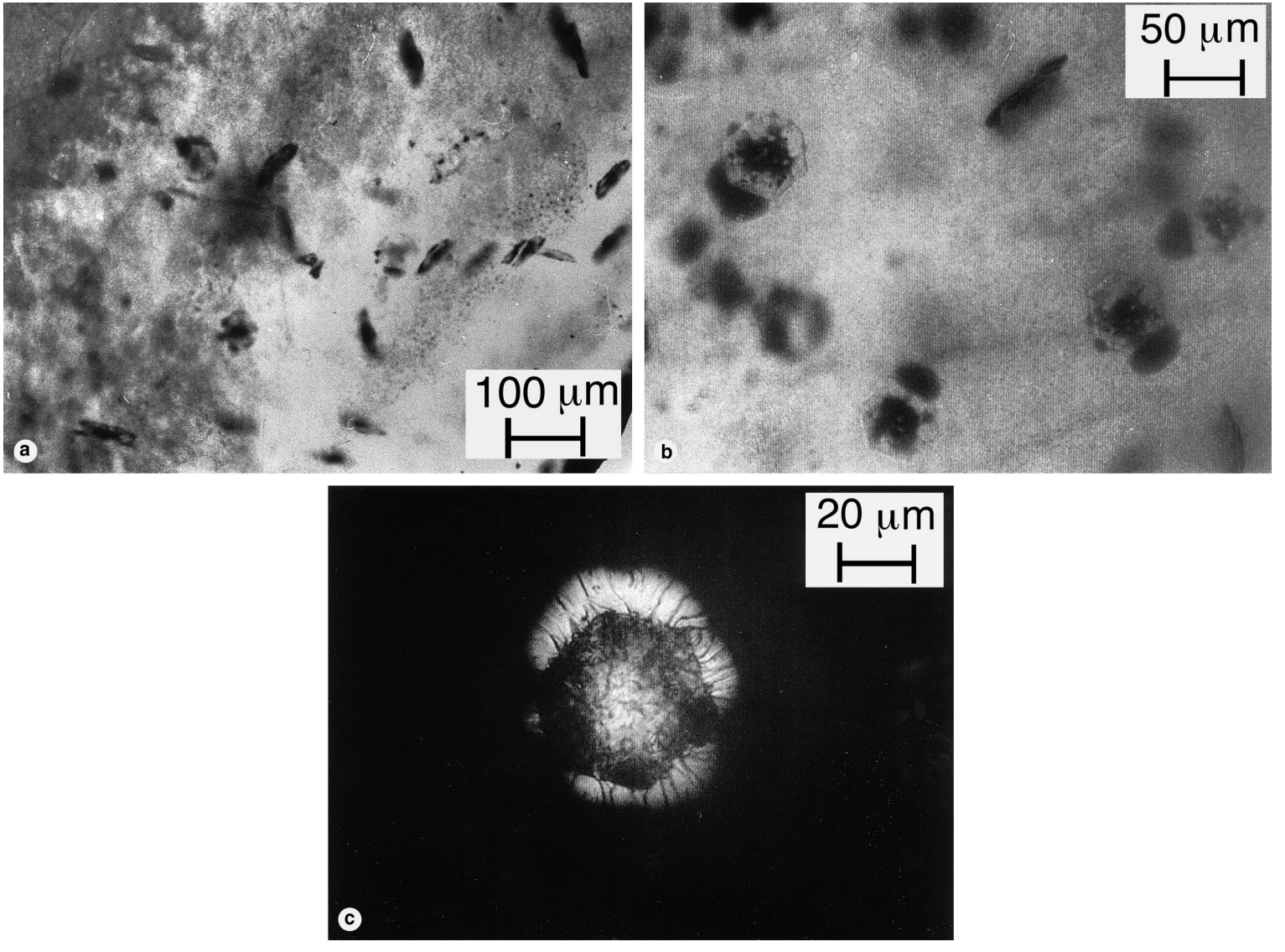

Fig. 7. Optical micrographs of a 95 μm thick Li_2O crystal cleaved parallel to (1 1 1), after electron irradiation (1 MeV, 5×10^{19} e^-/cm^2) at 275 K. (a) and (b): in transmission, showing the various {1 1 1} oriented colloids; (c): in reflection, showing the hexagonal cavity surrounded by metallic lithium.

3.1.3. Room-temperature irradiation

Polycrystalline samples, even when irradiated at room temperature or higher (upto 330 K) [3], do not usually exhibit the Dysonian line typical for large colloids. In a few favourable cases (possibly related to sample quality and/or geometry), we had succeeded to observe both signals in a polycrystal. Fig. 4 shows such an example, which bears qualitative resemblance with a single-crystal spectrum (cf. Fig. 5 below), though the intensity ratio of the two signals is here less in favour of the Dysonian.

Fig. 5 is a typical – one is tempted to call it classical – EPR spectrum of a high-quality single crystal irradiated near room temperature with a sufficient electron fluence, here with 5.3×10^{19} e^-/cm^2. Note the nicely separated Lorentzian and Dysonian lines both centered at $g = 2.0023$, the former (here shown saturated and overmodulated) with a linewidth of $\Delta H = 9.3$ μT, the latter of $\Delta H = 1.2$ mT. Their annealing behaviour is presented in Fig. 6. While the narrow line disappears at 300°C, following in that the comportment of the polycrystals [3], the broad line intensity keeps increasing up to a maximum near 400°C; it vanishes together with a bleaching and decomposition of the sample into powder above $T_{ann} \sim 450$°C. It has to be mentioned here that the intensity growth above $T_{ann} \sim 300$°C is accompanied by a strong increase in the Dysonian linewidth, making it difficult to analyze for the highest T_{ann}.

It is clear from the present discussion that the EPR line at $g = 2.003$ with a linewidth $\Delta H = 0.24$ mT observed by Noda et al. [2] in ion-irradiated Li_2O corresponds to F-center agglomerates as described in Sections 3.1.1 and 3.1.2. Neither can another 0.2 mT broad EPR line observed at $g = 2.01$ in fast-neutron irradiated Li_2O more recently by Masaki et al. [7] be attributed to metallic colloids; the striking similarity of its annealing behaviour (see also the discussion in Ref. [8]), including a negative recovery until ~400°C and disappearance at 600°C, with that of our $g = 2.0035$ line of Fig. 2, makes it a very good candidate for F-clusters. Hence, no alarm about the presence of liquid lithium metal is needed in the blanket working range of 450–650°C, since the last (and biggest) colloids have already recovered at these temperatures.

3.2. Optical microscopy

Having deduced the existence of large (>1 μm) colloids from the presence of the Dysonian line in EPR, it seemed natural to look for them under the microscope. Since the standard samples which contained after an irradiation a typical concentration of 10^{-3} Li in metallic form were completely opaque, we had to prepare a particularly thin crystal which remained semi-transparent even at such concentrations. A cleaved sample, polished down to 95 μm thickness and then irradiated to a dose of 5×10^{19} e^-/cm^2, provided the convenient characteristics and yielded the amazing micrographs shown in Fig. 7.

The first photograph (Fig. 7(a)), taken in transmission, exhibits disk-like species of $\leqslant 50$ μm in diameter, which are preferentially oriented parallel to the four {1 1 1} planes (including the surface cleavage plane). At a closer look (Fig. 7(b)), one notes that the disks consist of aligned transparent hexagons which are non-uniformly surrounded by opaque halos. Finally, the latter turn out to be brilliant metallically reflecting structures (Fig. 7(c)), whose volume in the sample corresponds roughly to the Li-concentration limit as determined from the EPR line intensity. The transparent hexagons are then either empty or oxygen-filled 5–10 μm thick cavities of candybox shape, preferentially forming in the open spaces between {1 1 1} planes of the antifluorite structure. The above observations concerning the anisotropy of colloid shape and distribution are in excellent agreement with the deductions made from the large increase of the dielectric constant after irradiation [5] and from the preliminary data obtained by us in neutron-scattering experiments.

4. Conclusions

1. Metallic Li colloids are created by irradiation of Li_2O near room temperature with electrons in the MeV range, at a fluence of the order of 10^{19}–10^{20} e^-/cm^2.
2. Two typical sizes of these colloids, $\ll 1$ μm and $\gg 1$ μm, are observed which recover in different temperature ranges: the small ones at 300°C and the large ones, which are disk-like and oriented along {1 1 1}, near 450°C.
3. The defect recovering at 650°C and described, among others, by Noda et al. [6–8] is not due to metallic Li but to F-center clusters.

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