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Lithium colloids and color center creation in electron-irradiated Li_2NH observed by electron-spin resonance

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Abstract

We have irradiated Li_2NH powder with MeV electrons at room temperature and investigated the introduced defects with electron spin resonance. CESR indicates the presence of nanosize metallic Li colloids seen as a Lorentzian line with a $g = 2.0023$ and a line width $\Delta H = 50 \mu\text{T}$. A second, broader, signal ($\Delta H = 3$ to 4 mT) appears superimposed upon the Li line at low T (Curie-type behavior) which exhibits complex T -dependence with a break near 180 K for its g -value and ΔH . We are suggesting for the latter a vacancy-type defect in the NH-sublattice, with freezing of its H-component below 180 K . When heated both the Li colloids and the color centers anneal around 100°C probably due to hydrogen evolution and subsequent chemical degradation.

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I. INTRODUCTION

In the search for a light-weight, cheap and easily practicable hydrogen-storage compound, the lithium amide/imide system had been recently rediscovered and has attracted notable interest^{1,2}, in particular in view of the reversible reaction $\text{Li}_2\text{NH} + \text{H}_2 \rightleftharpoons \text{LiNH}_2 + \text{LiH}$ occurring in the interesting range 150–200°C. Simultaneously, the crystal structure of Li_2NH has been revisited by neutron powder diffraction³ and by synchrotron X-ray diffraction⁴ and was established as a rather open cubic antiferroite structure, the NH-ions forming the f.c.c. cell with the Li-ions occupying its tetrahedral sites. The covalently bound hydrogen atoms were found hopping around their nitrogen atoms either on the 48h site within the $\text{Fm}\bar{3}\text{m}$ symmetry or on the 16e site within the $\text{F}\bar{4}3\text{m}$ symmetry, both variants exhibiting a large H-vacancy concentration. Later performed NPD experiments on a deuterated sample (quoted in Ref. 5) had shown the equivalence of the above description either in terms of a disordered cubic or a fully occupied orthorhombic structure. Both the charge-density analysis of Ref. 4 and the electronic structure calculation of Ref. 5 have established the binding between the Li ions and the NH complexes as essentially ionic, such as $[\text{Li}^{0.99+}]_2[\text{NH}]^{1.21-}$.

In the present work, we are interested in the defect aspect of Li_2NH , in particular concerning its stability towards energetic radiation. In fact, it was noted earlier by some of us in a detailed radiation damage investigation of the oxide Li_2O , also of antiferroite structure, that electron irradiation at room temperature had led among others to the formation of metallic Li colloids, which were detected and characterized by conduction electron spin resonance (CESR)⁶ and subsequently by NMR Knight shift measurements⁷. It was, therefore, tempting - in this context also - to undertake an irradiation of this equally ionic Li-rich antiferroite type compound and try to observe a possible creation of metallic Li under electron bombardment. As we shall see, we had indeed succeeded in forming metallic Li together with some color-center type defects when bombarding with high-energy electrons.

II. EXPERIMENTAL

Li_2NH powder was prepared from commercially obtained amide, LiNH_2 , by heating for 24 hours at 350°C in vacuum. The resulting white powder of the order of 30 mg was sealed under argon in a thin glass tube of 2 mm diameter and less than 0.1 mm wall thickness for

irradiation. The subsequent XR analysis has shown 95% pure Li_2NH , the rest mainly due to Li_2O .

The irradiation was performed at the Van de Graaff accelerator of the Laboratoire des solides irradiés, using 2.5 MeV electrons with a current of 3-5 $\mu\text{A}/\text{cm}^2$ in a helium gas atmosphere at a temperature between 300 and 310 K; the received dose was 0.5 C/cm^2 . The resulting damage distribution through the sample can be considered uniform since 2.5 MeV electrons only lose about 50 keV when traversing the tube. After irradiation, the sample was transferred in an argon glove box to another - more solid, 0.5 mm thick and defect free - glass tube, for EPR measurements. Part of the irradiated powder, of the order of 5 mg weight, was kept after the transfer in a further glass tube in air in order to test its stability and sensitivity to environment. Both the Ar-filled and the air-filled tubes were submitted to identical procedures such as the eventual annealing treatment in a furnace. (The two samples had shown very similar behavior through the whole study.)

The introduced defects were investigated by EPR with a Bruker EMX spectrometer, operating at 9.6 GHz, in the 4 – 300 K range. EPR spectra were taken under conditions where saturation does not occur, and were analyzed by performing least squares fits from which linewidths and intensities were calculated. Absolute intensities were obtained after comparison with a standard sample.

III. RESULTS

The initially white Li_2NH powder had turned completely black after irradiation and exhibited a relatively complex EPR spectrum already at room temperature. Since the glass tube had also changed color visibly, it was necessary to replace it as described above in order to separate the intrinsic sample spectrum. The latter is shown in Fig. 1 for four typical measuring temperatures, T_m , between 300 K and 10 K.

Fig. 1a represents a rather simple spectrum with a narrow central Lorentzian line superimposed upon a hardly noticeable, at this temperature, broad structure extending over about 10 mT. Fig. 1b, taken at $T_m = 120$ K, exhibits an unchanged central line and an emerging rather asymmetric broad structure. When lowering the temperature still further to $T_m = 50$ K (Fig. 1c) the broad signal becomes predominant and, moreover, exhibits some fine structure at higher fields - towards $H = 342 - 345$ mT. At the lowest shown $T_m = 10$ K

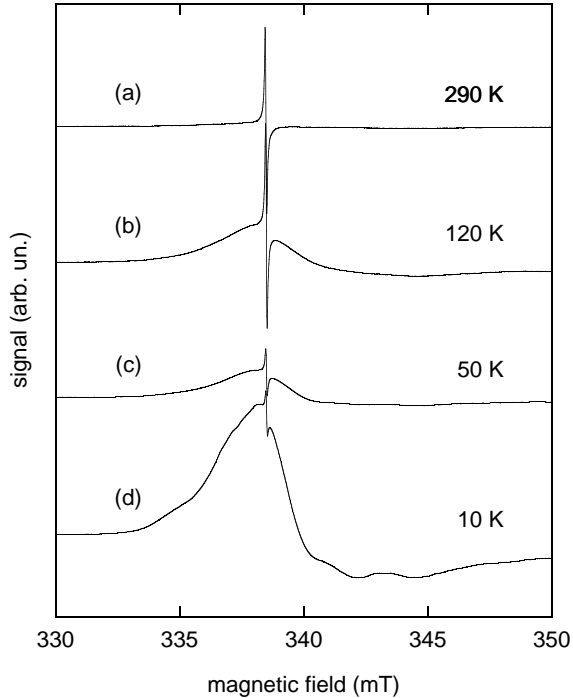


FIG. 1: EPR spectra of irradiated Li_2NH powder measured at different temperatures, T_m , with the same microwave power $P = 0.493$ mW and modulation $M = 20$ μT ; (a) $T_m = 290$ K, $G = 2 \times 10^4$; (b) $T_m = 120$ K, $G = 2 \times 10^4$; (c) $T_m = 50$ K, $G = 5 \times 10^3$; (d) $T_m = 10$ K, $G = 5 \times 10^3$.

(Fig. 1d), finally, the broad structure takes over completely, with the appearance of more additional shoulders at lower fields, but maintaining an unchanged central line.

A. Narrow line

Already now it seems clear that the central narrow line exhibits the typical Pauli-type temperature-independent behavior characteristic of conduction electron spins, in our case that of metallic Li electrons; the measured g -value of $g = 2.0023$ being close to that of free electrons is another strong argument in its favor.

In Fig. 2, we have collected all data concerning the narrow-line intensity for the T_m taken and show them together with the line width, ΔH . The Pauli-like T -independence of the spin concentration is nicely confirmed; the line width, $1/\gamma T_2$, is constant $\Delta H = 48$ μT down to $T_m \approx 100$ K and increases slightly below, by $\approx 10\%$ for the lowest T_m : this behavior, though not completely clear, could be connected with some magnetic impurities. The same

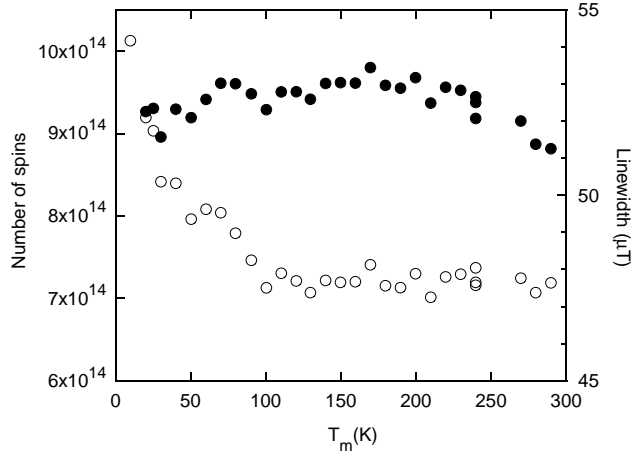


FIG. 2: Narrow line characteristics as a function of measuring temperature, T_m ; full signs - intensity, open signs - linewidth ΔH .

impurities could also be responsible for a linewidth value somewhat higher than observed in the best single crystals of Li_2O . (By the way, in the past⁸, we had observed in irradiated LiF crystals a large dispersion of conduction electron linewidth values.)

The measured number of spins corresponds to a concentration of 2.2×10^{-4} metallic Li in our ≈ 28 mg Li_2NH sample. [We wish to exclude here the possibility of the Li colloids as been formed in the Li_2O present here as $\approx 5\%$ “impurity”. There (see e.g. Ref. 6), the concentration of small colloids would be of the order of 2×10^{-5} , giving more than two orders of magnitude difference, in addition to a narrower line width, $\Delta H \approx 10 \mu\text{T}$.]

Concerning the size of the metallic Li precipitates observed, EPR gives an upper limit of about $1 \mu\text{m}$, from the non-Dysonian shape of the line, and a lower one of a few nm, due to the absence of quantum effects.

B. Broad signal

We have tried the analysis of the broad signal in the spectrum of Fig. 1 as a single structure, but due to its varying aspect with temperature this was not very satisfactory. The broad line shows a complicated shape which is surely related to an anisotropic signal averaged in the powder samples. In order to extract linewidth and intensity values, we used a fit containing mathematically an absorption and a dispersion part, without any particular physical meaning. We are showing in Fig. 3 the temperature dependence of the signal

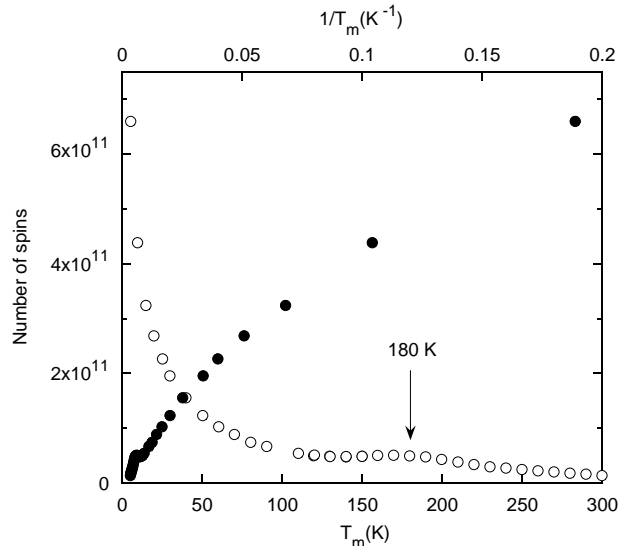


FIG. 3: T -dependence of the broad signal intensity in a direct plot (open signs, lower scale) and in a reciprocal plot (full signs, upper scale).

intensity as determined with such a fit, both in a direct $f(T_m)$ plot and in a reciprocal one, $f(1/T_m)$. The defect responsible for this rather Curie-like behavior is certainly a paramagnetic center, but seems to exhibit some anomalies, in particular seen as a break near 180 K in the direct plot and a change of slope at the same temperature, $1/T_m \approx 0.006 \text{ K}^{-1}$, in the reciprocal plot.

A further indication of a change in the behavior is expressed by the T_m -dependence of the linewidth, which we are showing in Fig. 4. It is clear that we are dealing here with (at least) two types of defect: one with a $\Delta H \approx 3 \text{ mT}$ at low T_m and up to $\approx 100 \text{ K}$; another with a $\Delta H \approx 4.5 \text{ mT}$ above $T_m \approx 180 \text{ K}$; the transition or transformation between the two is rather smooth over a range of about 100 K. (Interestingly and pointing into the same direction, the mean g -value resulting from the broad-signal fit varies also with T_m , from $g = 2.003$ at low T to $g = 1.999$ at room temperature.)

C. Annealing

We have tried to anneal the radiation defects by heating the samples in their sealed glass tubes from 50°C on in steps of 25°C for 30 minutes each and recording the spectra at 300 K after each T_{ann} . The sample bleaches progressively, losing signal intensity at the same time, with practically complete disappearance after $T_{ann} = 175^\circ\text{C}$.

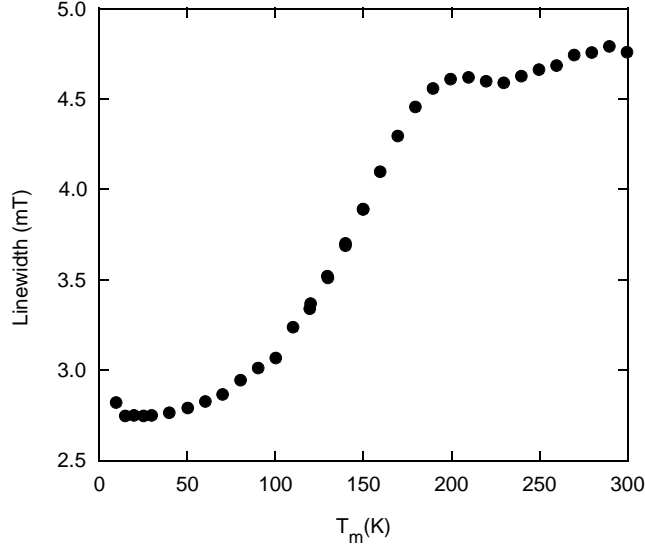


FIG. 4: T -dependence of the linewidth of the broad signal showing (at least) two defect domains.

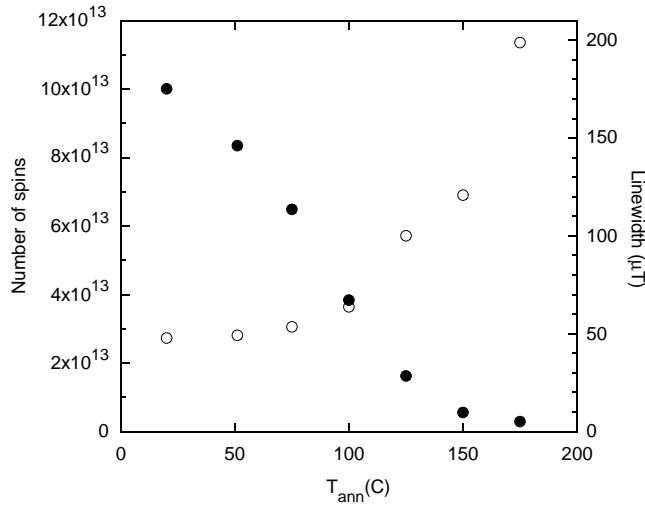


FIG. 5: Annealing behavior of the narrow line intensity (full signs) and its width (open signs), taken at 300 K after heating for 30 minutes at each T_{ann} .

Fig. 5 shows the evolution of the narrow line, both with regard to its intensity and the linewidth. (The g -value remained constant through the whole annealing treatment.) The annealing stage is rather broad and centered around $T_{ann} = 90^\circ\text{C}$; the linewidth which is constant, $\Delta H \approx 50 \mu\text{T}$, until $T_{ann} \approx 90^\circ\text{C}$ grows strongly above this temperature reaching $\approx 200 \mu\text{T}$ for the highest $T_{ann} = 175^\circ\text{C}$, where only 2% of the signal are left. Fig. 6 follows the evolution of the broad signal characteristics with annealing. Again, the signal intensity

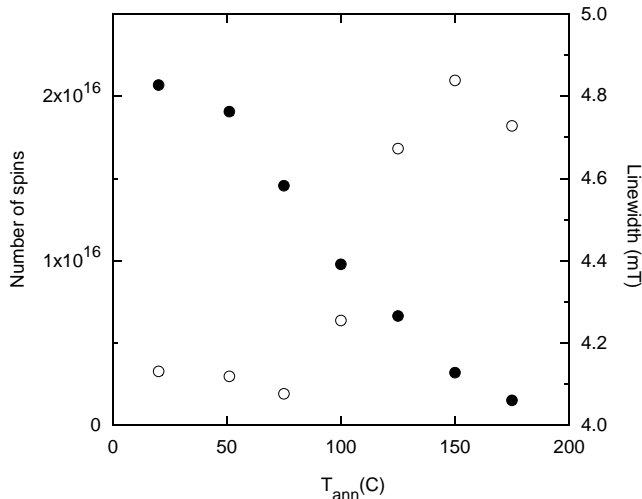


FIG. 6: Annealing behavior of the broad line intensity (full signs) and its width (open signs), taken at 300 K after heating for 30 minutes at each T_{ann} .

disappears progressively at the same time as the narrow line (together with the sample bleaching); its linewidth remains rather constant, $\Delta H \approx 4.1$ mT until $T_{ann} \approx 90^\circ\text{C}$ and grows afterwards by 10 – 15% before its near disappearance at $T_{ann} = 175^\circ\text{C}$, where 95% of the signal are gone. It is interesting to note that both line intensities clearly decrease after the first annealing at $T_{ann} = 50^\circ\text{C}$, which means that sample heating during the electron irradiation did not exceed this temperature.

In view of the very similar annealing behavior of both signals, it seems probable that we have here the result of chemical specimen degradation, with loss of components, rather than recovery of a specific defect. Especially the beginning linewidth increase, after $T_{ann} \approx 90^\circ\text{C}$, for both otherwise so different signals speaks for a degrading environment of the host matrix. This goes well conform with the fact that hydrogen evolution was reported above $\approx 150^\circ\text{C}$ in this system¹, another strong indication for its limiting stability.

IV. DISCUSSION

All the observed characteristics of the narrow signal, such as the T_m -independence of its intensity (Pauli-behavior), the $g = 2.0023$ value close to that of the free electrons, and the rather narrow width of $\Delta H \approx 50 \mu\text{T}$, are a clear indication of metallic Li colloids as responsible for its appearance. To explain this phenomenon and by analogy with the isostructural

Li₂O [6,7], we are suggesting the simultaneous creation and migration of anionic vacancy-type defects during irradiation which would leave behind neutral Li[°] species agglomerating to nano-size metallic colloids. The complementary NH anion cluster could end up as NH₃ bubble somewhere in the host or leave through the surface, though the latter does not seem to occur below 300°C in an undamaged system². On the other hand, we have noted sample degradation in anneals around 100°C, but also an isothermal decrease of the signal already at room temperature when it had diminished by a factor of ten in fifty days; it is most probably hydrogen leaving the sample during and/or after irradiation.

For the broad structure, we are suggesting some kind of complex anionic color center transforming from a simpler symmetric one at room temperature to a more structured of less symmetry at low temperatures; the break in the signal intensity (Fig. 3) and in the linewidth (Fig. 4) at $T_m \approx 180$ K together with a shift in the g -value are signs of this reversible transformation. When assuming an anionic vacancy-type defect (such as F) in the NH-sublattice a possible candidate for the above described behavior would be the hydrogen component in the covalent molecular NH group. As, indeed, shown in the structural analysis of Ref. 3,4 and explained in the introduction, the H atom is hopping around its N atom within a cage of various possible symmetries. Now, it is easily imaginable that this H hopping would freeze below a certain temperature, which could be the 180 K of our experiment, just like the rotating fullerene molecules in their f.c.c. cage.⁹ A similar phenomenon was expected though not observed in the NPD study by Ohoyama et al.³ and has been predicted (and is still expected) in a very recent density-functional analysis by Magyari-Köpe et al.¹⁰, namely the appearance of low-symmetry low-energy structures at low temperatures. On the other hand, the low stability of the H component in our imide has been amply demonstrated both in the isothermal and isochronal annealing described above.

V. CONCLUSIONS

High-energy electron bombardment of Li imide powder, Li₂NH, leads to the formation of metallic Li colloids as observed by CESR and to color centers. The latter exhibit a Curie-type behavior, but with a break in the temperature dependence near 180 K both for the linewidth and the g -value indicating a complex origin. We are suggesting an anionic type defect in the NH-sublattice, with freezing of the H component below ≈ 180 K, for its

interpretation.

Both the colloids and the color centers anneal simultaneously around 100°C probably because of chemical sample degradation due to hydrogen evolution.

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