Electron-Spin Paramagnetic Resonance Studies of Metallic Lithium in Neutron-Irradiated LiF†

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The electron-spin paramagnetic resonance absorption of conduction electrons in lithium metal in neutron-irradiated LiF has been observed. The dependence of the electron-spin paramagnetic resonance line shape and width on the temperature during irradiation and subsequent thermal annealing is discussed. An upper bound is set on the probability for flip of the spin in a collision with the metal surface.

THE appearance of lithium metal in neutron-irradiated LiF has recently been established by both x-ray[1] and nuclear magnetic resonance[2,3] (NMR) techniques. This communication concerns electron-spin paramagnetic resonance (ESPR) investigations of the lithium particles. A discussion is given of the ESPR line shape, width, and behavior under annealing, and an upper bound is set on the probability for flip of the electron spin in a collision with the particle surface.

Single crystals of LiF were obtained from the Harshaw Chemical Company, Dr. Karl Korth (Kiel, Germany) and Optovac Company. Some of these were heated in air at temperatures up to 600°C for times ranging from one-half hour to 54 hours. The crystals then received thermal neutron doses of between 10^{16} *nvt* and 5×10^{18} *nvt* at the Brookhaven Research Reactor facility. Irradiations were carried out at approximately 30°C. The ESPR absorption spectra were obtained at room temperature with a Varian Model 4500 spectrometer operating at 9.5 kMcps and about 3300 gauss. Samples were subsequently annealed in air at successively higher temperatures and cooled rapidly, and the effects of these treatments on their ESPR spectra observed. The experimental results appeared to be independent of the treatment of the samples prior to irradiation and of the choice of crystal supplier.

A marked variation of ESPR line shape with thermal neutron dose was noted. Samples which received 10^{16} *nvt* showed Gaussian absorption lines with $\Delta H=120$ gauss. ΔH is taken here as the separation of the inflection points of the absorption curve. The Gaussian lines were identical to spectra previously reported[4,5] for x-rayed and neutron-irradiated LiF. Integrated fluxes greater than 10^{16} *nvt* produced a new form of paramagnetic center which gave rise to Lorentzian ESPR absorption lines. The widths of the latter decreased with increasing integrated flux, from 68 gauss for 10^{17} *nvt*, to 52 gauss for 10^{18} *nvt*. At least five samples were examined for each of these doses. The scatter among the values of ΔH of samples which received a given dose was of the order of one gauss. Samples which received 5×10^{18} *nvt* showed symmetric resonances with ΔH between 52 and 78 gauss on which were superimposed sharp Lorentzian lines of width in the range one to five gauss (Fig. 1). Additional measurements were made on a crystal of LiF that received 5×10^{18} *nvt* at a temperature between 50 and 75°C and was found to be polycrystalline after irradiation. NMR studies[2] indicated the presence of lithium metal in this sample. Grains selected randomly from the polycrystalline form displayed Lorentzian ESPR lines having values of ΔH in the range 25 to 0.4 gauss.

Measurements of the ESPR absorption intensity showed a consistent growth of spin concentration with increasing neutron dose. For the resonance illustrated in Fig. 1, the estimated spin concentration contributing to the wide line was about 10^{20}/cc and for the narrow line, 10^{17}/cc. Measurements of the g values of the ESPR lines yielded, for the Gaussian shapes, 2.0027 ± 0.0004, and for the Lorentzian shapes, 2.0023 ± 0.0004. The g factors were isotropic within experimental error.

Two general modes of behavior of the irradiated crystals under thermal annealing were distinguished. All samples irradiated at approximately 30°C could be decolored at sufficiently high temperatures. In this group, samples whose ESPR line widths were initially greater than about 20 gauss showed a continual loss of resonance intensity with increasing temperature, with a marked acceleration of the loss rate in the vicinity of 320°C. However, absorption lines with ΔH initially between about one gauss and 20 gauss showed, in addition to their decreasing intensities, pronounced increases in ΔH when the temperature was raised to about 320°C. In contrast to this behavior was that of some of the grains of the polycrystalline sample, which could not be decolored at temperatures as high as 700°C. These grains showed ESPR lines with values of ΔH between 0.6 and 1.4 gauss. Annealing at successively higher temperatures caused these lines to peak and narrow in a manner such as to keep the intensity approximately constant. In a typical case, an absorption line initially 0.95 gauss wide at room temperature was narrowed to about 0.1 gauss after annealing at 560°C. The absorption intensity decreased by no more than a factor of two during this treatment.

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Theoretical[6] and experimental[7] studies have shown that lithium metal yields a Lorentzian ESPR absorption line with an isotropic g value equal to that of the free electron, if the dimensions of the metal are less than the skin depth of the exciting radio frequency field. Other possible sources of the Lorentzian lines observed in the present experiment have been considered, and it has been concluded that the paramagnetic centers consist of lithium metal of dimensions small compared to one micron, the skin depth for 9.5 kMcps radiation in the metal.

The structure of the metallic phase in the lattice appears to change with increasing neutron dose in a manner which tends to narrow the absorption line. In crystals irradiated at approximately room temperature, thermal annealing reverses this process, yielding lines of width several times the initial values. The observed "critical" temperature of 320°C compares closely with the position of the major thermoluminescence peak in neutron-irradiated LiF containing primarily F-type centers.[8] It would appear that thermal annealing of F centers and of the metallic phase observed in this experiment proceed via similar processes. The thermal stability of the coloring in some of the polycrystalline grains may be due to excess lithium resulting from loss of fluorine during the relatively high temperature irradiation. The large proportion of molecular fluorine in these samples,[2,3] of the order of 1% of the total halogen content, adds support to this hypothesis.

The data are as yet insufficient for a detailed discussion of the structure of the lithium metal in the lattice, and of the mechanism which dominates the relaxation of the electron spins in the metal. If the lithium atoms coagulate without the inclusion of an appreciable number of impurities, surface relaxation[6,7] will predominate. The narrowing of the absorption lines during annealing might then reflect a growth of the metal particles. The particle size was not known in this experiment, but an upper limit of one micron may be set by skin depth considerations. A simple calculation[9] then yields, for lines of width 0.1 gauss, the value 1×10^{-6} as an upper limit on ϵ, the probability for spin flip in a collision of an electron with the metal-lattice interface. If the relaxation mechanism is impurity-determined, ϵ must be even less than 1×10^{-6}.

The present results, which are consistent with the earlier NMR studies[2,3] and recent investigations[10] of ultraviolet-irradiated LiH, indicate a useful technique for obtaining finely dispersed particles of extremely pure alkali metal. Both NMR and ESPR techniques are being extended to other neutron-irradiated alkali halides and related compounds.

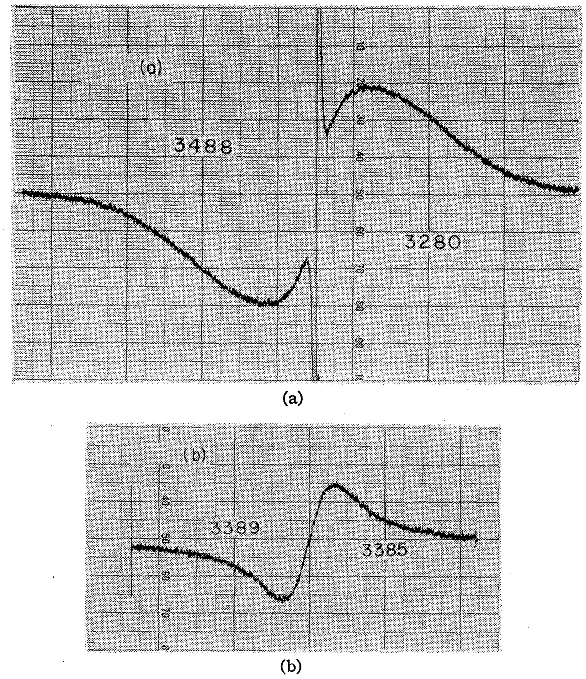

FIG. 1. ESPR spectra of Li metal in neutron-irradiated LIF ($5\times10^{18}nvt$). (a) An overall spectrum consisting of a 78 gauss wide symmetric resonance and a 1.5 gauss wide Lorentzian resonance. (b) The Lorentzian part in a slower scanning. For comparison with (a), the signal-to-noise ratio of this curve must be multiplied by 16.

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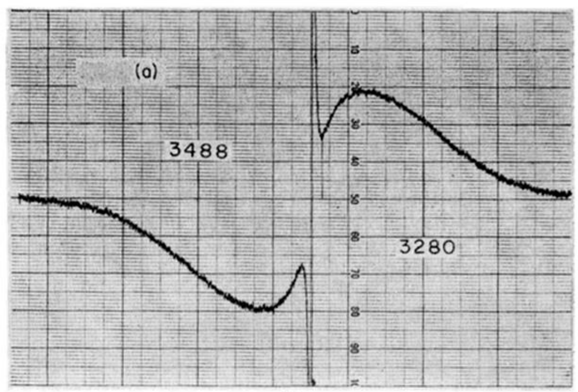
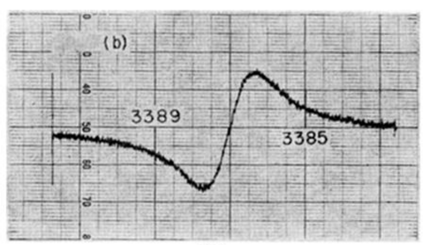
[9] Reference 6, Eqs. (107) and (108).
[10] Doyle, Ingram, and Smith, Phys. Rev. Letters **2**, 497 (1959).



(a)



(b)

FIG. 1. ESPR spectra of Li metal in neutron-irradiated LIF ($5\times10^{18}nvt$). (a) An overall spectrum consisting of a 78 gauss wide symmetric resonance and a 1.5 gauss wide Lorentzian resonance. (b) The Lorentzian part in a slower scanning. For comparison with (a), the signal-to-noise ratio of this curve must be multiplied by 16.