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Investigations on U.V. Irradiated Lithium Hydride Crystals by Electron Resonance

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I. INTRODUCTION.

During a general study of the types of bond breakage and defects that are produced by U.V. irradiation, it was found that very narrow electron resonance absorption lines are obtained from lithium hydride crystals [1]. These signals are observed after relatively short periods of irradiation with U.V. wavelengths. On studying the variation of the intensity of these signals with temperature, it was found that the signal strength remained constant and that there was no appreciable change between room temperature and 77° K. This fact, together with the narrow width of the absorption line, shows that the resonance is due to conduction electrons obeying Fermi-Dirac statistics, rather than electrons trapped in F-centres or other forms of defect. More recent work on the Knight Shift obtained for the lithium in these specimens has also confirmed its metallic nature [2]. It therefore appears that the energy of the U.V. quanta is sufficiently large to eject the individual lithium atoms from their lattice sites, and that they can then coalesce to form colloidal particles of metallic lithium. Confirmation of this mechanism is obtained from the optical absorption spectra of the irradiated specimens, when a large additional peak is obtained at 6500 Å, which can be explained as a colloidal or R' absorption band [3]. The size of the colloidal particles must be considerably smaller than the microwave skin depth at 9,000 Mc/s, since no distortion of the electron resonance line shape is detected.

Measurements have also been made on crystals of lithium aluminium hydride irradiated under the same conditions, and, in this case, only a very weak signal is produced after prolonged exposure. It would therefore seem that movement of the lithium atoms within this lattice is much more severely restricted.

II. EXPERIMENTAL.

The measurements on the irradiated samples were made with a transmission X band spectrometer incorporating 100 Kc/s field modulation with phase-sensitive detection. The absorption lines have been observed at room temperature and at low temperatures, and intensities of absorption were determined by comparison with the signals obtained from a standard free-radical sample containing 1.4×10^{16} spins, which was observed under identical conditions.

The lithium hydride crystals were irradiated with U.V. radiation of 2537 Å wavelength, produced by a mercury lamp with a discharge tube coiled into a spiral so that the radiation could be concentrated onto the specimen. Under such conditions fairly dark colouration of the crystals is produced after about fifteen minutes irradiation at room temperature. Detailed optical absorption plots were carried out on these samples and a new absorption peak was observed at 6500 Å. U.V. irradiation of the lithium aluminium hydride crystals was carried out in the same way but, as will be seen from the results below, much longer times of irradiation were required in this case, before an observable signal was obtained.

III. RESULTS.

Typical electron resonance signals obtained from irradiated lithium hydride crystals are shown in figure 1, together with a free radical signal from a calibrated carbon sample, observed under identical conditions. In all the irradiated samples a single resonance of $g = 2.002 \pm 0.001$ with a half width of 0.3 gauss was observed, this magnitude being determined primarily by the inhomogeneity of the magnetic field or other instrumental effects. No resonance signal was obtained from any of the samples before irradiation, and the extreme narrowness of the lines rules out the possibility that the signal is due to activated impurities or to any defect centres, since these give rise to wide inhomogeneously broadened absorption lines. These initial results therefore suggested that the absorption was due to conduction electrons in colloidal particles of lithium, and the temperature dependence of the signal strength was therefore studied to check this hypothesis. The results obtained are also summarised in figure 1, where curves (c) and (d) are those obtained at liquid oxygen temperatures, and it is evident that, although the intensity of the standard free-radical signal

increases in the normal way, that of the irradiated LiH sample remains the same. The only explanation for such a signal strength and susceptibility which does not vary with temperature is that the unpaired electrons must be obeying a Fermi-Dirac rather than a Maxwell-Boltzmann statistics, and must therefore be conduction electrons, and not those associated with crystal traps or defects.

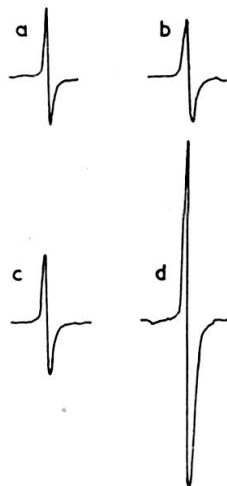


Fig. 1.

E.S.R. signals from lithium hydride after twenty minutes irradiation. Curves (a) and (b) are from the LiH and free radical standard respectively, at room temperature.

Curves (c) and (d) are the corresponding signals at 90° K.

These results are therefore definite proof that the effect of U.V. irradiation of the lithium hydride is to produce colloidal particles of lithium metal scattered throughout the specimen. Moreover the symmetry of the line shape shows that the size of the colloid particles must be small compared with the skin depth [4]. The observed optical absorption peak at 6500 Å, produced by the irradiation, can also be explained as a « colloid band » [5], and the resistance of the colouration to optical bleaching and heating of the specimen to 500° K also strongly suggest that it is due to colloidal metal.

Another interesting effect that has been observed is that the signal strength is very much enhanced if the crystals are ground before irradiation. This strongly suggests that the mechanism of colloid formation is mainly taking place at the surface due to the types of defect there [6]. The mechanism may therefore be analogous to the photographic process.

It would therefore appear that the energy of the U.V. quanta is sufficiently large to eject the individual lithium atoms from their lattice sites, and that they can then coalesce to form colloidal particles of metallic lithium. It is interesting to note, in this connection, that the spacing between atoms in a metallic lithium lattice is smaller than that in the lithium hydride lattice, and this feature will facilitate the formation of colloidal particles.

In order to pursue these ideas, crystals of lithium aluminium hydride were also studied, and irradiated under the same conditions. It was found

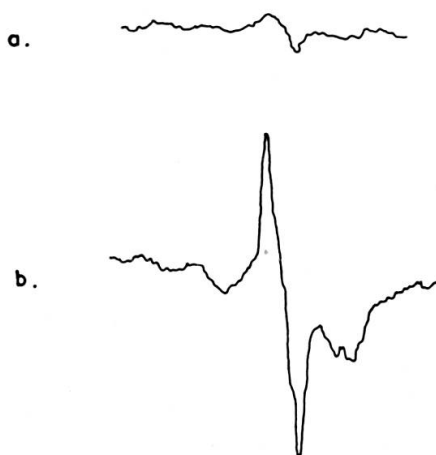


Fig. 2.

E.S.R. signals from crystals of lithium aluminium hydride after 10 hours U.V. irradiation.

- (a) Signal at room temperature.
- (b) Signal at 90° K.

that the irradiation had to be continued for about 15 hours before any observable electron resonance signal was observed in this case. The actual absorption then obtained is shown in figure 2 (a), and it has a large width of about 50 gauss, as compared with the very narrow line obtained from the irradiated lithium hydride. This, together with the long time of formation, suggests that the signal is due to crystal defects. The variation of the signal strength with temperature, as shown in figure 2, also confirms this, since the normal increase in intensity, as the temperature is lowered, is obtained.

It would therefore appear that the structure of the lithium aluminium hydride crystals is sufficiently strong to prevent the lithium atoms moving

any great distance in the lattice, and the formation of colloidal particles of metal does not take place.

IV. U.V. IRRADIATION OF OTHER COMPOUNDS.

Other simple compounds of similar nature have also been U.V. irradiated under the same conditions to see if colloidal particles of metal could be obtained. In general, no absorption signal is produced unless very long periods of irradiation are employed.

It has been found, however, that strong characteristic spectra can be produced if samples are X-irradiated before U.V. irradiation. For example silver bromide crystals were taken and X-irradiated for fifteen minutes at 10 cm distance from a standard 75 kV therapy unit. A small wide electron resonance absorption was just detectable from such specimens. If they were then U.V. irradiated for a short time, however, quite large electron resonance spectra are obtained with well resolved hyperfine structure. The fact that such spectra are not observed after either X-ray or U.V. irradiation alone, suggests that it is necessary first to form specific crystal defects or traps with the higher energy irradiation, and then to excite electrons within these by the U.V. quanta.

The fact that these signals are due to an unstable state in which the electrons, excited by the U.V. radiation, have become temporarily trapped is demonstrated by the complete disappearance of the signal once the specimens are warmed to room temperature. Further detailed measurements are now in hand on these compounds to see if the detailed nature of the trapping mechanism can be elucidated.

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DISCUSSION

M. Palma. — You have mentioned that U.V. quanta eject individual lithium atoms from lattice sites. I should be interested in knowing about the evidence

for the presence of lithium ions at interstitial positions at thermodynamical equilibrium in these crystals.

Furthermore, I should like to say that working on photographic image formation on silver halides, we have found at Palermo some evidence for the operation of vacancies as hole traps and therefore as sensitizing centres for photographic image formation. This is also apparent from the results that we have reported at this Colloquium (Communication No. 122). For this reason we have performed experiments by irradiation with X-rays and with U.V. light, in order to create vacancies with X-rays therefore obtaining an increased sensitivity. Our results are similar and consistent (as far as we have got) with yours.
