

mercury films which we have examined. (The transmission through the lead films in the normal state disagreed slightly with the value calculated from the dc resistance. The small ambiguity in the interpretation of the data which this introduces does not affect the qualitative features of the conductivity curve.)

It seems likely that the precursor hump in the conductivity curves for the films is due to the same cause as the dip in the power ratio curve for the bulk samples. For both of the metals under discussion, the structure in the film data and that in the bulk data occur at approximately the same frequency, relative to the frequency at which the main onset of absorption sets in. This structure may be associated with anisotropy of the energy gap. Such anisotropy has been observed in ultrasonic attenuation measurements⁴ on tin, and could also account for the observed nonexponential electronic specific heat, as has been pointed out, for instance, by Cooper.⁵ The electronic specific heat which is inferred for lead and mercury from critical field data shows a deviation from the exponential which is an order of magnitude greater than that for any of the other superconductors measured.^{6,7} This large deviation may well be associated with the marked structure that we observe for these two metals. On the other hand, the structure may be due to the production of collective excitations by the absorption of photons. Anderson has pointed out,⁸ on the basis of microscopic considerations, that collective excited states might have energies which lie below the top of the gap predicted by

the theory of Bardeen, Cooper, and Schrieffer.⁹ The collective excitations may perhaps also be described macroscopically in terms of longitudinal oscillations in the metal. In the case of bulk samples, transverse oscillations may also play a role in explaining the observed effects. Both of these possibilities have been proposed tentatively by Ferrell.¹⁰

The far-infrared experiments on these and other metals will be reported more fully in forthcoming publications.

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OVERHAUSER EFFECT IN METALLIC LITHIUM

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The enhanced nuclear polarization produced by the saturation of electron spin resonance in metals can be detected in two ways: (a) by observing the enhancement of the nuclear signal, a method widely used since the pioneer work of Carver and Slichter¹; (b) by observing the shift of the electron spin resonance brought about by the polarization of the nuclei, a method proposed by Overhauser² and analyzed by Kaplan³ but never carried out experimentally so far.

We present a preliminary report of a detection

of Overhauser nuclear polarization in lithium metal using both methods. The sample was lithium hydride heavily irradiated by pile neutrons. A sharp (0.3 gauss) electron spin resonance line, observed by Doyle *et al.*⁴ in LiH irradiated with ultraviolet radiation, was attributed by them to conduction electrons in colloidal particles of lithium metal. In our sample, with negligible inhomogeneous broadening, the electron spin resonance line had at room temperature and 10 000 Mc/sec a width of 0.125 gauss (peak to peak of

the absorption derivative). The metallic character of lithium was confirmed by the observation of the nuclear signal of Li^7 : the line, with a width of 0.4 gauss, is clearly diffusion-narrowed and presents a relative frequency shift of 0.024%, equal to the known Knight shift in lithium metal. The narrowness and the symmetrical shape of the electron spin resonance line at 300°K, exhibiting the unusual purity and smallness of metallic particles in irradiated LiH, make this sample particularly suitable for Overhauser experiments in high fields and at low temperatures.

(A) Experiments at 300°K: A sample of LiH surrounded by a nuclear magnetic resonance coil was placed inside a microwave cavity fed by a magnetron delivering up to two watts of continuous microwave power. The nuclear magnetic resonance of Li^7 was observed in a field of 3300 gauss while the electron resonance was being partially saturated. Because of the shielding of the sample from the microwave field by the nuclear magnetic resonance coil, no reliable estimate of the field at the sample could be made. The enhancement A of the nuclear polarization is given by

$$A - 1 = \frac{\gamma_e}{\gamma_{\text{Li}^7}} \frac{T_1}{T_{1e}} s = 1690 \frac{T_1}{T_{1e}} s, \quad (1)$$

where T_1 is the nuclear spin lattice relaxation time, T_{1e} the relaxation time caused by electron-nucleus coupling only and s the saturation parameter of the electron resonance, related to the microwave power P by $1/s = 1 + a/P$, where a is a constant depending on the apparatus and the sample. The maximum signal enhancement observed was approximately 100, the uncertainty being caused by the weakness of the unenhanced signal. A plot of $1/A_{\text{obs}}$ as a function of $1/P$ was, within experimental error, a straight line from which a value of $A_{\text{max}} \approx 150$ could be extrapolated. This would require $T_1/T_{1e} \approx 0.1$ rather smaller than the value $T_1/T_{1e} \approx 0.7$ at room temperature and 3300 gauss deduced from the results of Holcomb and Norberg.⁵ This discrepancy may be due to the presence of grains appreciably larger than the electronic (but not the nuclear) skin depth, which would give a full contribution to the natural signal but not to the enhanced signal.

(B) Experiments at 4.2°K: The relative shift D of the electron spin resonance frequency is related to the enhanced nuclear polarization $\langle I_z \rangle$

and to the Knight shift K by

$$D = K \gamma_n \hbar \frac{N}{\chi_p} \langle I_z \rangle \frac{1}{H_0}, \quad (2)$$

where χ_p is the electron susceptibility, N the number of nuclear spins per unit volume, and $\langle I_z \rangle$ is given by

$$\langle I_z \rangle = \frac{A \gamma_n}{\gamma_e} \frac{\gamma_e \hbar I(I+1) H_0}{3kT}, \quad (3)$$

where A is the enhancement (1). With $H_0 = 3300$ gauss, $T = 4.2^\circ\text{K}$, and $\chi_p = 2.1 \times 10^{-6}$,⁶ the absolute shift expressed in gauss is

$$\Delta = D H_0 = 7.2 A \gamma_n / \gamma_e. \quad (4)$$

The electron spin resonance was observed at 10 000 Mc/sec for various microwave levels up to 7 milliwatts, corresponding to an estimated rotating microwave amplitude $H_1 \approx 75$ milligauss, and to a saturation parameter $s \approx 0.3$ for grains smaller than the skin depth δ . For grains of dimension $d > \delta$, and for such a narrow line, it can be expected, because of electron spin diffusion, that the saturation parameter will be uniform within the grain but reduced by a factor of the order of $(\delta/d)^2$,⁷ resulting in a spread in the observed electron spin resonance shifts. As the microwave power is increased, two striking effects occur (Fig. 1): (a) The width and the shape of the line change considerably. (b) The shape depends on the direction of the sweep.

The spread of the curve 1(b), of the order of 2 gauss, agrees with the value of the shift pre-

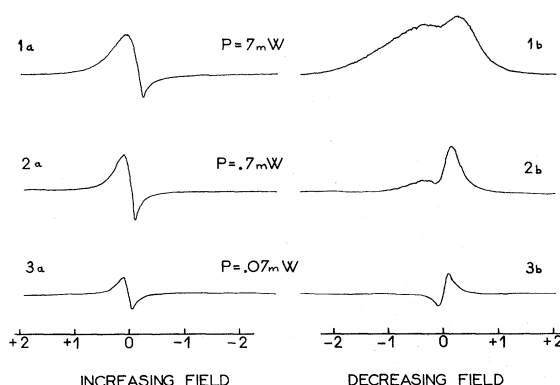


FIG. 1. Recorded electron spin resonance absorption derivative in neutron-irradiated LiH for various power levels P at 4.2°K and 10 000 Mc/sec. One division on the horizontal axis corresponds to one gauss; the sweep is 0.4 gauss/min.

dicted by Eq. (4) for a saturation parameter $s \approx 0.3$, that is for the smallest grains.

The dependence of the line shape on the direction of the sweep is in qualitative agreement with the prediction of Kaplan³ if the finite nuclear T_1 (10 sec at 4.2°K) and a spread in the size of the grains are taken into account.

The existence of a distribution of electron spin resonance shifts was also exhibited directly: after saturating the electron spin resonance line for several T_1 , a large field modulation (5 gauss) was introduced suddenly. The electron line being then saturated during a small fraction of the modulation cycle only, the enhanced nuclear polarization could relax back to approximately its normal value. The electron line observed on the scope presented immediately after the intro-

duction of the modulation, an asymmetrical broadening of the order of 0.4 gauss, which collapsed into a narrow line with a time constant of the order of $T_1 \approx 10$ sec.

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ELECTRON COLLISION FREQUENCIES IN NITROGEN AND IN THE LOWER IONOSPHERE*

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Attempts^{1,2} to correlate laboratory measurements of electron collision frequencies in nitrogen with the results of measurements using rockets passing through the *D*-layer of the ionosphere have not been very successful. Our measurements of the electron collision frequencies for thermal electrons in nitrogen, combined with an improved analysis of the data obtained with the rockets, appear to remove the discrepancies.

An improved version of the electron drift velocity tube used by Bradbury and Nielsen³ has been used to measure the mobility of electrons in nitrogen at such low electric fields that the electrons are in thermal equilibrium with the gas.⁴ The measured values of the product of electron mobility, μ , and gas density, N , are $\mu N = 1.10 \times 10^{24}$, 3.5×10^{23} , and 2.8×10^{23} cm⁻¹ volt⁻¹ second⁻¹ at 77°K, 300°K, and 373°K, respectively. Following Phelps, Fundingsland, and Brown⁵ (PFB) these results are analyzed by expressing the reciprocal of the momentum transfer collision frequency, $\nu_m(u)$, as a power series in the electron energy, u , and substituting into the standard expressions for electron mobility⁶ to obtain a power series in the most probable electron energy, kT/e . The power series for the mobility is then fitted to the experimental data to obtain the coefficients of the series for $\nu_m(u)$. The resulting $\nu_m(u)$ is shown by the lower solid curve in Fig. 1. The dashed curves show

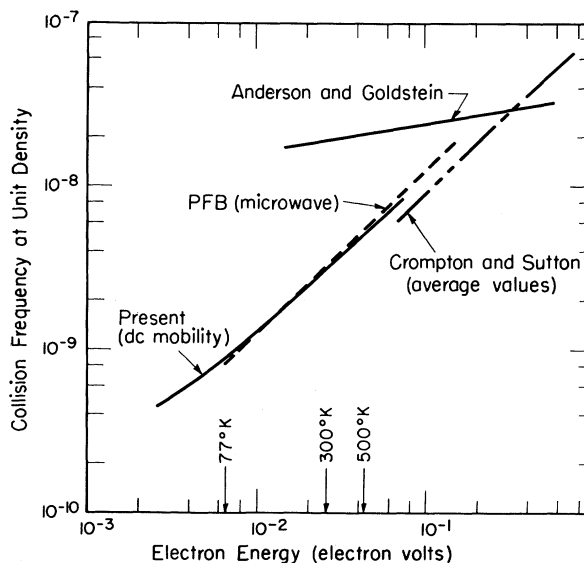


FIG. 1. Momentum transfer collision frequencies for monoenergetic electrons in nitrogen as a function of electron energy. The energy range of the thermal equilibrium experiments is shown by the values of kT/e at which the measurements were made and serves to indicate the range of validity of the curves of collision frequency as a function of energy. The mobility data are found to fit the relation $\mu N = 9.6 \times 10^{21} (kT/e)^{-1} - 1.39 \times 10^{19} (kT/e)^{-2}$ cm⁻¹ volt⁻¹ sec⁻¹ within the experimental error so that $N/\nu_m(u) = 8.2 \times 10^6 (u)^{-1} - 5.9 \times 10^3 (u)^{-2}$ cm³/sec.