NUCLEAR DYNAMIC POLARIZATION BY OPTICAL ELECTRONIC SATURATION AND OPTICAL PUMPING IN SEMICONDUCTORS*

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A nonresonant Overhauser effect by photoexcited conduction electrons is obtained on Si^{29} nuclei in silicon at 77°K in two different ways: (a) Saturation of the electronic magnetization is achieved with unpolarized light by exciting an equal number of spins up and spins down. (b) Polarized electronic spins are produced by optical pumping with circularly polarized light; the nuclear magnetization obtained in 1 G by optically pumped electrons corresponds to the equilibrium value at 77°K in 28 kG.

We report two different experiments of dynamic polarization of Si^{29} nuclei in silicon by intrinsic light irradiation. One is the usual Overhauser effect, but the saturation of the electronic magnetization is obtained by a nonresonant process: Photoexcitation of electrons with unpolarized light produces an equal number of electronic spins up and spins down. In the second experiment, the nuclear enhancement is achieved by polarized conduction electrons obtained by optical pumping with circularly polarized light. The effect is 8.5 times larger than the maximum enhancement expected in the usual Overhauser effect. We think that this is the first successful nuclear dynamic polarization obtained by optical pumping in solids.

(A) Optical electronic saturation.—In conductors, a strong relaxation mechanism for the nuclear spin $\vec{I}$ is the Fermi interaction $A\vec{I}\cdot\vec{S}$ with the electronic spin $\vec{S}$ of the free carriers. The Overhauser effect[1] is the dynamic enhancement of the nuclear polarization, obtained by maintaining the electronic polarization off its equilibrium value. If $\gamma_e\hbar\langle S_z\rangle$ and $\gamma_n\hbar\langle I_z\rangle$ are the electronic and nuclear magnetizations, respectively, and $\gamma_e\hbar S_0 = (\gamma_e\hbar)^2H_0/4kT$ and $\gamma_n\hbar I_0 = (\gamma_n\hbar)^2H_0/4kT$ (for $S = I = \frac{1}{2}$) their equilibrium values at temperature T in the magnetic field $\vec{H}_0$, the nuclear enhancement, in the high temperature limit, is given by[1]:

$$\langle I_z\rangle/I_0 = 1 - s\gamma_e/\gamma_n. \tag{1}$$

The saturation factor $s = (S_0 - \langle S_z\rangle)/s_0$ is the significant quantity which controls the nuclear enhancement. Saturation of the electronic spins $\vec{S}$ is usually achieved with a resonant field $\vec{H}_1$ at the electronic Larmor frequency in the external field $\vec{H}_0$.

In the present experiment, the electronic spins responsible for the nuclear relaxation are produced already saturated by photoexcitation.[2] Irradiation of silicon with intrinsic light (E_g = 1.2 eV at 77°K), in a magnetic field, creates an equal number of spins up and spins down without the need of any resonant field. However, spin-lattice relaxation tends to restore Boltzmann equilibrium among electronic spins. In our experiments the electronic spin-lattice relaxation time τ_1 is much shorter than the lifetime τ of the excited electrons, and the reduction of the saturation may be physically described as follows: The average value of the longitudinal component of an electronic spin is zero during a time τ_1 after its excitation in the conduction band and is restored to its equilibrium value S_0 for the remainder of its lifetime τ. The saturation factor is thus reduced to $s \approx \tau_1/\tau$. Exact solution of the rate equation yields, in the general case when τ_1 is not much smaller than τ,

$$s = \tau_1/(\tau + \tau_1). \tag{2}$$

In order to relax the Si^{29} nuclei by the photoexcited electrons and to avoid a short circuit by paramagnetic impurities,[3,4] the experiments are performed at T = 77°K in very pure n-type silicon ($N_d \approx 10^{13}$ phosphorus atoms/cm³). The presence of electrons trapped on donors is an efficient relaxation mechanism[5] but can be neglected in our experiments, the intensity of the light being sufficient to maintain a conduction-electron concentration 20 times higher than the donor concentration. The measured nuclear relaxation time T_1—more than 200 h without light at 77°K—is reduced to T_1 = 22 h ± 10% in the presence of light. Because of these long times we found it convenient to use a small permanent magnet of H_0 = 1.6 kG, the accessibility of which is well adapted for strong irradiation. The light source is an xenon high-pressure lamp of 900 W (OSRAM XBO 900). The

light is filtered and focused on the sample, giving about 1 W of efficient photons. The sample is a circular disc, 16 mm diam and 1 mm thick, at the bottom of a nitrogen Dewar. Because of the long nuclear relaxation times involved, the nuclear magnetization can be measured at room temperature[4] by adiabatic fast passage[6] in a Varian wide-line spectrometer.

By continuous irradiation during 37 h, we obtain a nuclear polarization enhancement extrapolated to infinite time: $\langle I_z\rangle/I_0 = -5.6$ which gives the saturation factor $s \approx \tau_1/\tau = 2\times10^{-3}$ ($\gamma_e/\gamma_n = 3310$ in silicon). An independent measurement of the lifetime ($\tau = 3\times10^{-5}$ sec at 77°K) gives the electronic relaxation time $\tau_1 \approx 6\times10^{-8}$ sec, which corresponds to a half-width of the resonance line of the conduction electrons, $\Delta H = (\gamma_e\tau_1)^{-1} \approx 1$ G. This value is in good agreement with the results obtained by direct electronic line-width measurements on n-type silicon with comparable free-carrier concentrations.[7]

(B) Polarization by optical pumping.—It has been predicted for a long time and discussed by Margerie[8] that optical pumping in solids could lead to dynamic nuclear polarization. He pointed out that the relaxation parameters in solids are usually not favorable, and no successful result has been reported so far. Very pure silicon appeared to us as particularly promising, especially because the nuclear relaxation is almost entirely due to the electrons created by light. We have succeeded in obtaining experimental enhancements as high as 28×10^3. The principle of the method is to produce highly polarized electrons in the conduction band by irradiation with circularly polarized light. Actually, a 100% electronic polarization is not obtained because, due to the band structure of silicon, both spin directions are created in the conduction band.[9] However, the proportions G_+ and G_- of transitions to spin-up and spin-down states are not equal, thus leading to a net polarization different from its equilibrium value, and in fact, much larger. Solution of straightforward rate equations[10] for steady-state conditions yields

$$s = \frac{\tau_1}{\tau+\tau_1}\left[\frac{G_- - G_+}{2S_0} + 1\right]. \tag{3}$$

As in section (A) the factor $\tau_1/(\tau+\tau_1)$ is the effect of the electronic relaxation which tends to restore the Boltzmann factor between electronic spins. The first term in the brackets is the optical pumping term and the second one is the saturation term discussed in section (A). Equations (1) and (3) yield

$$\langle I_z\rangle \approx \frac{\tau_1}{\tau+\tau_1}\left[\frac{G_+ - G_-}{2} - S_0\right]. \tag{4}$$

When optical pumping is strong enough to ensure that $\frac{1}{2}|G_+ - G_-|$ is much larger than the nuclear magnetization S_0, $\langle I_z\rangle \approx (\tau_1/\tau)\frac{1}{2}(G_+ - G_-)$ is no longer determined by statistical factors but is rather independent of external field and temperature. It depends on matrix-element ratios describing electronic transitions between valence and conduction bands, as well as on electronic recombination and relaxation rates. Therefore, the concept of nuclear enhancement is not significant and only the value of the nuclear magnetization obtained is meaningful. This situation is demonstrated in our optical pumping experiments, where about the same nuclear magnetization is obtained in $H_0 = 1$ G and $H_0 = 50$ G and reverses sign if the sense of the circularly polarized light is reversed. Figure 1 shows the magnetization measured after an irradiation time of 21 h in 1 G: The signal obtained corresponds to the equilibrium polarization in 15 kG at 77°K. The extrapolated magnetization to infinite time, taking into account that $T_1 \approx 27$ h [T_1 is larger than in section (A) because part of the light is absorbed in the polarizer] corresponds to the equilibrium polarization in a field of 28 kG at 77°K and leads to $\langle I_z\rangle = 3.7\times10^{-6}$. A direct measurement of τ_1/τ was given by the saturation method mentioned in the preceding section and the two experiments show us that we get only ≈0, 4% of what could be expected if only one kind of electronic spin had been created. This low polarization is due to the matrix elements describing the pumping

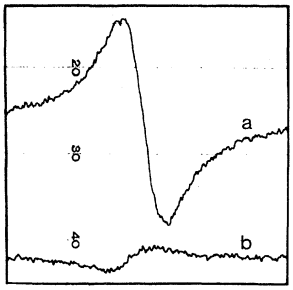

FIG. 1. Curve *a*: Signal proportional to the Si^{29} magnetization obtained in $H_0 = 1$ G after 21 h of irradiation with circularly polarized light at 77°K. Curve *b*: Signal proportional to the equilibrium Si^{29} magnetization in $H_0 = 6$ kG at 300 °K.

between valence and conduction bands in silicon.[5]

We are extending these studies to irradiation with extrinsic polarized light, with which similar effects are expected. This experiment was suggested by Professor I. Solomon and we wish to thank him for his constant interest in this work. The help of Professor C. Benoit à la Guillaume and his group at the Ecole Normale Supérieure, Paris, is gladly acknowledged.

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ZERO-POINT BUBBLES IN LIQUIDS*†

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Bubbles due to the zero-point motion of positronium atoms in liquid He, H_2, Ne, and Ar have been observed and their sizes determined.

Many years ago Ferrell[1] proposed that the long lifetime of positronium atoms in liquid helium was due to the fact that the positronium atoms were trapped in a "zero-point bubble" in the liquid. The argument is that any very light free particle cannot be confined in a small space because of the pressure of its zero-point motion. Indeed many observations of positron annihilation in liquids and dense gases have been discussed in terms of the zero-point motion picture. One of the most recent of these experiments, that of Roellig and Kelly,[2] has even determined some of the conditions of density and temperature for the formation of these zero-point motion bubbles, or "cavities," in the gaseous state.

Because of the strong repulsive interaction with He atoms, an electron is also known to form a zero-point bubble in dense He gas and liquid. Discussions of the mobility of electrons in helium have often been based upon this bubble idea. Recently Northby and Sanders,[3] in an interesting experiment, have observed the photoejection spectrum of electrons in the bubble state. From the photoejection energy they deduce that the potential well (assumed square) seen by an electron has a depth of about 1.0 eV and a diameter of about 42 Å.

In this Letter we present a direct measurement of the bubble size in He and other liquids when the entrapped particle is a positronium atom. The principle of the measurement is simple. The motion of the positronium atom is observed by the small departure from 180° of the angle between the annihilation gamma rays. The width of the momentum distribution of annihilation photons (and hence of positronium atoms) is inversely proportional to the size of the bubble.

The experiment was done in the usual long-slit angular-correlation apparatus for positron annihilation experiments. See Fig. 1. The source-detector distance was 250 in. and the slit width 0.050 in., subtending an angle at the source of 0.20×10^{-3} rad. For some higher resolution runs the angle was decreased to 0.15×10^{-3} rad. The angle was varied by moving one detector and coincidences were automatically recorded as a function of angle. As shown in Fig. 1, the source of positrons was two copper foils each mounted parallel to the long slit detectors and about $\frac{1}{16}$ to $\frac{1}{8}$ in. apart. The liquid specimen was defined by a fixed lead slit close to the cryostat with a gap of about 0.025 in. for all liquids and of about 0.050 in. for some He runs. On the other side of the cryostat, the corresponding slit was always slightly larger than the fixed specimen-defin-