

PHYSICAL REVIEW LETTERS

VOLUME 2

JUNE 1, 1959

NUMBER 11

DYNAMIC NUCLEAR POLARIZATION

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(Received April 13, 1959; revised manuscript received May 8, 1959)

Saturation of the microwave electron paramagnetic resonance of impurities in various materials produces enhanced and reversed nuclear polarization throughout the material, an effect discovered by Erb, Motchane, and Übersfeld¹ and Abragam and Proctor.²

Figure 1 shows the levels in a magnetic field of a single electron spin loosely coupled to a nu-

cleus of spin $\frac{1}{2}$. Full arrows denote the allowed transitions, presumably also the fastest relaxation processes. Saturation of the partially forbidden line *A* at a frequency $\nu_e - \nu_n$ leads to the population distribution shown in column *A* on the right of the figure. The resulting ratio of the populations of nuclear substates with m_I positive to those with it negative is

$$x_1 \approx (2 + \Delta)/(2 - \Delta) \approx 1 + \Delta,$$

compared with the equilibrium ratio

$$x_0 \approx 1 + \delta,$$

where Δ and δ are the electronic and nuclear Boltzmann factors. Saturation of *B* yields

$$x_2 \approx 1 - \Delta.$$

Thus *A* leads to a positive enhancement Δ/δ and *B* to a reversal $-\Delta/\delta$.

In the materials investigated, the lines *A* and *B* are not resolved since their separation $2\nu_n$ is considerably less than the width $\Delta\nu_e$ of the electron line. If this is inhomogeneously broadened, a plot (Fig. 2) of the electron absorption line is equivalent to a plot of the number N of paramagnetic centers whose allowed frequency is ν in a particular field. An applied signal ν_0 saturates the allowed transition of N_0 centers, the transition *A* of N_1 centers whose allowed frequency is $\nu_0 + \nu_n$, and the transition *B* of N_2 centers. In the case illustrated, the net effect is a reversal depending on the difference between N_2 and N_1 . The points of maximum enhancement and reversal coincide with the points of maximum slope of the

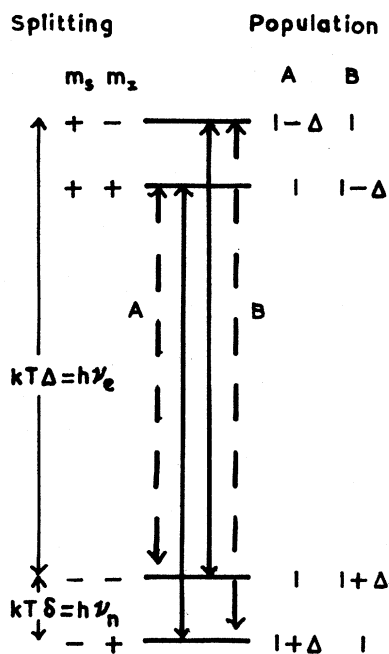


FIG. 1. Levels of an electron and a nucleus in a magnetic field.

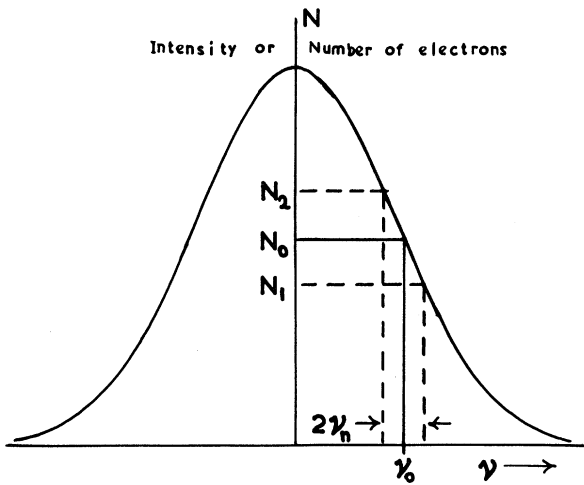


FIG. 2. Effect of electron line width.

electron absorption line. Enhancement at a fixed field occurs at electron frequencies below the line center (field above at fixed frequency), and reversal vice versa. For $\nu_n \ll \Delta\nu_e$, the maximum effect is proportional to $\nu_n/\Delta\nu_e$. Since the possible enhancement is $\Delta/\delta = \nu_e/\nu_n$, the over-all effect depends only on $\nu_e/\Delta\nu_e$ and not at all on the nuclear gyromagnetic ratio g_n .

In Fig. 3 we show the intensity at 1.6°K of the Li^7 nuclear resonance absorption signal in a single crystal of LiF containing F centers produced by x-rays. The microwave frequency is constant at 9.41 kMc/sec and the static magnetic

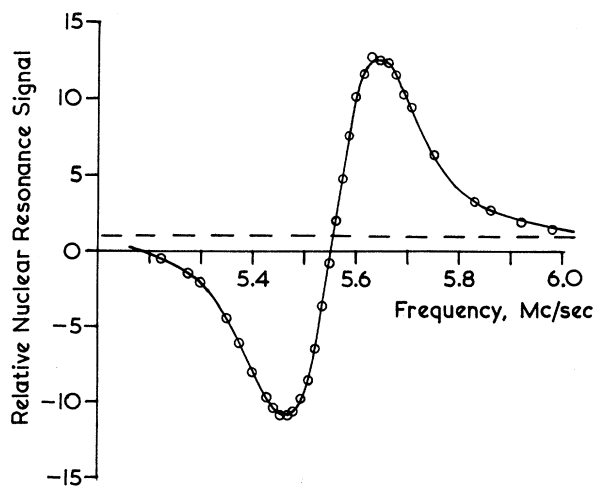


FIG. 3. Enhancement of Li nuclear resonance signal at 1.6°K as a function of the nuclear resonance frequency (or magnetic field) at a fixed microwave frequency 9.41 kMc/sec.

field and nuclear resonance frequency are varied. Each point represents the ratio of the signal with the microwave power on to the signal in its absence. The signal-to-noise ratio of the unenhanced signal was greater than 5:1.

The results fit the theory outlined above, and the separation 0.18 Mc/sec or 108 gauss between the two maxima agrees well with the paramagnetic resonance result, 111 gauss, of Lord.³ Exactly similar results obtain for the F^{19} resonance, confirming the independence of the effect on g_n . Preliminary results on another crystal show an increase in the maximum effect from 17:1 at 9.4 kMc/sec to 58:1 at 36 kMc/sec. This increase is less than the increase in ν_e but is at least partly explained by incomplete saturation of the resonance at the higher frequency. The nuclear resonance spectrometer would not operate above 25 Mc/sec and so we were unable to observe the increase in the F^{19} resonance. If we assume that this is also 58:1, then at the temperature 1.4°K of this experiment the F^{19} polarization exceeded 10% in a volume of 1/8 cc.

The measurements were made using a specially designed self-oscillating nuclear resonance detector, and we observed no change in the relative enhancement in going from levels well below nuclear saturation to levels well above. The effect depends to some extent on the field modulation amplitude if this approaches the electron line width. The measurements we quote used much smaller sweeps approximately equal to twice the nuclear line width.

The effect increases with increasing F -center concentration. It is absent in pure crystals characterized by a nuclear spin lattice relaxation time T_1 in excess of 45 seconds at room temperature. It is 3:1 in crystals exposed to x-rays but not visibly colored with $T_1 \sim 5$ sec and 17:1 in dark brown crystals.

The results for other materials at microwave frequencies between 8 and 10 kMc/sec and temperatures between 1.2 and 1.6°K are presented in Table I. The variety of materials yielding a measurable effect suggests that this is a very general way of polarizing nuclei. Almost any type of paramagnetic impurity produces an effect, provided only that the principal nuclear spin lattice relaxation process is via the impurities. With the exception of sapphire and cobalticyanide, the results are similar to those in Fig. 3. In these two materials the effects are much more complex. In sapphire, for example, each line of the Al^{27} quadrupole spectrum is en-

Table I. Maximum enhancement of nuclear resonance absorption in several materials.

Material		Nucleus	Enhancement
Ce ₂ Mg ₃ (NO ₃) ₆ ·24H ₂ O	Ce ⁺⁺⁺	H ¹	25:1
La ₂ Mg ₃ (NO ₃) ₆ ·24H ₂ O	5 % Ce ⁺⁺⁺ impurity	H ¹	60:1
Synthetic sapphire	0.1 % Cr ⁺⁺⁺ impurity	Al ²⁷	5:1
K ₃ Co(CN) ₆	2.5 % ferric impurity	Co ⁵⁹	2:1
Polytetrafluoroethylene	Centers due to electron bombardment	F ¹⁹	38:1
CaF ₂	0.01 % Ce ⁺⁺⁺ impurity	F ¹⁹	2:1
LiF	<i>F</i> centers due to x-rays	Li [†] F ¹⁹	17:1
LiF	<i>F</i> centers, 36 kMc/sec	Li ⁷	58:1

hanced or reversed to the same extent but, at a fixed field, on sweeping the microwave frequency from 8 to 10 kMc/sec a series of peaks in the enhancement are seen below 9 kMc/sec and a series of peaks in the reversal at frequencies above. These peaks extend over the whole range 2 kMc/sec of our microwave source.

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²A. Abragam and W. G. Proctor, *Compt. rend.* **246**, 2253 (1958).

³N. W. Lord, *Phys. Rev.* **105**, 756 (1957).

STRAIN-INDUCED CHANGES IN THE SEEBECK COEFFICIENT OF *n*-TYPE GERMANIUM

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(Received April 29, 1959)

We have measured the strain-induced changes in the Seebeck coefficient of oriented specimens of *n*-type germanium (with carrier concentration $3 \times 10^{14}/\text{cc}$) at mean temperatures of 82°K and 95.5°K. Large changes parallel to the applied stress were observed on [111] and [110] oriented specimens. The corresponding effects for [100] specimens were negligibly small in comparison, thus indicating that the changes are brought about solely as a consequence of the strain-induced changes in the carrier populations of the different valleys. The effect leads in a fairly direct way to an estimate of the anisotropy of the phonon-drag part of the Seebeck tensor for a single valley.

The theory of elasto-resistance under these conditions (Herring and Vogt¹) leads to expressions for the components of the variation of the conductivity with strain which are functions of the deformation potential constants and of $K (= \mu_{\perp}/\mu_{\parallel})$, the ratio of mobilities perpendicular

and parallel to the symmetry axis of a single valley. A closely parallel theory can be set up for the components of the variation with strain of the product of the conductivity and Seebeck tensors. These components involve the same parameters as the elasto-resistance components together with another parameter L which it is convenient to define as Q_{\parallel}/Q_{\perp} , the ratio of the components of the partial Seebeck tensor parallel and perpendicular to the symmetry axis of a valley. The theory is not completely analogous to the theory of elasto-resistance because the electronic part of the Seebeck tensor for a single valley changes with the carrier concentration. This change however is just k/e times the relative change in the conductivity of the corresponding valley, and thus the combined effect of such changes is simply related to the total conductivity change.

In view of this analysis, we have measured the relative resistivity changes $(\Delta\rho)/\rho_0$ under conditions of stress and temperature distribution