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## THE OVERHAUSER EFFECT AND RELATED PHENOMENA

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### 1. INTRODUCTION

THE production of oriented nuclei is of considerable interest. It is enough to note that the most important phenomenon discovered during the last few years, namely parity nonconservation in  $\beta$  decay, was observed by measuring the angular asymmetry of the  $\beta$  radiation of  $\text{Co}^{60}$  nuclei polarized by the Gorter-Rose method. Although almost complete information has been obtained in the last three years on the Hamiltonian of the  $\beta$  interaction, the production of oriented nuclei has not lost its significance. Actually, for example, we can determine the numerical values of nuclear matrix elements from Wu-Ambler experiments performed with other nuclei, by comparing the theoretical results with the experimental data. This is important for the verification of nuclear models. It is furthermore interesting to produce nuclear reactions with polarized incident nucleons and polarized targets. Measurement of the angular distribution of the  $\alpha$  radiation of oriented nuclei makes possible an investigation of the nonsphericity of nuclei. Of considerable interest are experiments on the production, scattering, and absorption of strange particles on polarized protons.

Finally, experiments with polarized nuclei are interesting also from the point of view of investigation of the properties of solids.

The methods first proposed for the production of oriented nuclei (polarization by means of an external field, the methods of Gorter-Rose, Pound, or Bleaney; see, for example, the reviews in references 1, 2, and 3) are based on the creation of conditions under which different nuclear-spin directions correspond to energies that differ by amounts greater than or of the order of  $kT$ . However, in view of the smallness of the nuclear magnetic and quadrupole moments, extremely low temperatures, (on the order of several hundredths of a degree) are necessary to obtain a considerable degree of orientation by these methods.

In 1953 Overhauser proposed<sup>4</sup> a very original and clever method of obtaining polarized nuclei, realizable at helium temperatures rather than at extremely low ones. Overhauser stated that his method was applicable only to metals. It was found later, however, that the Overhauser method can be used to polarize nuclei in many nonmetals, too.

We shall assume the reader to be familiar with the phenomenon of paramagnetic resonance (see surveys,

references 5-9). We shall nevertheless discuss briefly resonance saturation and its hyperfine structure, since the Overhauser effect is based on these phenomena. We shall also touch upon the so-called contact interaction between the electron and nuclear spins.

## 2. CONTACT INTERACTION BETWEEN ELECTRON AND NUCLEAR SPINS

We denote by  $\mathbf{S}$  and  $\mathbf{I}$  the spin operators of the electron and nucleus, respectively, and by  $\beta$  and  $\beta_n$  the operators of their magnetic moments. We have

$$\beta = -2\beta S, \quad \beta_n = \frac{\beta_n}{i} \mathbf{I} \quad (2.1)$$

( $\beta$  is the Bohr magneton while  $\beta_n$  and  $\mathbf{I}$  are the maximum projections of the magnetic moment and of the nuclear spin).

For the matrix element of the energy of interaction between the magnetic moments of the electron and the nucleus (electron transition  $i \rightarrow f$ ) we can write

$$V_{fi} = -\frac{1}{c} \int \mathbf{A} \mathbf{j}_i d\tau, \quad (2.2)$$

where  $\mathbf{j}$  is the current density due to the magnetic moment of the electron and  $\mathbf{A}$  is the vector potential of the field produced by the nuclear magnetic moment.

Furthermore

$$\mathbf{A} = \frac{[\beta_n \times \mathbf{r}]}{r^3} = -\left[ \beta_n \times \nabla \frac{1}{r} \right] = \text{curl} \frac{\beta_n}{r} \quad (2.3)$$

( $\mathbf{r}$  is the radius vector of the electron relative to the nucleus), and thus

$$V_{fi} = \frac{1}{c} \beta_n \int \left[ \nabla \frac{1}{r} \times \mathbf{j}_i \right] d\tau. \quad (2.4)$$

We denote by  $\psi_i$  and  $\psi_f$  the initial and final wave functions of the electron. For  $\mathbf{j}_i$  we have<sup>10</sup>

$$\mathbf{j}_i = -2\beta c \text{curl}(\psi_i^* \mathbf{S} \psi_i). \quad (2.5)$$

Thus,

$$V_{fi} = -2\beta \beta_n \int \left[ \nabla \frac{1}{r} \times \text{curl}(\psi_i^* \mathbf{S} \psi_i) \right] d\tau.$$

This expression can be converted to the following form (see reference 10, p. 548):

$$V_{fi} = -\frac{8\pi}{3} \psi_i^*(0) (\beta \beta_n) \psi_i(0) - \int \psi_i^*(\mathbf{r}) \frac{3(\beta \mathbf{r})(\beta_n \mathbf{r}) - r^2(\beta \beta_n)}{r^5} \psi_i(\mathbf{r}) d\tau, \quad (2.6)$$

so that we can obtain an expression for the operator  $V$

$$V = -\frac{8\pi}{3} (\beta \beta_n) \delta(\mathbf{r}) - \frac{3(\beta \mathbf{r})(\beta_n \mathbf{r}) - r^2(\beta \beta_n)}{r^5}. \quad (2.7)$$

It is customary to call the first term of the last expression the contact or hyperfine-structure term, while the second is known as the dipole-dipole term.

We shall henceforth be interested in cases when the initial and final wave functions of the electron  $\psi_i$  and  $\psi_f$ , are almost identical with regards to the spatial state. In this case the contact term is proportional to  $|\psi(0)|^2$ . It is known that  $\psi(0)$  differs from zero in

the  $s$  state and vanishes in the  $p, d, \dots$ , states. On the other hand, the dipole-dipole term vanishes in the  $s$  state, in view of the spherical symmetry of the wave function.

The operator of the energy of interaction of the magnetic moments of the electron and the nucleus reduces thus to the contact term in the case of the  $s$  state, and to the dipole-dipole term in the case of the  $p, d, \dots$  states. A very important circumstance in this case is that in the  $s$  state  $|\psi(0)|^2$  is usually sufficiently large, and therefore the energy of interaction of magnetic moments of the electron and the nucleus is usually much greater in the  $s$  state than in the  $p, d, \dots$  states.

It happens frequently that the electron wave function does not have a definite azimuthal quantum number. In this case we expand  $\psi$  in wave functions with definite azimuthal quantum numbers:

$$\psi = \alpha_s \psi_s + \alpha_p \psi_p + \alpha_d \psi_d + \dots$$

It follows from the foregoing that if  $\alpha_s$  is not anomalously small, in other words, if  $|\psi(0)|^2$  is sufficiently large, then the contact term is much greater than the dipole-dipole term and the latter can be neglected. In this case

$$V = -\frac{8\pi}{3} \beta \beta_n \delta(\mathbf{r}) = \frac{16\pi}{3} \frac{\beta \beta_n}{i} \text{Si} \delta(\mathbf{r}). \quad (2.8)$$

Let us analyze a few examples, which will be found useful later on.

### a) Atom of Hydrogen or of an Alkali Metal

In the ground state of an atom of hydrogen or of an alkali metal, the valence electron is in the  $s$  state. Therefore the dipole-dipole term will be exactly equal to zero and only the contact term remains.

### b) Metals of the First Group

We are interested in the magnetic interaction between the nucleus and an electron located in the conduction band and of energy close to the Fermi boundary. It is known from the theory of metals that in the case of metals of the first group the conduction band is a hybrid  $s + p$  band. Therefore the fraction of the  $s$  state in the wave function of the electron will not be small,  $|\psi(0)|^2$  will be large (as confirmed by experiments on the so-called Knight shift<sup>11</sup>), and the dipole-dipole term will be negligibly small.

### c) Silicon or Germanium with Pentavalent Donor or Trivalent Acceptor Impurity

The model which explains the properties of germanium or silicon with a pentavalent or a trivalent impurity is well known. To be specific, we shall discuss only arsenic or aluminum doped silicon.

The arsenic atom replaces a silicon atom; in this case the four valence electrons of the arsenic are sufficient to saturate the covalent bonds with the four

nearest atoms of the silicon. At sufficiently low temperatures the fifth electron is localized near the arsenic ion; at high temperatures it is not localized and causes the electronic conduction. Thus, at low temperatures we have the system  $\text{As}^+ + \text{electron}$ , and we speak of a magnetic interaction between the electron and the nucleus of the arsenic. This system is analogous to the hydrogen atom, the only difference being that, firstly, account must be taken of the dielectric constant of the medium, and secondly, the effective mass of the electron is used instead of the true mass. Both circumstances lead to an increase in the orbit dimensions, i.e., to a reduction in  $|\psi(0)|^2$ , but  $|\psi(0)|^2$  remains still sufficiently large to be able to neglect the dipole-dipole term in the magnetic interaction in the spins of the electron and the nucleus.

At high temperatures, one speaks of magnetic interaction between the spins of the nucleus and the non-localized electron, a situation similar to that in a metal. In this case, too, the contact term is expected to predominate.

The situation is analogous for aluminum doped silicon, except that the positive arsenic ion and the "excess" electron are replaced by a negative ion of aluminum with an "excess" hole.

According to experiment, the ionization energy of the trivalent or pentavalent impurity is on the order of 0.05 eV in the case of silicon and 0.01 eV in the case of germanium. At helium temperatures, therefore, almost all the "excess" electrons or holes in the silicon are localized near the impurity ions, whereas in the case of germanium a considerable part of the impurity atoms is ionized. On the other hand, at hydrogen temperatures the greater part of the impurity atoms is ionized in the case of silicon, too.

#### d) F center in Alkali-Halide Crystals

To be specific, we shall discuss the KCl crystal.

It has been well established that the F center is a chlorine-ion vacancy that has captured an electron. According to the LCAO (linear combination of atomic orbitals) model the  $\psi$  function of the electron of the F center has approximately the following form:<sup>12</sup>

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{6}} \sum_{i=1}^6 \varphi(\mathbf{r} - \mathbf{r}_i), \quad (2.9)$$

where  $\mathbf{r}$  is the radius vector of the electron relative to the center of the vacancy, and  $\mathbf{r}_i$  is the radius vector of the  $i$ -th of the potassium ions surrounding the vacancy. The summation is over the six potassium ions located on the first coordination sphere. In other words, it is assumed that the electron is localized with equal probabilities on the six potassium ions nearest the vacancy. The function  $\varphi$  in (2.9) is the wave function of the electron in the field of the potassium ion (whose shell is deformed by the vacancy field).

If  $|\psi(\mathbf{r}_i)|^2$  is sufficiently large [in other words, if  $|\psi(0)|^2$  is sufficiently large], we can neglect in the

magnetic interaction between the spins of the electron and of the  $i$ -th potassium nucleus the dipole-dipole term compared with the contact term. The validity of this neglect is confirmed by experiment;<sup>12</sup> experiment yields a value of approximately 0.5–0.6 for the fraction of the  $s$  state in the wave function  $\varphi$ .

#### e) Free Radical

By way of an example, let us consider the free radical of diphenyl picryl hydrazil (abbreviated DPPH). The structural formula of this radical is of the form



The dot signifies that one of the covalent bonds of the nitrogen is not saturated, i.e., it is produced by only one electron. One can expect the magnetic interaction of this uncompensated electron with the two neighboring nitrogen nuclei to be essentially a contact interaction, while the interaction with the hydrogen nuclei is dipole-dipole [since  $|\psi(0)|$  is large in the former case and small in the latter].

#### f) Paramagnetic Ion Containing a Spinning Nucleus

Let us consider a hydrated paramagnetic salt. In this case the magnetic interaction of the nearest paramagnetic ions is relatively small, and can be further reduced by diluting the salt.

Let us ponder on the magnetic interaction between the nucleus and electrons of the partially filled shells. It would appear at first glance that there should be no contact term in this case. Actually, the paramagnetic ion has a partially filled 3d (ions of the iron group) or 4f (ions of the rare-earth group) shell, and  $\psi(0) = 0$  for the d and f electrons. A weak magnetic interaction is therefore expected.

The magnetic interaction between the nucleus and the electrons appears in the hyperfine structure of the paramagnetic-resonance spectrum (see Sec. IV). Experiment shows that in many cases the hyperfine structure is considerably greater than expected for 3d or for 4f electrons. The only explanation for this fact was the hypothesis, advanced by Abragam,<sup>14</sup> that a noticeable role is played by the shell states with unpaired electrons. According to this hypothesis, for example in the case of elements of the iron group, the ground state of the paramagnetic ion, contains, in addition to the  $3s^2 3d^n$  state, the state  $3s 3d^{n-1} 4s$ , with small weight. In spite of the smallness of the weight, the second term will play a predominant role in the magnetic interaction. This mixing is called configuration mixing.

It must be noted that it is still unknown whether configuration mixing exists in all cases, and it is therefore unclear whether it is permissible in all cases to retain for paramagnetic salts the contact term in the magnetic interaction between the nucleus and the electron shell of the paramagnetic ion.

We shall confine ourselves henceforth to an examination of paramagnetic salts for which the effective spin of the shell of the paramagnetic ion is  $1/2$ . This means that in the absence of an external magnetic field we have one doubly degenerate level (disregarding the degeneracy connected with the nuclear spin); the remaining levels have energies considerably greater than  $kT$  and are therefore not populated. The case of effective spin equal to  $1/2$  is quite frequent. For example, this occurs for salts of cobalt, copper, titanium, praseodymium, neodymium, etc.

We have seen earlier that the contact term in the energy of magnetic interaction of an electron with a nucleus is proportional to  $\mathbf{S}\mathbf{I}$ . On the other hand, it is easily seen that  $\mathbf{S}\mathbf{I}$  commutes with the expression  $\mathbf{S} + \mathbf{I}$ .<sup>\*</sup> The operators  $3(\mathbf{S}\mathbf{r})(\mathbf{I}\mathbf{r}) - r^2\mathbf{S}\mathbf{I}$  and  $\mathbf{S} + \mathbf{I}$  do not commute, however. Thus, the contact term commutes with the total spin, while the dipole-dipole term does not.

Denoting by  $M$  and  $m$  the eigenvalues of the operators  $S_z$  and  $I_z$ , we have the following selection rules for transitions due to the contact interaction:

$$\Delta M = -\Delta m = \pm 1.$$

Transitions with such selection rules are called flip-flop transitions. The dipole-dipole term, causes in addition to flip-flop transitions also the following transitions:

|                                  |                        |
|----------------------------------|------------------------|
| $\Delta M = \Delta m = \pm 1$    | flip-flop transitions  |
| $\Delta M = \pm 1, \Delta m = 0$ | vertical transitions   |
| $\Delta M = 0, \Delta m = \pm 1$ | horizontal transitions |

(the reason for the terms "vertical" and "horizontal" will be explained later).

Finally, in the case of nuclear spin greater than  $1/2$ , an important role can also be played by quadrupole transitions

$$\Delta M = 0, \quad \Delta m = \pm 2,$$

due to the interaction between the nuclear quadrupole moment and the electric field of the surrounding charges. (We note that there will be also quadrupole transitions with the same selection rules as the horizontal transitions.)

### 3. SATURATION OF PARAMAGNETIC RESONANCE

Let us consider the case  $S = 1/2$  ( $S$  is either the spin of the electron or the effective spin of the shell of the paramagnetic ion) and no hyperfine structure. When an external magnetic field  $H$  is applied, we obtain two Zeeman levels corresponding to projections  $+1/2$  and  $-1/2$  of  $\mathbf{S}$  on the field (Fig. 1). The energy difference between these levels is  $g\beta H$ , where  $g$ , generally speaking, depends on the orientation of the external field relative to the crystallographic axes.

<sup>\*</sup>It is easy to see that  $S_z + I_z$  commutes also with the expression

$$A S_z I_z + B (S_x I_x + S_y I_y).$$

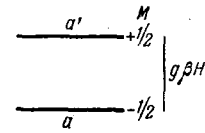


FIG. 1

We denote the level populations by  $N(a)$  and  $n(a')$ , the total number of spins in the sample by  $N$ , and the excess of spins in the lower state by  $D$ . We have

$$N(a) + N(a') = N, \quad (3.1)$$

$$N(a) - N(a') = D. \quad (3.2)$$

The probabilities of relaxation transitions (i.e., transitions caused by the spin-lattice interaction)  $a \rightarrow a'$  and  $a' \rightarrow a$  per unit time will be denoted by  $W(aa')$  and  $W(a'a)$ . In the case of Boltzmann statistics, we can assume that<sup>\*</sup>

$$\frac{W(a'a)}{W(aa')} = e^{2\delta}, \quad (3.3)$$

where

$$\delta = \frac{g\beta H}{2kT}. \quad (3.4)$$

We introduce the quantity

$$W = [W(aa')W(a'a)]^{1/2}. \quad (3.5)$$

Generally speaking,  $W$  will be a function of the temperature and of the external field. We have

$$W(aa') = W e^{-\delta}, \quad W(a'a) = W e^{\delta}. \quad (3.6)$$

We readily obtain for the equilibrium excess

$$D_0 = N \tanh \delta. \quad (3.7)$$

We furthermore have

$$\begin{aligned} \dot{D} &= -2N(a)W(aa') + 2N(a')W(a'a) \\ &= -2W \cosh \delta [D - N \tanh \delta], \end{aligned}$$

or

$$\dot{D} = \frac{1}{T_1} (D_0 - D), \quad (3.8)$$

where

$$T_1 = \frac{1}{2W \cosh \delta} = \frac{1}{W(aa') + W(a'a)}. \quad (3.9)$$

The solution of (3.8) is of the form

$$D(t) = D_0 + [D(0) - D_0] e^{-t/T_1}.$$

$T_1$  is therefore called the spin-lattice relaxation time.

Assume that, in addition to the constant field, an alternating field is applied to the sample, of frequency  $\omega$  close to  $g\beta H/h$  and of amplitude much less than that of the constant field. We denote by  $W(a)$  the proba-

<sup>\*</sup>Actually, in equilibrium  $N^0(a)W(aa') = N^0(a')W(a'a)$  (the superscript 0 denotes the equilibrium value). On the other hand,  $N^0(a)/N^0(a') = e^{2\delta}$ . Therefore  $W(a'a)/W(aa') = e^{2\delta}$ . But since the transition probabilities are independent of whether equilibrium exists, the last equation holds also in the absence of equilibrium.

bility per unit time of the transition  $a \leftrightarrow a'$ , due to the alternating field (the alternating field produces transitions  $a \rightarrow a'$  and  $a' \rightarrow a$  with equal probability\*). In the stationary case we have

$$N(a)[W(a) + W e^{-\delta}] = N(a')[W(a) + W e^{\delta}],$$

which yields

$$D = \frac{NW(e^{\delta} - e^{-\delta})}{2W(a) + W(e^{\delta} + e^{-\delta})} = \frac{D_0}{1 + 2W(a)T_1}. \quad (3.10)$$

We introduce the parameter of saturation of a magnetic resonance,  $s$ , by means of the following formula

$$s = 1 - \frac{D}{D_0} = 1 - \frac{N(a) - N(a')}{N^0(a) - N^0(a')}. \quad (3.11)$$

We can readily obtain

$$s = \frac{2W(a)}{2W(a) + W(e^{\delta} + e^{-\delta})} = \frac{2W(a)T_1}{1 + 2W(a)T_1}. \quad (3.12)$$

For the power absorbed by the sample (from the source that produces the alternating field) we can write

$$P = W(a) D g \beta H,$$

which can be readily transformed to

$$P(s) = D_0 \frac{g \beta H}{2T_1} s. \quad (3.13)$$

Let us analyze the physical meaning of the above results. Equation (3.12) shows that  $s \ll 1$  when  $W(a)T_1 \ll 1$  and  $s = 1$  when  $W(a)T_1 \gg 1$ . This can be readily understood, considering that  $W(a)T_1$  is the probability of reorientation of the spin under the influence of the alternating field during a time  $T_1$ . Actually, two factors influence the spin system. On the one hand, the interaction between the spins and the lattice tends to establish a Boltzmann distribution of the spins over their Zeeman levels. On the other hand, the interaction between the spins and the alternating field tends to establish equality of  $N(a)$  and  $N(a')$ , i. e., to make  $s$  equal to unity. Which of these factors predominates depends on  $W(a)T_1$ .

We say that there is no saturation when  $s \ll 1$ , the resonance saturation is complete when  $s = 1$ , and the saturation is partial when  $s \lesssim 1$ .

The physical meaning of Eq. (3.13) for the absorbed power is also quite clear. Actually, when  $s = 1$ , i. e., for complete saturation, the alternating field should flip  $D_0/2$  spins within a time  $T_1$  from the lower level to the upper one, corresponding to an absorbed power equal to  $D_0 g \beta H / 2T_1$ .

We can derive the following expression for  $W(a)$ :<sup>15</sup>

$$W(a) = W(\omega) = \frac{\pi}{2} (\gamma H_1)^2 \varphi(\omega), \quad (3.14)$$

where  $\gamma$  is the gyromagnetic ratio of the spin,  $2H_1$  the amplitude of the alternating field (it is assumed applied perpendicular to the main field), and  $\varphi(\omega)$  a

\*In the radio and microwave regions we can neglect the spontaneous transitions.

function that defines the shape of the absorption line and is normalized by the condition

$$\int_0^{\infty} \varphi(\omega) d\omega = 1. \quad (3.15)$$

Substitution of (3.14) in (3.12) yields

$$s(\omega) = \frac{\pi (\gamma H_1)^2 T_1 \varphi(\omega)}{1 + \pi (\gamma H_1)^2 T_1 \varphi(\omega)} = \frac{1}{1 + \left[ \frac{H_1^c(\omega)}{H_1} \right]^2}, \quad (3.16)$$

where

$$H_1^c(\omega) = \frac{1}{\gamma \sqrt{\pi T_1 \varphi(\omega)}}. \quad (3.17)$$

Let, in particular, exact resonance take place

$$\omega = \omega_0 = \gamma H.$$

We consider that<sup>15</sup>

$$\pi \varphi(\omega_0) = T_2, \quad (3.18)$$

where  $1/T_2$  is the width of the absorption line based on the true frequency (the width being taken to be the width of a rectangle, whose height is equal to half the height of the maximum, and whose area is unity). We obtain

$$W(\omega_0) = \frac{1}{2} (\gamma H_1)^2 T_2, \quad (3.19)$$

$$s = s(\omega_0) = \frac{1}{1 + \left( \frac{H_1^c}{H_1} \right)^2}, \quad (3.20)$$

where

$$H_1^c = H_1^c(\omega_0) = \frac{1}{\gamma \sqrt{\pi T_1 T_2}}. \quad (3.21)$$

When  $H_1 \ll H_1^c$  we have  $s \approx 0$ , whereas when  $H_1 \gg H_1^c$  we have  $s \approx 1$ . For this reason  $H_1^c$  is called the critical field, or more accurately, the critical half-amplitude of the alternating field.

The physical meaning of (3.21) is clear; this formula indicates that  $H_1^c$  increases with decreasing  $T_1$  and  $T_2$ . Actually, the stronger the relaxation and the broader this line, the more difficult it is to saturate the absorption line.

Let us discuss briefly the nonstationary case. It is easy to set up an equation for  $D$

$$\frac{dD}{dt} = \frac{1}{T_1} (D_0 - D) - 2W(a)D, \quad (3.22)$$

whose solution yields

$$D(t) = \frac{D_0}{1 + 2W(a)T_1} + \left[ D(0) - \frac{D_0}{1 + 2W(a)T_1} \right] e^{-\frac{t}{\tau}}, \quad (3.23)$$

where  $\tau$  is given by

$$\frac{1}{\tau} = \frac{1}{T_1} + 2W(a). \quad (3.24)$$

$\tau$  is the time of approach to the stationary state. It is less than  $T_1$ . In the limiting cases we have

$$\tau = T_1 \quad \text{for } H_1 \ll H_1^c,$$

$$\tau = \frac{1}{2W(a)} \sim H_1^{-2} \quad \text{for } H_1 \gg H_1^c.$$

Thus, at sufficiently large  $H_1$ , the stationary state is reached quite rapidly.

The foregoing theory of saturation of magnetic resonance is not quite exact. It needs a generalization for excessive values of  $H_1$  (see reference 16) and also for the case of the so-called inhomogeneous broadening (see reference 17). We shall not discuss these questions, however.

Let us touch briefly on a question which will be very important in what follows, of the so-called "adiabatically fast" passage through resonance. Assume that we pass through resonance between two levels by changing the external main magnetic field (the frequency of the alternating field is fixed). If the passage through resonance is sufficiently rapid, the relaxation effects will be insignificant during the time of passage. The question of rapid passage through resonance was considered theoretically by Bloch,<sup>18</sup> who showed that in rapid passage an exchange takes place between the populations of two levels, or, as is customarily said, an inversion of two levels takes place. In order for the passage to be rapid, the following condition must be satisfied

$$\frac{H_1}{T_2} \ll \left| \frac{dH}{dt} \right| \ll |\gamma| H_1^2. \quad (3.25)$$

We obtain from this, in particular, that  $H_1$  must be considerably greater than  $1/\gamma T_2$ , i.e., than the width of the absorption line. Furthermore, if we take the time of passage through resonance to mean the expression  $H_1 \left| \frac{dH}{dt} \right|^{-1}$ , it follows from (3.25) that this time should be considerably smaller than  $T_2$ .

The distribution obtained as a result of a rapid passage will naturally not be in equilibrium, and a relaxation to the equilibrium state will take place, with a relaxation time  $T_1$ .

#### 4. HYPERFINE STRUCTURE OF PARAMAGNETIC RESONANCE

Let us consider first the case of a paramagnetic salt. If the nucleus of the paramagnetic ion has a spin, the paramagnetic resonance will have a hyperfine structure.

Let us analyze the case when the external field is sufficiently large, namely much larger than the field with which the nucleus acts on the shell spin (the Back-Goudsmit case). For this it is usually sufficient that the external field be greater than 2 or 3 kilooersteds.

In a strong field, the projections  $M$  and  $m$  of the spins of the electron and of the nucleus on the field are good quantum numbers. The selection rules for paramagnetic resonance are of the form  $\Delta M = \pm 1$  and  $\Delta m = 0$ . But the projection of the nuclear spin  $m$  has  $2I + 1$  possible values. Therefore the total field acting on the spin of the shell will have  $2I + 1$  possible values, and for this reason the paramagnetic resonance will have  $2I + 1$  hfs components. In the case of a strong field these components will be equidistant and of equal intensity.

For details concerning the hyperfine structure of paramagnetic resonance in paramagnetic salts we refer the reader to the survey by Bleaney and Stevens.<sup>5</sup> We note merely that to resolve the hyperfine structure the experiments must be carried out with dilute salts.

The situation is quite analogous at low temperatures in the case of silicon or germanium with pentavalent donor or trivalent acceptor impurity, if the nucleus of the impurity has a spin. Let us consider, for example, silicon with an arsenic impurity. Among the isotopes of arsenic, only  $As^{75}$ , with spin  $3/2$ , is stable. Therefore the total field acting on the "fifth excess" electron of the arsenic will have four possible values, and consequently the hyperfine structure will have four components.

Analogously, in the case of phosphorus doped silicon we obtain a hyperfine structure with two components ( $P^{31}$  has spin  $1/2$ ).

Both in the case of a paramagnetic salt and in the case of silicon or germanium with pentavalent or trivalent impurities (at low temperatures), the problem reduces to the analysis of a system consisting of an electron shell of a paramagnetic ion with effective spin  $S$  (we confine ourselves to  $S = 1/2$ ), or an electron, or a hole and a nucleus with spin  $I$ , placed in an external magnetic field  $H$ . Abragam and Pryce<sup>19</sup> have shown that such a system can be described by a so-called spin Hamiltonian, which in the case of axial symmetry of the intracrystalline field has the form

$$\mathcal{H} = \beta [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + [A S_z I_z + B (S_x I_x + S_y I_y)] + P \left[ I_z^2 - \frac{1}{3} I(I+1) \right] - g_I \beta H I, \quad (4.1)$$

where  $z$  is the symmetry axis of the intercrystalline electric field,  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A$ ,  $B$ , and  $P$  are constants determined by comparison with experimental data, and  $g_I \beta = \beta_n / I$  ( $\beta$  is the nuclear magnetic moment).

In the case of silicon or germanium with pentavalent or trivalent impurities, the symmetry is spherical (more accurately, cubic) and therefore  $A = B$  and  $g_{\parallel} = g_{\perp}$ . In the case of paramagnetic salts, generally speaking,  $A \neq B$  and  $g_{\parallel} \neq g_{\perp}$ .

In the case of a strong field ( $g\beta H \gg A, B$ ), the energy levels of the spin Hamiltonian have the form<sup>20</sup>

$$E_{Mm} = Mg\beta H + KMm + O\left(\frac{A^2, AB, B^2}{g\beta H}, P, g_I \beta H\right), \quad (4.2)$$

where

$$g = \sqrt{g_{\parallel}^2 \cos^2 \vartheta + g_{\perp}^2 \sin^2 \vartheta}, \quad (4.3)$$

$$Kg = \sqrt{A^2 g_{\parallel}^2 \cos^2 \vartheta + B^2 g_{\perp}^2 \sin^2 \vartheta} \quad (4.4)$$

( $\vartheta$  is the angle between the directions of  $H$  and  $z^*$ ).

For the transition energies of the paramagnetic resonance we obtain

\*A detailed investigation shows<sup>20</sup> that if the external magnetic field is not directed along one of the principal directions of the tensor  $g_{ik}$ , then the quantization axes of  $I$  and  $S$  do not coincide with the direction of the external field.

$$g\beta H + Km,$$

i.e., as indicated above, we have  $2\dot{I} + 1$  equidistant components.

All the foregoing pertains to the ordinary (or allowed) paramagnetic resonance. In addition to ordinary paramagnetic resonance, so-called forbidden paramagnetic resonance is possible, in which the projection of the nuclear spin  $m$  also changes by  $\pm 1$ . These transitions are due to mixing of states with different  $m$ , resulting from the term proportional to  $B$  in the spin Hamiltonian (4.1). The theory of forbidden paramagnetic resonance is considered in references 21 and 22.

If the spin Hamiltonian has an axial symmetry, and the external field is directed along the symmetry axis of the intracrystalline electric field, we obtain the following selection rules for the transitions of the forbidden paramagnetic resonance (we denote the levels by their quantum numbers in a strong field)

$$\Delta M = -\Delta m = \pm 1.$$

It is easily seen that in order for such transitions to take place, the resonating field must have a non-zero component along the main field. It is also easy to see that the forbidden paramagnetic resonance will have a hyperfine structure consisting of  $2\dot{I}$  components with transition energies approximately equal to

$$g_{\parallel}\beta H + \left(\dot{I} - \frac{1}{2}\right)A, \\ g_{\parallel}\beta H + \left(\dot{I} - \frac{3}{2}\right)A, \dots, g_{\parallel}\beta H - \left(\dot{I} - \frac{1}{2}\right)A.$$

A simple estimate shows that the probability of a forbidden transition is, in order of magnitude,  $(g_{\parallel}\beta H/A)^2$  times smaller than the probability of the allowed transition.

We note finally that if the external field is not directed along the symmetry axis of the intracrystalline field, or else if the spin Hamiltonian does not have axial symmetry, forbidden transition with selection rules  $\Delta M = \Delta m = \pm 1$  will also be possible.

Let us turn now to the question of the hyperfine structure in the case of other systems, confining ourselves to the case of ordinary (allowed) paramagnetic resonance.

We consider the hyperfine structure in the case of resonance on F centers.<sup>12</sup> Specifically, we shall again discuss the KCl crystal. The electron of the F center experiences magnetic interactions with the nuclei of the six potassium ions surrounding the vacancy, and also with more remote nuclei. In first approximation we can confine ourselves to a calculation of the interaction with the six nearest potassium nuclei. Because of the large number of possibilities of distribution of spin directions of these nuclei, we usually obtain an unresolved hyperfine structure. In other words, the individual components of the hyperfine structure overlap, and considerable broadening of the absorption line takes place. For example, in the case of KCl, the

width of the absorption line is approximately 100 oersteds. In individual cases, in particular in the case of LiF, a resolved hyperfine structure is obtained.

A hyperfine structure is obtained also in the case of paramagnetic resonance on a free radical, provided a nucleus with spin is located near the uncompensated bond. For example, owing to the two nitrogen nuclei, paramagnetic resonance on highly dilute DPPH produces a hyperfine structure with five components.<sup>13</sup>

In the case of paramagnetic resonance on a metal, i.e., on the conduction electrons, no hyperfine structure is observed. The reason for the absence of a hyperfine structure in this case is that the conduction electrons are not localized, but wander over the entire crystal, and the field produced by the nucleus and acting on the conduction electron is therefore averaged.

There is likewise no hyperfine structure in resonance on doped silicon or germanium at high temperatures. The point is that at high temperatures the "excess" electrons and holes, as we have seen above, are not localized near the impurity atoms.

Nor is there any hyperfine structure in the case of resonance in a liquid containing paramagnetic ions, provided the nuclei of the paramagnetic atoms have no spin. The reason for the absence of hyperfine structure is the same as in the case of metals.

### 5. OVERHAUSER EFFECT WITH COMPLETE SATURATION OF ALL THE COMPONENTS

Let us consider a system consisting of an electron or an electron shell with effective spin  $S = \frac{1}{2}$  and a nucleus with spin  $\dot{I}$ , placed in an external magnetic field  $H$ . We assume the external field to be sufficiently strong. The energy levels of the system are given by (4.2). When calculating the Boltzmann populations, we neglect the spin-spin interaction energy. Then the level picture assumes the form shown in Fig. 2, i.e., we obtain  $2\dot{I} + 1$  pairs of levels, and the difference in the energies of the components of each pair is  $g\beta H$ . For the sake of brevity, the state  $M = -\frac{1}{2}$ ,  $m$  will be denoted by  $m$ , and the  $M = \frac{1}{2}$ ,  $m$  will be denoted by  $m'$ .

In the case of statistical equilibrium, the respective populations of each lower and upper level are

$$N^0(m) = \frac{N}{2\dot{I} + 1} \frac{e^{\delta}}{e^{\delta} + e^{-\delta}}, \quad N^0(m') = \frac{N}{2\dot{I} + 1} \frac{e^{-\delta}}{e^{\delta} + e^{-\delta}}, \quad (5.1)$$

and the approximate nuclear polarization is zero.

If all the components of the hyperfine structure are completely saturated, we obtain

$$N(m) = N(m') \quad \text{for all } m.$$

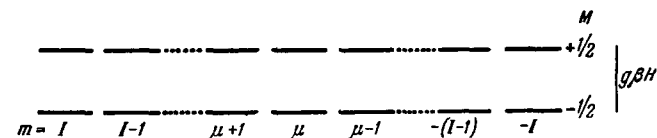


FIG. 2

If it is assumed that the nuclear spin interacts only with the electron spin, and that this interaction is of the contact type, equilibrium will exist in the stationary case for all the flip-flop transitions, and we obtain

$$N(\dot{I}) : N(\dot{I} - 1) = N(\dot{I} - 1) : N(\dot{I} - 2)$$

$$= \dots = N(-\dot{I} + 1) : N(-\dot{I}) = e^{2\delta},$$

where  $\delta$  is given by (3.4).

Using these conditions we readily obtain

$$N(m) + N(m') = \text{const} \cdot e^{2m\delta}, \quad (5.2)$$

where the constant is independent of  $m$ .

We thus find that the states with different nuclear-spin projections have a Boltzmann distribution, but with a Boltzmann factor  $\exp(g\beta H/kT) = \exp(\hbar\gamma_e H/kT)$ , instead of the  $\exp(\hbar\gamma_n H/kT)$ , obtained in statistical equilibrium in the absence of saturation;  $\gamma_n$  denotes the paramagnetic ratio of the nucleus;  $\gamma_e$  denotes the absolute value of the gyromagnetic ratio of the electron, or, in the case of a paramagnetic salt, the gyromagnetic ratio of the spin of the shell. This shows that, with total saturation of all the hfs components of paramagnetic resonance, the effective gyromagnetic ratio of the nucleus is equal to the gyromagnetic ratio of the electron (or of the shell of the paramagnetic ion):

$$\gamma_{\text{eff}} = \gamma_e. \quad (5.3)$$

This is the Overhauser effect. More generally, the Overhauser effect is the increase of nuclear polarization upon saturation of the electron paramagnetic resonance.

If the quantization of the nuclear spin has an axial symmetry, the degree of orientation of the nuclei can be characterized quantitatively by  $2\dot{I}$  quantities  $f_k$  ( $k = 1, 2, \dots, 2\dot{I}$ ).<sup>23</sup> The most important of these are

$$f_1 = \frac{1}{\dot{I}} \langle m \rangle, \quad (5.4)$$

$$f_2 = \frac{3}{\dot{I}(2\dot{I}-1)} \left[ \langle m^2 \rangle - \frac{1}{3} \dot{I}(\dot{I}+1) \right] \quad (5.5)$$

(the symbol  $\langle \rangle$  denotes averaging over nuclei of a given type in the sample).

It is easy to write all the values of  $f_k$  for total saturation of all the hfs components of paramagnetic resonance. For this purpose we must replace  $\gamma_n$  with  $\gamma_e$  in the expressions for  $f_k$  in the case of polarization with an external field.<sup>23</sup> In particular we obtain

$$f_1 = B_{\dot{I}}(2\dot{I}\delta), \quad (5.6)$$

$$f_2 = \frac{2(\dot{I}+1)}{2\dot{I}-1} - \frac{3}{2\dot{I}-1} \coth \delta B_{\dot{I}}(2\dot{I}\delta), \quad (5.7)$$

where  $B_{\dot{I}}(y)$  is the so-called Brillouin function.

It appears at first glance that the above deduction holds only when the sample contains individual systems, each of which consists of a nucleus with spin  $\dot{I}$  and an electron (or a hole, or an electron shell with  $S = 1/2$ ). This is the case at sufficiently low tempera-

tures, for example, for silicon or germanium with pentavalent donor or trivalent acceptor impurities. We have a similar situation in the case of a paramagnetic salt in which the nuclei of the paramagnetic atoms have spins. We note that in these cases the paramagnetic resonance has a hyperfine structure.

There exist other cases, however. For example, in the case of a metal, in view of the non-localization of the conduction electrons, the electrons will change in the vicinity of a given nucleus. The same situation will prevail in the case of silicon or germanium with donor or acceptor impurity at high temperatures, when the excess electrons or excess holes are not localized. The situation is also analogous in the case of a solution containing paramagnetic atoms, if one speaks of polarization of the solvent nuclei. We note that in all these cases the paramagnetic resonance does not have a hyperfine structure.

It is easily seen, however, that with total saturation of paramagnetic resonance the aforementioned result will remain in force in these cases, too, for as soon as the resonance of all the electrons is saturated, their exchange near a given nucleus will not play any role. The result remains true also in the case of a metal, since the foregoing proof remains valid also in the case of Fermi statistics.\*

Thus, if the paramagnetic resonance is completely saturated (all the components are saturated in the presence of a hyperfine structure), and if we can neglect the non-contact terms in the nuclear spin interactions, then  $\gamma_{\text{eff}} = \gamma_e$  in all cases. This takes place independently of the sign of  $\gamma_n$ , and thus, a positive polarization of the nuclei is obtained in this case ( $f_1 > 0$ ), i.e., the average spin is directed along the external field.

In the sections that follow we shall analyze in detail systems of different types. We shall see that if the saturation is incomplete or if the non-contact terms in the relaxation of the nuclear spin cannot be neglected, the results will be different for different substances. In further calculations we shall also take into account the Zeeman energy of the nucleus.

Before we proceed to a detailed analysis of the Overhauser effect in the case of specific substances, it will be useful to clarify the physical nature of this effect. Let us turn again to Fig. 2. When all the paramagnetic resonance components are saturated, we artificially increase the population of the upper levels. If the nuclear spin experiences only flip-flop relaxation, then we obtain after saturation the transitions  $\mu' \rightarrow \mu + 1$  ( $\mu = \dot{I}, \dot{I} - 1, \dot{I} - 2, \dots, -\dot{I}$ ), as a result of which the states with large  $m$  will be more strongly populated, i.e., we obtain nuclear polarization;

\*This is connected with the fact that  $g_F/(1 - g_F) = g_B$ , where  $g_F$  and  $g_B$  are the Fermi and Boltzmann distribution functions, respectively.



the foregoing calculation shows that with complete saturation  $\gamma_{\text{eff}} = \gamma_e$ .\*

If, on the other hand, the nuclear spin experiences only flip-flip relaxation, then the transitions  $\mu' \rightarrow \mu - 1$  ( $\mu = \dot{i}, \dot{i} - 1, \dots, -\dot{i} + 1$ ) take place, and we obtain  $\gamma_{\text{eff}} = -\gamma_e$ .

If the relaxation of the nuclear spins is not connected with the interaction with electrons (for example, if the relaxation is quadrupole) or, more generally, if relaxation processes in which the projection of the electron spin does not change strongly predominate, then the nuclear polarization will correspond to the true gyromagnetic ratio of the nucleus, i.e., the Overhauser effect will not take place in this case. Nor will there be any Overhauser effect when the probabilities of the flip-flop and flip-flip transitions are equal.

Thus, in order for the Overhauser effect to take place it is necessary that either the flip-flop or the flip-flip transitions play a noticeable role in the nuclear magnetic relaxation, and their probabilities must not be equal.

In order for the Overhauser effect to take place, still another condition must be satisfied. There must be a possibility of transferring to the lattice the energy connected with the flip-flop or flip-flip transitions of the nucleus and the electron.

The importance of the Overhauser effect lies in the fact that upon saturation of the paramagnetic resonance the effective gyromagnetic ratio of the nucleus increases by three orders of magnitude. Therefore, whereas exceedingly low temperatures must be used to obtain considerable polarizations of nuclei by an external field, in the Overhauser method it is enough to employ liquid-helium temperatures.

For example, in the case of a proton ( $\dot{i} = 1/2$ ,  $\beta_n = 2.79$  nuclear magnetons) at  $H = 10^4$  oersteds,  $T = 2^\circ \text{K}$ , and complete saturation of the electron resonance,  $f_1 = \tanh \delta = 0.33$ , whereas for the same  $J$  and  $T$ , but in the absence of saturation,  $f_1 = \tanh(\hbar\gamma_n H/kT) = 5 \times 10^{-4}$ .

## 6. THE OVERHAUSER EFFECT IN METALS

### a) Relaxation of the Conduction Electrons

In analyzing the Overhauser effect in metals we shall follow Overhauser's papers.<sup>4,24</sup> This method makes it possible to obtain not only the magnitude of the effect, but also the value of the relaxation time.

We shall use the simplest model of a metal, that of an electron gas. According to this model, the state of the conduction electron is determined by the wave vector  $\mathbf{k}$  and by the spin direction. The kinetic energy of the electron is expressed as follows:

$$\epsilon = \frac{\hbar^2 k^2}{2m}. \quad (6.1)$$

\*The Overhauser effect can take place also if one or several hfs components are saturated, but its value will be less (see Sec. 8).

When an external magnetic field is applied, the total energy of the electron  $E$  will equal the sum of the kinetic and magnetic energies:

$$E = \epsilon \pm \beta H, \quad (6.2)$$

where the upper sign takes place for an electron with a spin parallel to the field, and the lower for an electron with a spin antiparallel to the field.

We can represent the aggregate of the conduction electrons of a metal as an aggregate of two gases, namely gases of electrons with spins parallel and antiparallel to the field, respectively. Each of these groups of electrons will have its own Fermi distribution. The chemical potentials of these two gases will be denoted by  $\mu_+$  and  $\mu_-$ , while the chemical potential in the absence of an external magnetic field will be denoted by  $\mu_0$ .

The introduction of two different Fermi distributions is advantageous, because the equilibrium within each individual gas is reached much more rapidly than equilibrium between the gases. This is connected with the fact that no electron spin flip is necessary to obtain equilibrium in an individual gas. Therefore the relaxation time  $\tau_R$  for reaching equilibrium in an individual gas is equal to the relaxation time encountered in the theory of resistance of metals. At room temperature this time is on the order of  $10^{-14} - 10^{-13}$  second in the case of alkali metals. On the other hand, establishment of equilibrium between two electron gases entails electron spin flips and is therefore much slower.

We denote the total number of electrons with spins parallel and antiparallel to the field (all quantities are per unit volume of metal) by  $N_+$  and  $N_-$ , the total number of electrons by  $N$ , and the excess of electrons with antiparallel spins by  $D$ . We denote by  $g(\epsilon, \mu)$  the Fermi distribution function. We then have for the two groups of electrons

$$g_{\pm} = g(\epsilon \pm \beta H, \mu_{\pm}) = g(\epsilon, \mu_{\pm} \mp \beta H). \quad (6.3)$$

Furthermore

$$N_{\pm} = \int g(\epsilon, \mu_{\pm} \mp \beta H) G(\epsilon) d\epsilon, \quad (6.4)$$

where  $G(\epsilon) d\epsilon$  is the number of quantum states of the electron in the kinetic energy interval  $(\epsilon, d\epsilon)$ . It is known that

$$G(\epsilon) = \frac{3N}{4\mu_0^{3/2}} \epsilon^{1/2}. \quad (6.5)$$

The calculation of the integral entails no difficulty (we assume  $\beta H \ll \mu_0$  and  $kT \ll \mu_0$ ). We obtain

$$N_{\pm} = \frac{N}{2} + \frac{3N}{4\mu_0} (\mu_{\pm} - \mu_0 \mp \beta H). \quad (6.6)$$

Since

$$N_+ + N_- = N, \quad (6.7)$$

we obtain from (6.6)

$$\mu_+ + \mu_- = 2\mu_0. \quad (6.8)$$

Furthermore, we have for the excess  $D$

$$D = \frac{3N}{4\mu_0} (\mu_- - \mu_+ + 2\beta H). \quad (6.9)$$

In the case of complete equilibrium, the chemical potentials of the two electron gases are the same

$$\mu_+ = \mu_- = \mu_0$$

and we obtain for the equilibrium excess

$$D_0 = \frac{3}{2} N \frac{\beta H}{\mu_0}. \quad (6.10)$$

If there is no equilibrium, i.e., if  $\mu_+ \neq \mu_-$ , the interactions between the electron spins and the lattice give rise to processes that restore the equilibrium. This raises the question of calculating the corresponding relaxation time.

Overhauser calculated<sup>24</sup> the relaxation time of the conduction-electron spins for six processes. The most effective of these six mechanisms was found to be the interaction between the conduction-electron spin and the current due to the translational motion of the other electrons. Calculation shows, for example, that this mechanism leads to a relaxation time of approximately  $8 \times 10^{-7}$  sec for lithium at room temperature. This, however, is two orders of magnitude greater than the experimental value (see below).

Elliott calculated<sup>25</sup> still another mechanism, which was found to be more effective. It is known that the orbital momentum of the electron is strongly coupled to the lattice. On the other hand, the electron spin is coupled to its orbital momentum, and consequently the electron spin will ultimately interact with the lattice. Elliott obtained an expression for the relaxation time  $T_1$  of the electron spins. This time includes  $\tau_R$  and  $\Delta g$ , where  $\Delta g$  is the deviation of the conduction-electron  $g$ -factor from the value of the  $g$  factor of the free electron (2.023). The fact that  $T_1$  contains  $\Delta g$  is readily understood, since the value of  $\Delta g$  is connected with the value of the spin-orbit interaction.

According to the Elliott theory,  $T_1$  is inversely proportional to the temperature at high temperatures, whereas at low temperatures  $T_1$  is inversely proportional to the cube of the temperature.

The question of magnetic relaxation of the conduction electron by the Elliott mechanism was considered theoretically by Andreev and Gerasimenko by solving the quantum kinetic equation.<sup>26</sup> It was shown, firstly, that  $T_1 = T_2$ . It was further shown that at all temperatures  $T_1$  should be approximately inversely proportional to the temperature.

Experiments on paramagnetic resonance on the conduction electrons of a metal are made difficult by the skin effect. It is well known that the thickness of the skin layer  $\delta$  is given by

$$\delta = \frac{c}{\sqrt{2\pi\sigma\omega}}, \quad (6.11)$$

where  $\sigma$  is the specific electric conductivity of the metal.

For frequencies used in paramagnetic resonance,  $\delta$  is on the order of several microns at room temperature (for alkali metals), and diminishes with decreasing temperature. The experiments are therefore carried out with minute particles of metal, dispersed in paraffin or in transformer oil (minute particles with dimensions 5–10 microns are obtained by using ultrasound and centrifuges), or with thin films of metal.

Feher and Kip<sup>27</sup> investigated paramagnetic resonance in lithium, sodium, potassium, and beryllium in the temperature interval from 4 to 300°K (no resonance was observed in other metals, particularly aluminum, magnesium, palladium, and tungsten). Experiment has yielded, first, the fact that the absorption line has a Lorentz form, with  $T_1 = T_2$ . According to the experiment, the relaxation time in the case of sodium is  $9 \times 10^{-9}$  sec at room temperature, which agrees in order of magnitude with the theoretical results of Andreev and Gerasimenko. In the case of sodium, experiment shows  $T_1$  to be approximately inversely proportional to the temperature, also in agreement with theory. In the case of lithium and beryllium, on the other hand, the experimentally measured relaxation times  $T_1$  were almost independent of the temperature. This is attributed by the authors to effects due to impurities.

## b) Polarization of Nuclei in Metals

One of the mechanisms considered by Overhauser<sup>24</sup> is the relaxation due to the hyperfine interaction of the electron spin with the nuclear spin. There are much faster relaxation processes for the electron spin, and therefore hyperfine relaxation for electrons is of no importance. For nuclear spins, however, this relaxation is fundamental.

Let the degree of saturation of paramagnetic resonance of the conduction electrons be  $s$ . We then have for the excess of electrons in the lower state

$$D = D_0(1 - s). \quad (6.12)$$

Using (6.9), (6.10), and (6.12) we readily obtain

$$\mu_+ - \mu_- = 2\beta Hs. \quad (6.13)$$

Thus, the saturation of resonance causes an increase in  $\mu_+$  and a decrease in  $\mu_-$ . In particular, in total resonance saturation is  $\mu_+ - \mu_- = 2\beta H$ , and we obtain two Fermi distributions, shifted by  $2\beta H$  relative to each other.

In order not to complicate unnecessarily the theoretical analysis, we shall carry out the calculations for the case of nuclear spin  $1/2$ . We denote by  $n_+$  and  $n_-$  the number of nuclei with spins parallel and antiparallel respectively to the external field, by  $n$  the total number of nuclei, and by  $\Delta$  the excess

$$\Delta = n_+ - n_-. \quad (6.14)$$

Denoting furthermore by  $W(+ \rightarrow -)$  and  $W(- \rightarrow +)$

the probabilities of relaxation nuclear-spin transitions  $+ \rightarrow -$  and  $- \rightarrow +$  per unit time, respectively. We then obtain

$$\dot{\Delta} = 2[W(- \rightarrow +)n_- - W(+ \rightarrow -)n_+] = [W(- \rightarrow +) + W(+ \rightarrow -)] \left[ n \frac{W(- \rightarrow +) - W(+ \rightarrow -)}{W(- \rightarrow +) + W(+ \rightarrow -)} - \Delta \right]$$

Introducing

$$\Delta_s = n \frac{W(- \rightarrow +) - W(+ \rightarrow -)}{W(- \rightarrow +) + W(+ \rightarrow -)}, \quad (6.15)$$

$$T_n = \frac{1}{W(- \rightarrow +) + W(+ \rightarrow -)}, \quad (6.16)$$

we obtain

$$\dot{\Delta} = \frac{\Delta_s - \Delta}{T_n}. \quad (6.17)$$

It is clear therefore that  $\Delta_s$  is the stationary value of  $\Delta$  and  $T_n$  is relaxation time of the approach of  $\Delta$  to  $\Delta_s$ .

It is logical to assume that in a metal the nuclei relax exclusively through interaction with the conduction electrons. On the other hand, as we have seen above, in the case of a metal the magnetic interaction between the nucleus and the conduction electron reduces practically to the contact term only. Therefore the nuclear spin will experience only flip-flop relaxation transitions and we obtain

$$\Delta_s = n \frac{W(\pm \rightarrow \mp) - W(\mp \rightarrow \pm)}{W(\pm \rightarrow \mp) + W(\mp \rightarrow \pm)}, \quad (6.18)$$

$$T_n = \frac{1}{W(\pm \rightarrow \mp) + W(\mp \rightarrow \pm)}, \quad (6.19)$$

where  $W(\pm \rightarrow \mp)$  is the probability of a simultaneous  $+ \rightarrow -$  transition electron and  $- \rightarrow +$  nuclear transition, averaged over the electron energy.  $W(\mp \rightarrow \pm)$  is analogously defined.

It remains to calculate these probabilities. The energy of the perturbation causing the transitions is the energy of the hfs interaction between the electron and nuclear spins

$$V = \frac{32\pi}{3} \beta\beta_n \text{SI}\delta(\mathbf{r}). \quad (6.20)$$

For the matrix element of  $V$  we obtain

$$V_{fi} = \frac{16\pi}{3} \beta\beta_n \psi_f^*(0) \psi_i(0),$$

where  $\psi_i$  and  $\psi_f$  are the spatial parts of the initial and final states of the conduction electron. However, in view of the smallness of the Zeeman energy of the electron, the initial and final states of the electron are almost the same (with the exception of the spin direction). Therefore

$$V_{fi} = \frac{16\pi}{3} \beta\beta_n |\psi(0)|^2. \quad (6.21)$$

We denote by  $W(\mathbf{k} \pm, \mathbf{k}' \mp)$  the probability of the (per unit time)  $\pm \rightarrow \mp$  transition, in which the wave vector of the conduction electron experiences a change  $\mathbf{k} \rightarrow \mathbf{k}'$ . We have

$$W(\mathbf{k} \pm, \mathbf{k}' \mp) = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho_f,$$

where  $\rho_f$  is the density of the final states per unit energy interval

$$\rho_f = \frac{k'^2 dk' d\Omega'}{(2\pi)^3 de'} = \frac{mk' d\Omega'}{(2\pi)^3 \hbar^2}.$$

Since  $k' \cong k$ , we can replace here  $k'$  by  $k$ . We then obtain

$$W(\pm \rightarrow \mp) = \int W(\mathbf{k} \pm, \mathbf{k}' \mp) \frac{k^2 dk d\Omega}{(2\pi)^3} g(\epsilon + \beta H, \mu_+) \times [1 - g(\epsilon' - \beta H, \mu_-)]$$

or, integrating over the angles and using the relation between  $\epsilon$  and  $k$

$$W(\pm \rightarrow \mp) = \frac{m^3}{\pi^3 \hbar^7} |V_{fi}|^2 \int_0^\infty g(\epsilon + \beta H, \mu_+) \times [1 - g(\epsilon' - \beta H, \mu_-)] \epsilon d\epsilon, \quad (6.22)$$

where  $\epsilon$  and  $\epsilon'$  are connected by the energy conservation law

$$\epsilon + (\beta + \beta_n) H = \epsilon' - (\beta + \beta_n) H. \quad (6.23)$$

We obtain analogously

$$W(\mp \rightarrow \pm) = \frac{m^3}{\pi^3 \hbar^7} |V_{fi}|^2 \int_0^\infty g(\epsilon' - \beta H, \mu_-) \times [1 - g(\epsilon + \beta H, \mu_+)] \epsilon d\epsilon, \quad (6.24)$$

where  $\epsilon$  and  $\epsilon'$  are connected by the same relation.

Calculation of the integrals yield

$$W(\pm \rightarrow \mp) = \frac{m^3}{\pi^3 \hbar^7} |V_{fi}|^2 2\mu_0 \frac{\beta'H}{1 - \exp\left(-\frac{2\beta'H}{kT}\right)}, \quad (6.25)$$

$$W(\mp \rightarrow \pm) = \frac{m^3}{\pi^3 \hbar^7} |V_{fi}|^2 2\mu_0 \frac{\beta'H}{\exp\left(\frac{2\beta'H}{kT}\right) - 1}, \quad (6.26)$$

where

$$\beta' = \beta_{\text{eff}} = \beta_n + s\beta. \quad (6.27)$$

Using (6.18), (6.19), (6.25), and (6.26) we obtain

$$\Delta_s = n \tanh \frac{\beta'H}{kT}, \quad (6.28)$$

$$T_n = \frac{9\pi}{2^9} \frac{\hbar^7 \tanh \frac{\beta'H}{kT}}{m^3 (\beta\beta_n)^2 \mu_0 \beta'H |\psi(0)|^4}. \quad (6.29)$$

(6.28) shows that  $\beta_{\text{eff}}$  is the effective magnetic moment of the nucleus. From this we find for the effective gyromagnetic ratio

$$\gamma_{\text{eff}} = \gamma_n + s\gamma_e. \quad (6.30)$$

Overhauser<sup>4</sup> has shown that for an arbitrary nuclear spin  $\dot{\mathbf{I}}$ , expression (6.30) remains valid for the effective gyromagnetic ratio while the formula for  $T_n$  becomes

$$T_n = \frac{9\pi}{2^7} \frac{\hbar^7 \dot{I}^2 \tanh \frac{\beta'H}{kT}}{m^3 (\beta\beta_n)^2 \mu_0 \beta'H |\psi(0)|^4}, \quad (6.31)$$

where

$$\beta' = \beta_{\text{eff}} = hI\gamma_{\text{eff}} = \beta_n + 2Is\beta. \quad (6.32)$$

In extreme cases,  $T_n$  assumes the following form (see reference 28)

$$T_n = \frac{9\pi}{2^7} \frac{h^2 I^2}{m^3 (\beta\beta_n)^2 \mu_0 kT |\psi(0)|^4}, \quad \text{if } \beta'H \ll kT, \quad (6.33)$$

$$T_n = \frac{9\pi}{2^7} \frac{h^2 I^2}{m^3 (\beta\beta_n)^2 \mu_0 \beta'H |\psi(0)|^4}, \quad \text{if } \beta'H \gg kT. \quad (6.34)$$

Substituting in (6.31) the numerical values of the constants, we obtain

$$T_n = 1.9 \cdot 10^{-22} \frac{j^2}{\beta_n^2 \mu_0 |\psi(0)|^4} \frac{\tanh \frac{\beta'H}{kT}}{\beta'H}, \quad (6.35)$$

where  $\beta_n$  is in nuclear magnetons.

Let us estimate the order of  $T_n$  in case of lithium and sodium. For lithium we put  $I = \frac{3}{2}$  (isotope  $\text{Li}^7$ ),  $\beta_n = 3.25$  nuclear magnetons,  $\mu_0 = 4.70 \text{ ev} = 0.75 \times 10^{-11} \text{ erg}$  and  $|\psi(0)|^2 = 28$ .<sup>\*</sup> In particular, at room temperature we obtain  $T_n = 0.17 \text{ sec}$ . At  $2^\circ \text{K}$ , 10,000 oersteds, and complete saturation,  $T_n = 20 \text{ sec}$ . For sodium  $I = \frac{3}{2}$ ,  $\beta_n = 2.21$  nuclear magnetons,  $\mu_0 = 3.1 \text{ ev} = 5 \times 10^{-12} \text{ erg}$ , and  $|\psi(0)|^2 = 160$ . At room temperature we obtain  $T_n = 0.02 \text{ sec}$ . At  $2^\circ \text{K}$  and a field of 10,000 oersteds, we obtain for complete saturation  $T_n = 2 \text{ sec}$ .

Equation (6.31) shows that  $T_n$  first increases with decreasing  $T$ , but then, when  $\beta'H > kT$ , it tends to a constant limit. Since all other mechanisms of relaxation of the nuclear spin lead to an increase in  $T_n$  with decreasing  $T$  over the entire temperature interval, the hfs relaxation will predominate (if  $s \neq 0$ ) at low temperatures, even though other mechanisms do predominate at high temperatures.

It is shown in Overhauser's paper that if the nuclear relaxation which is not connected with the interaction with the conduction electrons is substantial, the equation for the effective gyromagnetic ratio becomes

$$\gamma_{\text{eff}} = \gamma_n + s \frac{T_n}{T_n'} \gamma_e, \quad (6.36)$$

where  $T_n$  is the total time of nuclear relaxation and  $T_n'$  is the relaxation time due to the hfs interaction with the conduction electrons, i.e., the time given by (6.31). If other mechanisms are essential, then  $T_n < T_n'$  and a decrease takes place in the effective gyromagnetic ratio.

We note that the Overhauser effect in a metal is possible because the change in energy due to the reorientation of the spins of the electron and nucleus can be offset by the kinetic energy of the electron. An important circumstance in this case is the fact that the conduction electrons have a continuous spectrum.

In the case  $\gamma_n < 0$  a unique situation obtains. In the absence of saturation of the electron resonance, the nuclei will have very small negative polarization. If resonance occurs, the nuclear polarization first de-

creases in absolute magnitude, passes through zero, and then increases to a large positive value.

### c) Resonance Shift

It is easy to see that the frequency of the electron resonance should shift upon saturation. Actually, the magnetic energy of the conduction electron has the form

$$-\beta_e \left[ \mathbf{H} + \frac{8\pi}{3} |\psi(0)|^2 \sum_n \beta_n \right].$$

The expression in the square brackets can be considered as an overall magnetic field acting on the conduction electron. We thus obtain\* for the overall magnetic field, with which the nuclei act on the electron,

$$\Delta \mathbf{H} = \frac{8\pi}{3} |\psi(0)|^2 \sum_n \beta_n.$$

This expression can be rewritten

$$\Delta \mathbf{H} = f_1 (\Delta \mathbf{H})_0, \quad (6.37)$$

where  $f_1$  is the degree of polarization of nuclei and  $(\Delta \mathbf{H})_0$  is given by

$$(\Delta \mathbf{H})_0 = \frac{8\pi}{3} |\psi(0)|^2 n \beta_n. \quad (6.38)$$

We note that in the case of lithium  $(\Delta \mathbf{H})_0 = 180$  oersteds.

If  $\gamma_n > 0$ ,  $\Delta \mathbf{H}$  is parallel to  $\mathbf{H}$ , and therefore the resonance frequency of the electron shifts towards the larger frequencies if the external field is constant. If, however, we fix the frequency, then the resonant value of the external field shifts towards the smaller fields. When  $\gamma_n < 0$ , the direction of the shift will be opposite.

It is known that a so-called Knight shift of the frequency of nuclear resonance is observed in nuclear magnetic resonance in metals.<sup>11</sup> This shift is produced by the magnetic field with which the conduction electrons act on the nucleus. The Knight shift, like the Overhauser shift, is also proportional to  $|\psi(0)|^2$ .

Let us note the following interesting circumstance. In the absence of saturation of the electric paramagnetic resonance, the Knight shift has a maximum, whereas the Overhauser shift is equal to zero. With increasing degree of saturation, the Knight shift diminishes (since the saturation causes depolarization of the spins of the conduction electrons), while the Overhauser shift increases (since the nuclear polarization increases).

### d) Comparison with Experiment

An experimental investigation of the Overhauser effect in metals has been carried out by Carver and Slichter.<sup>30</sup> Let us describe these experiments briefly. The authors have not set out to obtain considerable nuclear polarization. Their purpose was more modest, namely to observe the increase in nuclear resonance

\*The  $\psi$  function of the conduction electron is normalized to unit volume. The summation is therefore carried out over the nuclei per unit volume of the metal.

\*We take from reference 29 a value of 0.8 for the parameter  $\xi$ .

brought about by saturation of the electron resonance. For this reason the experiments were carried out at room temperature, and relatively low frequencies were used.

The experiments were performed with lithium. The samples were minute metal particles (measuring approximately  $5 - 10 \mu$ ), dispersed in transformer oil. The alternating field, with which the nuclear resonance was investigated had a frequency of 50 kcs. This frequency determines the value of the main field, while the latter determines the frequency of the alternating field, with which the electron resonance was saturated. The absorbed power was approximately 60 watts, causing a rise in the sample temperature to  $70^\circ \text{C}$ .

Special experiments have shown that the width of the nuclear-resonance line does not change upon saturation of the electron resonance. Therefore the intensification of the nuclear signal gives directly the increase in the nuclear polarization.

Let us introduce the quantity  $A(s)$ , equal to the ratio of the nuclear-resonance signal when the electron-resonance saturation parameter has a value  $s$ , and when there is no saturation. It is obvious that  $A(s)$  should equal the ratio of the degree of polarization of the nuclei at a saturation parameter  $s$  to the degree of polarization in the absence of saturation. In the case when  $\beta_{\text{eff}}H \ll kT$ , the nuclear polarization is proportional to the gyromagnetic ratio. If we neglect in (6.30) the quantity  $\gamma_n$ , we obtain

$$A(s) = \frac{\gamma_{\text{eff}}}{\gamma_n} = s \frac{\gamma_e}{\gamma_n}. \quad (6.39)$$

On the other hand, when the resonance condition is exactly satisfied [see (3.20) and (3.21)] we have

$$s = \frac{(\gamma_e H_1)^2 T_1 T_2}{1 + (\gamma_e H_1)^2 T_1 T_2} \quad (6.40)$$

and thus

$$A(H_1) = \frac{\gamma_e}{\gamma_n} \frac{(\gamma_e H_1)^2 T_1 T_2}{1 + (\gamma_e H_1)^2 T_1 T_2}. \quad (6.41)$$

In particular, we obtain

$$\frac{1}{A} \sim 1 + \frac{1}{(\gamma_e H_1)^2 T_1 T_2}. \quad (6.42)$$

In other words, a plot of  $1/A$  vs  $1/H_1^2$  should be a straight line, and, in the case of metals, as indicated above,  $T_1 = T_2$ . Therefore, by measuring in the experiment the width of the electron-resonance line, we obtain the dependence of  $s$  on  $H_1$  from (6.40).

In the experiments with lithium, the external field  $H$  was 30.3 oersteds and the frequency saturating the electron resonance was 84 Mcs (the electron resonant frequency corresponding to a field of 30.3 oersted). In the absence of saturation resonance, it was impossible to measure the nuclear signal, since it was so small that it was lost in the background. It was possible, nevertheless, to measure the dependence of  $A$  on  $H_1$ , by comparison with the resonance of protons in gly-

cerine. The maximum value of  $H_1$  in these experiments was 3.3 oersteds, which according to (6.40) yields  $s = 0.7$ . Considering that  $\gamma_e/\gamma(\text{Li}^7) = 1690$ , one might expect  $A_{\text{max}} = 1200$ , whereas experiment yielded  $A_{\text{max}} \cong 110$ . The authors' attempted to explain the discrepancy between theory and experiment by introducing not too convincing considerations of other possibilities of relaxation.

In the experiments with sodium the external field  $H$  was 44.2 oersteds, corresponding to a resonant frequency of 124 Mcs. The nuclear resonance was observed in the absence of saturation of the electron resonance, and thus the function  $A(H_1)$  was measured directly. The electron-resonance line was much broader in the case of sodium than in the case of lithium, its width being 12 oersteds. The maximum value of  $H_1$  in experiments with sodium was 2 oersteds. The corresponding value of  $s$  is 0.01. Since  $\gamma_e/\gamma(\text{Na}^{23}) = 2400$ , one expects  $A_{\text{max}} = 24$ , while experiment yields  $A_{\text{max}} \cong 10$ .

We see therefore that there is a considerable discrepancy between theory and experiment. This discrepancy is on the order of a factor of ten in the case of lithium and two in the case of sodium. The discrepancy could be ascribed to nuclear relaxation mechanisms not connected with electrons. However, considering that there are many conduction electrons in a metal and that  $|\psi(0)|^2$  is large in the case of alkali metals, such an explanation is little likely (particularly since the quadrupole moment of the nucleus  $\text{Li}^7$  is small).

Worthy of mention among the other experiments are those of Bekeshko and Kondorskii<sup>31</sup> who measured the temperature dependence of the Overhauser effect in lithium in the temperature range  $0 - 100^\circ \text{C}$ .

Let us also note the theoretical paper by Azbel', Gerasimenko, and Lifshitz,<sup>32</sup> in which it is shown that if the condition

$$H_1 > \frac{8\pi\delta_{\text{eff}}}{c^2 |Z| T_2} H$$

is satisfied ( $\delta_{\text{eff}}$  is the depth to which the electron penetrates by diffusion in a time  $T_2$ , and  $Z$  is the surface impedance), then the nuclei should be polarized not in a layer of thickness of the order of the skin layer, but in a much thicker layer, on the order of  $\delta_{\text{eff}}$ ; in other words, the Overhauser effect should be considerably intensified. It is also shown that in resonance saturation the metal film should exhibit selective transparency.

In a later paper<sup>33</sup> the same authors presented a general theory of magnetic resonance and of the Overhauser effect in metals.

Let us note, finally, the paper by Kastler,<sup>34</sup> in which it is proposed to saturate a pair of electron levels with the aid of ultrasound. The advantage of this method is that the skin effect will not play any role and it becomes possible to polarize nuclei in a considerable volume of metal.

## 7. OVERHAUSER EFFECT IN LIQUID AND SOLID DIAMAGNETS WITH PARAMAGNETIC IMPURITIES

### a) General Considerations

Consider a diamagnetic medium containing paramagnetic impurities. We shall discuss now the Overhauser effect on the nuclei of the diamagnetic atoms. This analysis is due to Abragam.<sup>35</sup>

In order not to complicate the problem, we confine ourselves to the case of nuclear spin  $i = 1/2$ , particularly since our experiments have been performed with protons.\*

The nucleus of the diamagnetic atom and the electron with uncompensated spin belong to different atoms, and on the average these atoms are sufficiently far from each other. Therefore, if the external field is not too weak, the energy of the magnetic interaction of the electron with the nucleus will be considerably less than the Zeeman energy of the nucleus. For this it is necessary that the external field be considerably greater than the average field in which the electron acts on the nucleus (the Paschen-Back case). If the foregoing condition is satisfied, we have individual Zeeman levels for the nucleus and the electron, and the spin-spin interaction energy can be neglected in the energy levels.

The Zeeman levels of the nucleus and the electron, together with their populations, are shown in Fig. 3.

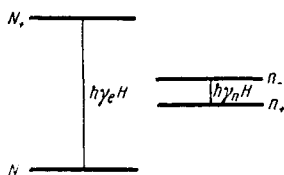


FIG. 3

The figure pertains to the case  $\gamma_n > 0$ . As before, the populations of the electron levels will be denoted by  $N_+$  and  $N_-$ , those of the nuclear levels by  $n_+$  and  $n_-$ , and their excesses in the lower states by  $D$  and  $\Delta$ . We introduce the symbols

$$\delta = \frac{g\beta H}{2kT} = \frac{\hbar\gamma_e H}{kT}, \quad (7.1)$$

$$\delta_n = \frac{\beta_n H}{kT} = \frac{\hbar\gamma_n H}{kT}. \quad (7.2)$$

In order for the Overhauser effect to take place, it is necessary that a noticeable fraction of the nuclear relaxation be due to processes connected with the interaction between the nuclei and the electrons of the paramagnetic impurities. In the calculations that follow we shall first assume that the nuclei interact not directly with the lattice, but through electrons of the paramagnetic impurities.

In order for the Overhauser effect to take place, it

\*In addition, we assume the effective spin of the ion of the paramagnetic impurity to be  $1/2$ , and for the sake of brevity we refer to an electron instead of an ion of the paramagnetic impurity.

is necessary, in addition, that it be possible to compensate for the change in the energy due to the change in the orientation of the electron and nuclear spins. Let  $H_e(t)$  represent the magnetic field with which the electron acts on the nucleus. This field will be a fluctuating function of time. We introduce the correlation function

$$\varphi(\tau) = \langle H_e(t) H_e(t - \tau) \rangle \quad (7.3)$$

(averaging over  $t$ ). According to reference 15, the aforementioned second condition necessitates that the spectral intensity  $j(\omega)$ , corresponding to  $\varphi(\tau)$ , be different from zero at a frequency  $\omega$  equal to the nuclear Larmor frequency  $\omega_n$ .

We note that two cases are possible:

I. The change in  $H_e$  is due to motion, i.e., to the change in the distance between the electron and the nucleus as they move.

II. The change of  $H_e$  is due to re-orientation of the electron spin. Each such re-orientation is effected on the average, within a time  $T_e$ , equal to the electron spin relaxation time.

The nuclear spin relaxations due to these causes were called by Abragam relaxations of the first and second kind respectively. We note that relaxation of type I predominates in liquids of low viscosity, owing to the fast Brownian motion, whereas relaxation of type II usually predominates in solids.\*

We note furthermore that in the present section, unlike the preceding one, we use Boltzmann statistics for the electrons.

### b) General Analysis

Let us assume that the magnetic interaction of the spins of the electron and nucleus is dipole-dipole. The operator of dipole-dipole interaction between a nucleus and an electron can be written in the following form:<sup>36</sup>

$$V = -4\beta\beta_n r^{-3} (A + B + C + D + E + F), \quad (7.4)$$

where  $\mathbf{r}$  is the radius vector of the electron relative to the nucleus, and the operators  $A, B, C, D, E,$  and  $F$  are of the form

$$\left. \begin{aligned} A &= S_z \dot{I}_z (1 - 3 \cos^2 \vartheta), & \Delta M = \Delta m &= 0, \\ B &= -\frac{1}{4} (S_+ \dot{I}_- + S_- \dot{I}_+) (1 - 3 \cos^2 \vartheta), & \Delta M = -\Delta m &= \pm 1, \\ C &= -\frac{3}{2} (S_z \dot{I}_+ + S_+ \dot{I}_z) \sin \vartheta \cos \vartheta e^{-i\varphi}, & \Delta(M + m) &= +1, \\ D &= -\frac{3}{2} (S_z \dot{I}_- + S_- \dot{I}_z) \sin \vartheta \cos \vartheta e^{i\varphi}, & \Delta(M + m) &= -1, \\ E &= -\frac{3}{4} S_+ \dot{I}_+ \sin^2 \vartheta e^{-2i\varphi}, & \Delta M = \Delta m &= +1, \\ F &= -\frac{3}{4} S_- \dot{I}_- \sin^2 \vartheta e^{2i\varphi}, & \Delta M = \Delta m &= -1. \end{aligned} \right\} \quad (7.5)$$

\*When the nuclear spin is greater than  $1/2$ , the quadrupole relaxation of the nuclear spin, which is not due to interactions with electrons, predominates in diamagnetic solids. In this case there will be no Overhauser effect.

In these formulas  $\vartheta$  and  $\varphi$  are the polar angle and the azimuth of the vector  $\mathbf{r}$  relative to the external field. Furthermore, in these formulas there are introduced the operators

$$I_{\pm} = \dot{I}_x \pm i\dot{I}_y \quad S_{\pm} = S_x \pm iS_y, \quad (7.6)$$

whose non-vanishing matrix elements are

$$(m \pm 1 | \dot{I}_{\pm} | m) = \sqrt{(\dot{I} \mp m)(\dot{I} + 1 \pm m)} \quad (7.7)$$

and analogously for  $S_{\pm}$ .

The right side of (7.5) indicates the selection rules for the non-vanishing matrix elements of the operators A, B, C, D, E, and F.

We shall denote by  $(+, -)$  the state  $M = +1/2$ ,  $m = -1/2$  of the electron-plus-nucleus system. We denote the remaining states analogously. Let us set up the kinetic equation for  $n_{\pm}$ :

$$\begin{aligned} \frac{dn_{\pm}}{dt} = & pN_{\pm}n_{\pm}e^{\delta+\delta_n} - pN_{\mp}n_{\pm}e^{-\delta-\delta_n} \\ & + q(N_{+} + N_{-})n_{\pm}e^{\delta_n} - q(N_{+} + N_{-})n_{\pm}e^{-\delta_n} \\ & + rN_{-}n_{\pm}e^{-\delta+\delta_n} - rN_{+}n_{\pm}e^{\delta-\delta_n}. \end{aligned} \quad (7.8)$$

$p$ ,  $q$ ,  $r$  are functions of the temperature and of the external field;  $pe^{\delta+\delta_n}$  gives the probability of relaxation

transition  $(+, -) \rightarrow (-, +)$  per unit time, and  $pe^{-\delta-\delta_n}$  is the probability of the inverse process. We take it into account here that the probabilities of the direct and inverse relaxation transitions are related by the Boltzmann equation. Furthermore, it is clear that  $p$  is connected with the operator B,  $q$  with the operator C and D, and  $r$  with the operators E and F.

In the stationary case we obtain

$$\frac{n_{+}}{n_{-}} = e^{2\delta_n} \frac{pN_{+}e^{\delta} + q(N_{+} + N_{-}) + rN_{-}e^{-\delta}}{pN_{-}e^{-\delta} + q(N_{+} + N_{-}) + rN_{+}e^{\delta}}. \quad (7.9)$$

If the degree of saturation of the electron resonance is  $s$ , we have

$$\left. \begin{aligned} N_{+} &= \frac{N}{2} [1 - (1-s) \tanh \delta], \\ N_{-} &= \frac{N}{2} [1 + (1-s) \tanh \delta] \end{aligned} \right\} \quad (7.10)$$

and we obtain

$$\frac{n_{+}}{n_{-}} = e^{2\delta_n} \frac{pe^{\delta} + 2q + re^{-\delta} - (1-s)(pe^{\delta} - re^{-\delta}) \tanh \delta}{pe^{-\delta} + 2q + re^{\delta} + (1-s)(pe^{-\delta} - re^{\delta}) \tanh \delta}. \quad (7.11)$$

The degree of polarization of the nuclei, by definition, is

$$f_1 = \frac{n_{+} - n_{-}}{n_{+} + n_{-}}, \quad (7.12)$$

which yields

$$f_1 = \frac{p \sinh(\delta + \delta_n) + 2q \sinh \delta_n - r \sinh(\delta - \delta_n) - (1-s) \tanh \delta [p \cosh(\delta + \delta_n) - r \cosh(\delta - \delta_n)]}{p \cosh(\delta + \delta_n) + 2q \cosh \delta_n + r \cosh(\delta - \delta_n) - (1-s) \tanh \delta [p \sinh(\delta + \delta_n) + r \sinh(\delta - \delta_n)]}. \quad (7.13)$$

If the condition

$$s \gg \frac{\delta_n}{\delta} \sim 10^{-3},$$

is satisfied, we can neglect in (7.13) the small quantity  $\delta_n$ . We then obtain

$$f_1 = s \frac{p-r}{p+r} \tanh \delta \left[ 1 + \frac{2q}{(p+r) \cosh \delta} - (1-s) \tanh^2 \delta \right]^{-1}. \quad (7.14)$$

If, in particular,  $s = 1$  and  $q = 0$ , we get

$$f_1 = \frac{p-r}{p+r} \tanh \delta. \quad (7.15)$$

According to (7.14), the polarization is positive if  $p > r$ , in other words, if the flip-flop transitions are more probable than the flip-flip transition; it is negative in the opposite case. It is easy to understand the physical cause of this fact. In the saturation of the electron resonance we increase  $N_{+}$  and decrease  $N_{-}$ . Therefore, if the flip-flop transitions predominate, the processes  $(+, -) \rightarrow (-, +)$  will predominate over the inverse processes, leading to an increase in  $n_{+}$  and to a decrease in  $n_{-}$ .

Let us analyze in greater detail the case  $\delta \ll 1$ , which is the most interesting from the point of view of the experiments performed to date. In this case (7.11) and (7.13) yield

$$\frac{n_{+}}{n_{-}} = 1 + 2\delta_n - 2sq\delta, \quad (7.16)$$

$$f_1 = \delta_n - sq\delta, \quad (7.17)$$

where we introduce

$$q = -\frac{p-r}{p+2q+r}. \quad (7.18)$$

$\rho$  depends on the relative fractions of the flip-flop, flip-flip transitions and the horizontal relaxation of the nuclear spin.

We can readily transform (7.17) to the following form

$$\langle \dot{I}_z \rangle - \dot{I}_0 = -\rho (\langle S_z \rangle - S_0), \quad (7.19)$$

where  $\dot{I}_0$  and  $S_0$  are the equilibrium values of  $\langle \dot{I}_z \rangle$  and  $\langle S_z \rangle$  in the absence of saturation (we note that  $S_0$  and  $\langle S_z \rangle$  are negative, while the sign of  $\dot{I}_0$  coincides with the sign of  $\gamma_N$ ).

### c) Case of Hyperfine Interaction

The results obtained in the preceding section are valid also when the magnetic interaction of the nucleus and of the electron reduces to a contact term; in this case  $q = r = 0$  and, for example, (7.13) yields

$$f_1 = \frac{(2-s) \sinh \delta_n + s \sinh(2\delta + \delta_n)}{(2-s) \cosh \delta_n + s \cosh(2\delta + \delta_n)}. \quad (7.20)$$

In the case of hyperfine interaction we have  $\rho = -1$ .

It is easy to see, furthermore, that the equation (6.30) obtained in the case of a metal for the effective gyromagnetic ratio of the nucleus holds in this case, too, since we have either  $s = 1$  or  $\delta \ll 1$ . In general, the result of the Overhauser effect cannot be described in terms of the effective gyromagnetic ratio.

Let us note, however, that usually in a liquid or solid diamagnet with magnetic impurities, it is not the hfs term which predominates, but the dipole-dipole term. This is due to the fact that the distance between the nucleus and the electron is on the average sufficiently large, and consequently  $\psi(0)$  is small.

**d) Diamagnetic Liquid with Paramagnetic Impurities**

Let us consider a low-viscosity diamagnetic liquid, containing paramagnetic impurities. It is sensible to assume that the magnetic interaction between the nucleus and the electron is dipole-dipole and that the relaxation of the nuclear spins is a relaxation of the first kind.

We can, following reference 15, write down the spectral intensities corresponding to the expressions A, B, C, D, E, and F. In view of the rapid Brownian motion of the molecules of the liquid, we can assume that these intensities are independent of the frequency. If, furthermore, we assume that the isotropy of the liquid allows us to average the intensities over the angles, we obtain<sup>35</sup>

$$p : q : r = 2 : 3 : 12.$$

Substitution in (7.18) yields  $\rho = 1/2$ . We find therefore that if the small quantity  $\delta_n$  is neglected, the Overhauser effect has the opposite sign and its absolute value is one half as large as in the case of the hfs interaction.

**e) Solid Diamagnet with Paramagnetic Impurities**

Abraham<sup>35</sup> has shown that in case of a solid diamagnet the result differs substantially from the result obtained above for a liquid diamagnet. The magnetic interaction of the nucleus with the electron can again be considered dipole-dipole. The difference, however, lies in the fact that in the case of a solid diamagnet the relaxation of the nuclear spin will at least in the main, be of the second type.<sup>36</sup>

The electron-plus-nucleus system has four spin states:  $(+, +)$ ,  $(-, -)$ ,  $(+, -)$ , and  $(-, +)$ . However, mixing of the states results in dipole-dipole interaction, which has non-vanishing matrix elements over these states. Here, according to perturbation theory, the states mixed will in the main be those with nearly equal energies, i.e., with equal  $M$  and different  $m$ . The mixing will, however, be weak since the energy of the dipole-dipole interaction is small compared with the nuclear Zeeman energy. The operator causing the mixture has the form [see (7.4) and (7.5)]:

$$V = -4\beta\beta_n r^{-3} (C' + D'), \tag{7.21}$$

where

$$\left. \begin{aligned} C' &= -\frac{3}{2} S_z \hat{I}_+ \sin \vartheta \cos \vartheta e^{-i\varphi}, & \Delta M = 0, & \Delta m = +1, \\ D' &= -\frac{3}{2} S_z \hat{I}_- \sin \vartheta \cos \vartheta e^{i\varphi}, & \Delta M = 0, & \Delta m = -1. \end{aligned} \right\} \tag{7.22}$$

According to perturbation theory, the wave function

of the state obtained from the zeroth-approximation state  $(-, +)$  has the form

$$a = (-, +) - \frac{(-, -|V|-, +)}{E(-, -) - E(-, +)} (-, -).$$

Analogously, we can make up the other perturbed states and obtain

$$\left. \begin{aligned} a &= (-, +) + \alpha(-, -), & a' &= (+, +) - \alpha(+, -), \\ b &= (-, -) - \alpha^*(-, +), & b' &= (+, -) + \alpha^*(+, +). \end{aligned} \right\} \tag{7.23}$$

where

$$\alpha = \frac{3}{2} \frac{\beta \sin \vartheta \cos \vartheta e^{i\varphi}}{H r^3} = \frac{3}{4} \frac{\gamma_e \gamma_n \hbar \sin \vartheta \cos \vartheta e^{i\varphi}}{\omega_n^3}. \tag{7.24}$$

These four states are shown in Fig. 4. We indicate on the left the approximate quantum numbers of these states.

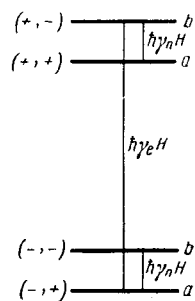


FIG. 4

We note that

$$\alpha \sim \frac{H_{loc}}{H}, \tag{7.25}$$

where  $H_{loc}$  represents the magnetic field produced by the electron on the nucleus. As indicated above, we are considering the case  $H \gg H_{loc}$ , i.e.,  $|\alpha| \ll 1$ .

In subsection a) of the present section we indicated that in relaxation of type II the fluctuating magnetic field, causing the relaxation of the nuclear spin, is itself caused by periodic reorientation of the electron spin. The reorientation of the electron spin is caused in turn by its interaction with the lattice. The operator which causes these reorientations can be represented in the form  $2\beta H'S$ , where  $H'$  is so to speak the fluctuating effective magnetic field caused by the lattice fluctuations.  $H'$  has components both parallel and perpendicular to the  $z$  axis. It is easily seen that the parallel component causes no transitions, while the perpendicular component causes transitions with selection rules

$$\Delta M = \pm 1, \quad \Delta m = 0.$$

We see thus that  $H'$  causes, first, the transitions (strong)

$$a \leftrightarrow a', \quad b \leftrightarrow b',$$

which cause relaxation of the electron spin. Furthermore, it also causes the transitions (weak)

$$a \leftrightarrow b', \quad a' \leftrightarrow b,$$



which cause the relaxation of the nuclear spin.

Using (7.22) we readily find that the ratio of the probability of the transition  $a \rightarrow b'$  or  $b \rightarrow a'$  to the probability of the transition  $a \rightarrow a'$  or  $b \rightarrow b'$  is equal to  $4|\alpha|^2$ . For this reason we obtain (compare with results obtained in reference 36)

$$\frac{1}{T_n} = \frac{4|\alpha|^2}{T_e}, \quad (7.26)$$

where  $T_e$  and  $T_n$  are the relaxation times of the electron and nuclear spins.

The transitions  $a \rightarrow b'$  and  $b \rightarrow a'$  have equal probabilities, since the matrix elements of the operator  $2\beta H'S$  are the same for these transitions (in absolute value). In other words, in this case the probabilities of flip-flop and flip-flip transitions are the same, and therefore the Overhauser effect will not take place. The coefficient  $\rho$  in (7.19) will in this case be equal to zero.

We note, however, that if the relaxation of type I makes a certain contribution to the relaxation of the nuclear spin, an Overhauser effect of smaller absolute value will take place.

We mention also the paper by Tomita,<sup>37</sup> in which a general analysis is given of a system consisting of two types of spins. Let one of the spin systems become saturated, while the second is investigated by magnetic resonance without saturation. It is shown that if the fluctuating part of the magnetic interaction of the two unlike spins predominates over the static part, the Overhauser effect will take place. In the opposite limiting case, on the other hand, there will be no Overhauser effect, but a narrowing of the resonance of the second system (the so-called narrowing by saturation).

#### f) Generalization of the Results Obtained

Equation (7.19) is valid if the relaxation of the nuclear spin is due in its entirety to its interaction with the electron spin. If the nucleus has also other means of relaxation, the magnitude of the Overhauser effect will be reduced. If, in particular, the other mechanisms of relaxation (for example, quadrupole relaxation) greatly predominate, the Overhauser effect will not take place.

All this can be described by adding to (7.19) an additional factor, called by Abragam the leakage coefficient

$$f = \frac{T_n}{T_n'} = 1 - \frac{T_n}{T_n''}, \quad (7.27)$$

where  $T_n$  is the total time of relaxation of the nuclear spin,  $T_n'$  is the relaxation time due to its interaction with the electrons, and  $T_n''$  is the relaxation time due to other causes.\* The value of  $f$  is unity if the other mechanisms of nuclear relaxation are negligibly small ( $T_n \cong T_n'$ ), and is equal to zero if they strongly predominate.

\*We note that  $1/T_n = 1/T_n' + 1/T_n''$

We thus obtain

$$\langle \dot{I}_z \rangle - \dot{I}_0 = -f\rho (\langle S_z \rangle - S_0), \quad (7.28)$$

where the formula is valid only if  $\delta \ll 1$ .

Reference 38 contains a generalization of this formula to include the case of arbitrary  $I$  and  $S$  in the form

$$\langle \dot{I}_z \rangle - \dot{I}_0 = -f\rho \frac{I(I+1)}{S(S+1)} (\langle S_z \rangle - S_0). \quad (7.29)$$

#### g) Comparison with Experiment

Abragam, Combrisson, and Solomon carried out experiments<sup>39</sup> (see also references 40 and 41) at 77°K with a sample of phosphorus doped silicon. At this temperature the "excess" electrons are not localized around the impurities, but wander over the crystal. In other words, in analogy with a metal, we have here a gas of free electrons. The difference is that in view of their small concentration, they obey the Boltzmann statistics. In addition, the skin effect will play a small role.

In natural silicon, containing approximately 4.7% of the isotope  $\text{Si}^{29}$  with spin  $I = 1/2$  and with magnetic moment  $\beta_n = -0.55$  nuclear magnetons. It is to be expected that the magnetic interaction between the electron and  $\text{Si}^{29}$  will be essentially hyperfine. Therefore we put  $\rho = -1$  in (7.28). Assuming  $f = 1$  and neglecting the small quantity  $\dot{I}_0$  we obtain at full saturation of electron resonance

$$\frac{\langle \dot{I}_z \rangle}{\dot{I}_0} = -\frac{S_0}{I_0} = -3300,$$

i.e., the nuclear resonance should increase by 3300 times and reverse its sign. In other words, after the stationary state is established, we should have not resonant absorption but resonant emission.

The experiment was carried out with a silicon sample containing  $5 \times 10^{10}$  atoms of phosphorus per cubic centimeter. An external field of 3000 oersteds was applied. The half-width of paramagnetic resonance was found to be 4 oersteds. The relaxation time of  $\text{Si}^{29}$  was found to be large, 5 minutes, owing to the small concentration of the electrons. So large a relaxation time facilitates the experiment. Actually, one can separate in space and in time the polarization of the nuclei by saturation of electron resonance and the measurements of this polarization by nuclear resonance. The authors could not fully saturate the electron resonance, and consequently the amplification of the nuclear resonance was found to be on the order of one hundred.

Beljers et al.<sup>42</sup> investigated the Overhauser effect on protons of the free radical of diphenyl picryl hydrazil. Bennett and Torrey<sup>43</sup> investigated the Overhauser effect on protons in a solution of sodium and naphthalene in 1, 2 dimethoxyethane. Paramagnetic resonance in this solution is attributed to the formation of the free ion radical through the transfer of the valence electron from sodium to the naphthalene molecule. An

external field of 17.8 oersteds was applied, corresponding to an electron frequency of 50 Mcs and a nuclear frequency of 76.8 kcs. The authors measured the dependence of the intensification of the nuclear resonance on  $H_1$ . The results of the experiments agree with the formula [compare with (6.41)]

$$A(H_1) = \frac{1}{2} \frac{\gamma_e}{\gamma_n} \frac{(\gamma_e H_1)^2 T_1 T_2}{1 + (\gamma_e H_1)^2 T_1 T_2},$$

i.e., exact agreement was obtained with theory in the case of dipole-dipole interaction and type I relaxation. Here, according to theory, application of the saturating alternating field caused the nuclear spin to decrease, pass through zero, and then to increase in absolute value until the aforementioned stationary state was reached.

Let us note also the work of Abragam, Combrisson, and Solomon<sup>44</sup> (see also references 40 and 41) in which the Overhauser effect was investigated on protons in an aqueous solution of the free radical of nitrodisulphonate of potassium [(SO<sub>3</sub>)<sub>2</sub>NOK<sub>2</sub>]. None of the nitrogen bonds are saturated in the radical. For this reason, the paramagnetic resonance has a hyperfine structure consisting of two components which are 13 oersteds apart.

Let us determine first the leakage coefficient  $f$ . According to measurements, the relaxation time of protons in the absence of free radicals  $T_n'' = 2$  sec, and in their presence  $T_n = 0.4$  sec. From (7.27) we obtain  $f = 0.8$ .

The authors saturated one of the hfs components. It is easy to see that when it is completely saturated  $\langle S_z \rangle = (\frac{2}{3}) S_0$ . Using (7.28) and assuming  $\rho = \frac{1}{2}$ , we obtain

$$\frac{\langle j_z \rangle}{j_0} = -90.$$

Such an intensification of proton resonance was observed at all three values of the external field corresponding to the three peaks of the paramagnetic resonance absorption curve.

Owing to the presence of the hyperfine structure, spin splitting will take place also in the absence of an external field. In this case we obtain two levels (corresponding to values of  $\frac{1}{2}$  and  $\frac{3}{2}$  for  $F$ , the total spin of the radical). The authors have observed an Overhauser effect upon saturation of the transition between these two levels, and the amplification of the proton signal was very large. For details we refer the reader to reference 44.

Codrington and Bloembergen investigated the Overhauser effect on protons in an aqueous solution of MnCl<sub>2</sub> in weak fields.<sup>38</sup> The experimental data agree with the theory if the interaction of the proton spin with the spin of the Mn<sup>2+</sup> ion is assumed hyperfine.

In those cases when the nuclear polarization reverses sign upon saturation of the electron resonance, the Overhauser effect can be used to produce a crystal amplifier.<sup>44,45</sup>

Finally, we mention the paper by Solomon,<sup>46</sup> in which the relaxation processes and the Overhauser effect are considered theoretically for a system of two spins coupled by dipole-dipole interaction, and the Overhauser effect is experimentally investigated in HF.

### b) Induced Dynamic Polarization of Nuclei

Let us consider now a phenomenon which was observed by Erb, Motchane, and Uebersfeld<sup>47,48</sup> and explained by Abragam and Proctor.<sup>39</sup> In this phenomenon, the Overhauser effect does not take place in certain substances, but an amplification of the nuclear resonance signal is observed when an alternating field of frequency equal to the sum or difference of the electron and nuclear resonant frequencies is applied.

In subsection e) of the present section we have shown that the Overhauser effect should not take place in a solid diamagnet with paramagnetic impurities. In the same subsection we calculated the wave functions of four stationary states [see (7.23) and Fig. 4]. The mixing is due to the dipole-dipole interaction. Because of this mixing, application of an alternating field of suitable frequency perpendicular to the main field makes possible the obtained "forbidden" transitions

$$a \leftrightarrow b' \text{ and } b \leftrightarrow a'.$$

In the notation for the quantum numbers of the main components, these transitions are written in the following form

$$\Delta M = -\Delta m = \pm 1 \text{ and } \Delta M = \Delta m = \pm 1$$

or

$$(+, -) \leftrightarrow (-, +) \text{ and } (+, +) \leftrightarrow (-, -).$$

The probabilities of such transitions are of the same order as the probabilities of the main resonant transition, multiplied by a small quantity  $|\alpha|^2$ . It is easy to see that these two types of transition have identical probabilities under identical conditions. For resonant frequencies corresponding to these transitions we obtain

$$\Omega = \omega_e + \omega_n \text{ and } \Omega = \omega_e - \omega_n, \quad (7.30)$$

where  $\omega_e$  and  $\omega_n$  are the electronic and nuclear resonant frequencies, respectively.

As is well known, however, it is more convenient to fix the frequency and to vary the main field. Let us obtain the values of the main field corresponding to these two forbidden resonances. We have

$$\omega_e \pm \omega_n = (\gamma_e \pm \gamma_n) H = \omega,$$

where  $\omega$  is a frequency fixed in the experiment. From this we obtain for the resonant values of the field

$$H = \bar{H} \mp \Delta H, \quad (7.31)$$

where  $\bar{H} = \omega/\gamma_e$  is the resonant value of the field corresponding to the allowed transition, and  $\Delta H$  is given by the formula

$$\Delta H = \frac{\gamma_n}{\gamma_e} \bar{H}. \quad (7.32)$$

In particular, in the case of the proton

$$\Delta H = \frac{\bar{H}}{660}.$$

We have three parameters of the dimension of time:  $T_e$  — the time of relaxation of the electron spin,  $T_n$  — the time of relaxation of the nuclear spin, and  $T_f$  — the time to produce the transition due to the alternating field. As we have seen in subsection e) of the present section, the flip-flop and flip-flip transitions cancel each other out in nuclear relaxation. We can therefore assume that the nuclear relaxation is due to the “horizontal” transitions  $\Delta M = 0$ ,  $m = \pm 1$ .

Since the electron relaxation is considerably faster than the nuclear relaxation, we have

$$T_e \ll T_n.$$

Let us consider first the case  $T_f \ll T_n$ . Then there is no nuclear relaxation in practice. In the stationary case we have

$$\left. \begin{aligned} N_+ n_- = N_- n_+ \quad \text{при} \quad H = \bar{H} - \Delta H, \\ N_+ n_+ = N_- n_- \quad \text{for} \quad H = \bar{H} + \Delta H, \end{aligned} \right\} \quad (7.33)$$

which corresponds to total saturation of the forbidden transition. Since the numbers of the direct and inverse transitions are equal, these transitions, produced by the alternating field, will not influence the relaxation of the electron spin (independent of the relationship between  $T_e$  and  $T_f$ ), and consequently

$$\frac{N_+}{N_-} = e^{-2\delta}. \quad (7.34)$$

Solution of (7.33) and (7.34) yields

$$\left. \begin{aligned} \frac{n_+}{n_-} = e^{-2\delta} \quad \text{for} \quad H = \bar{H} - \Delta H, \\ \frac{n_+}{n_-} = e^{2\delta} \quad \text{for} \quad H = \bar{H} + \Delta H. \end{aligned} \right\} \quad (7.35)$$

In other words, the effective gyromagnetic ratio of the nucleus will be in these two cases  $-\gamma_e$  and  $+\gamma_e$ . We therefore obtain a nuclear emission signal when  $H = \bar{H} - \Delta H$  and a nuclear absorption signal when  $H = \bar{H} + \Delta H$ . The absolute values of the signals will be  $\tanh \delta / \tanh \delta_n$  times stronger than in the absence of saturation ( $\gamma_e/\gamma_n$  times stronger if  $\delta \ll 1$ ). The degree of the polarization of the nuclei will be

$$f_1 = \mp \tanh \delta. \quad (7.36)$$

The physical cause of the present effect is as follows: when  $H = \bar{H} - \Delta H$  the alternating field causes at first more  $(-, +) \rightarrow (+, -)$  transitions than the reverse transitions, since at first  $N_- n_+ > N_+ n_-$ . On the other hand, because of the electron relaxation, the electron spins will return from the state “+” to the state “-.” As a result, the nuclei will jump over from the state “+” to the state “-.” The result will be the opposite for  $H = \bar{H} + \Delta H$ .

If  $T_f \sim T_n$  or  $T_f > T_n$ , (7.33) will no longer hold, i.e., the saturation of the forbidden transition will be incomplete. But, since in this case  $T_e \ll T_f$ , the electronic relaxation will be considerably faster than the transitions due to the alternating field, and consequently (7.34) will remain in force.

In the stationary case we have

$$W_n e^{\delta n} n_- - W_n e^{-\delta n} n_+ + W_f (N_+ n_- - N_- n_+) = 0,$$

where  $W_n e^{\delta n}$  and  $W_n e^{-\delta n}$  are the probabilities of the nuclear relaxation transitions  $- \rightarrow +$  and  $+ \rightarrow -$ ;  $W_f N_+ n_-$  and  $W_f N_- n_+$  are the respective numbers of  $(+, -) \rightarrow (-, +)$   $(-, +) \rightarrow (+, -)$  transitions under the influence of the alternating field of frequency  $\omega = \omega_e + \omega_n$  (all these quantities are per unit time). Since (7.34) is satisfied, we have

$$N_+ = \frac{N}{2} \frac{e^{-\delta}}{e^{\delta} + e^{-\delta}}, \quad N_- = \frac{N}{2} \frac{e^{\delta}}{e^{\delta} + e^{-\delta}}$$

and we obtain in the stationary case

$$\frac{n_+}{n_-} = \frac{NW_f \frac{e^{-\delta}}{e^{\delta} + e^{-\delta}} + W_n e^{\delta n}}{NW_f \frac{e^{\delta}}{e^{\delta} + e^{-\delta}} + W_n e^{-\delta n}}. \quad (7.37)$$

For nuclear polarization we have

$$f_1 = \frac{-NW_f \tanh \delta + 2W_n \sinh \delta_n}{NW_f + 2W_n \cosh \delta_n}. \quad (7.38)$$

In the case of  $(+, +) \rightarrow (-, -)$  transition we obtain an analogous expression, except that the plus sign is in front of the first term of the numerator.

Setting  $\delta_n$  equal to zero, in view of its smallness, we have

$$f_1 = \mp \frac{\tanh \delta}{1 + \frac{2W_n}{NW_f}} \quad (7.39)$$

or, introducing the times

$$T_n = \frac{1}{2W_n \cosh \delta_n} \cong \frac{1}{2W_n}, \quad (7.40)$$

$$T_f = \frac{1}{NW_f}, \quad (7.41)$$

we obtain

$$f_1 = \mp \frac{\tanh \delta}{1 + \frac{T_f}{T_n}}. \quad (7.42)$$

It remains to determine the expression  $W_f$ . Using (7.23), we readily find that the ratio of the squares of the absolute values of the matrix elements of the forbidden and allowed transitions is  $4|\alpha|^2$ , where  $\alpha$  is given by (7.24). Taking (3.19) into account we obtain

$$NW_f \cong 2|\alpha|^2 (\gamma_e H_1)^2 T_2, \quad (7.43)$$

where  $T_2$  is the reciprocal of the width of the forbidden transition.

We finally have for the magnitude of the amplification of the signal of the nuclear resonance

$$A(H_1) = \mp \frac{\tanh \delta}{\delta_n} \frac{H_1^2}{H_1^2 + a}, \quad (7.44)$$

where

$$a = \frac{2W_n}{NW_f} H_1^2 = H_1^2 \frac{T_f}{T_n} \cong \frac{1}{2|\alpha|^2 \gamma_e^2 T_e T_n} \quad (7.45)$$

The first experiments were performed by Erb, Motchane, and Uebersfeld.<sup>47,48</sup> The sample was carbon with an adsorbed liquid (benzene or toluene) or gas (ammonia or hydrogen sulfide). Paramagnetic resonance was obtained in the carbon, because the carbon contains paramagnetic centers.

The experiments were carried out first at room temperature. The specimen was then cooled by placing it in liquid nitrogen, causing solidification of the adsorbed substance. The measurements were repeated for this case, too.

The experiments performed by these authors can be divided into two groups. In one group of experiments samples of coal were used, giving a paramagnetic absorption line with a width ranging from 4 to 10 oersteds. The authors observed the amplification of the proton resonance signal upon application of an alternating field of frequency approximately 9000 Mcs (with variation of the main field). It was found that when  $\omega = \omega_e$  more amplification effect is produced, but at  $\omega = \omega_e \pm \omega_n$  the aforementioned effects take place, and the amplification of the proton resonance is approximately 15 or 20. The effect takes place both at room and at nitrogen temperatures. The effect occurs also if the carbon is replaced by an organic substance (Plexiglas, glycol) bombarded by  $\gamma$  quanta.

In the second group of experiments, the coal samples gave paramagnetic absorption lines less than 2 oersteds wide. In these specimens there was no dynamic induced polarization, but the ordinary Overhauser effect took place instead. This problem was investigated in greater detail by Abragam, Landesman, and Winter,<sup>50</sup> in whose opinion the strong exchange interaction between the electron spins contributes to the Overhauser effect (it is known that the exchange interaction narrows down the resonance absorption line).

Borghini and Abragam<sup>51</sup> investigated the induced dynamic polarization of protons in samples of polystyrene containing diphenyl picryl hydrazil. Different samples contained different concentrations of DPPH, the optimum concentration being 10% (corresponding to one electron with uncompensated spin for every 300 protons). The experiments were carried out at 4.2° K. The external field was approximately 12,000 oersteds, the nuclear resonant frequency was near 50 Mcs, and the width of the electron resonance was near 20 Mcs. The maximum amplification of proton resonance was approximately 50, corresponding to an approximate degree of polarization of 1.5%.

Analogous experiments were made by Lomkatsi<sup>52</sup> with DPPH at 4° K. The amplification of the proton signal at  $H = \bar{H} \pm \Delta H$  was approximately 15–20.

It was noted in several interesting papers<sup>53,54</sup> that if the width of the (allowed) electron resonance ex-

ceeds the nuclear Larmor frequency, the theoretical analysis above must be modified. This is due to the fact that the transitions of the two types considered above overlap, causing a reduction in the values of the signals. In addition, the distance between the maxima will increase and will become of the order of the width of the electron resonance.

The same papers report a few experiments. In particular, Abraham, McCousland, and Robinson<sup>53</sup> investigated the effect of induced dynamic polarization of nuclei in a LiF crystal containing F centers (according to the authors' statement, they obtained approximately 10% polarization of F<sup>19</sup>) and in nitrate of cerium. The investigations by Combrisson and Solomon<sup>54</sup> were on silicon with donor impurities.

We note, finally, that Abragam and Proctor<sup>39</sup> observed induced dynamic polarization in the case of a system of two nuclear spins coupled by dipole-dipole interaction. The sample was a LiF crystal. The application of an alternating field of frequency  $\omega$  (F<sup>19</sup>)  $\pm \omega$  (Li<sup>6</sup>) has made it possible to intensify the resonance signal of Li<sup>6</sup>.

## 8. OVERHAUSER EFFECT IN PARAMAGNETIC SALTS AND SEMICONDUCTORS

### a) General Considerations

Let us proceed to the case when the sample can be considered as consisting of individual systems, each comprising a nucleus with spin  $I$  and an electron, or hole, or more generally an electron shell with effective spin of  $1/2$ . In Sec. 2 we indicated that such a situation is obtained, for example, in the following cases:

- 1) Silicon or germanium with pentavalent donor impurity at low temperature. The elementary system in this case is the impurity nucleus together with the "excess" electron localized near it.
- 2) Silicon or germanium with trivalent acceptor impurity at low temperature. The elementary system is the impurity nucleus together with an "excess" hole localized near it.
- 3) Free radical. The elementary system comprises a nucleus, whose atom has a non-saturated bond, and an electron with uncompensated spin [for example, the electron and the nitrogen nucleus in the case of free radical (SO<sub>3</sub>)<sub>2</sub>NOK<sub>2</sub>].
- 4) Paramagnetic salt with the paramagnetic ion shell of spin  $1/2$  when the nucleus of the paramagnetic ion also has a spin. The elementary system will consist of the spins of the shell and the nucleus of the paramagnetic ion.

Unlike the cases discussed in Secs. 6 and 7, in the present case the energy of the magnetic interaction of nuclear and electron spins exceeds the nuclear Zeeman energy. It becomes meaningless therefore to speak of individual Zeeman levels of the nucleus and of the shell, and compatible levels of a system

consisting of two spins  $\mathfrak{S}$  and  $\mathfrak{I}$  must be introduced. This was the procedure in Sec. 5. We shall employ the same notation in the present section.

In Sec. 5 we discussed the case of total saturation of all the paramagnetic-resonance hfs components. It was assumed there that only vertical and flip-flop relaxation take place. In the present section we consider first the case of equal partial saturation of all the components, and the case of the saturation of one of the components of the hyperfine structure.

The first question to arise is whether one can neglect all the nuclear relaxations with the exception of the flip-flop relaxation. We have seen in Sec. 2 that the hyperfine interaction with non-diagonal matrix elements for only the flip-flop transition exceeds considerably the dipole-dipole interaction, if the wave function of the electron (or the hole, or shell with  $S = \frac{1}{2}$ ) on the nucleus is not anomalously small. In the same section we have indicated that this condition is satisfied in the case of silicon or germanium with a pentavalent or trivalent impurity, and also in the case of a free radical. Because of the configuration mixing, this condition is satisfied for many paramagnetic salts.

We must note, however, the following. Owing to the motion of the particles, and also owing to the reorientation of the electron spin, both the hyperfine and the dipole-dipole interactions will be functions of the time. The energy of each of these interactions can be represented as a sum of constant and fluctuating (in time) terms, with the relaxation due to the fluctuating term. If  $|\psi(0)|$  is sufficiently large, then the total energy of the contact interaction exceeds considerably the total energy of the dipole-dipole interaction. However, cases are quite possible when the fluctuating parts of the contact in dipole-dipole interaction are of the same order, and then the role of the flip-flip and horizontal relaxation becomes comparable with the role of the flip-flop relaxation. For example, in the paper by Abragam<sup>35</sup> (see also reference 55) it is shown that in paramagnetic salts the horizontal relaxation can frequently make a substantial contribution.

Next, in nuclear spin greater than  $\frac{1}{2}$ , a sizeable fraction of the nuclear relaxation can be due to quadrupole processes.

In order not to complicate the analysis excessively, however, we assume in most of this section that only the vertical and flip-flop relaxation take place. Later, for the case  $\mathfrak{I} = \frac{1}{2}$ , we shall discuss effects due to relaxations of other types.

The results of the present section for the case  $\mathfrak{I} = \frac{1}{2}$ ,  $s = 1$ , and  $\delta \ll 1$  were obtained by Abragam<sup>35</sup> and, for the general case, by the author of the present article.<sup>56,57,58</sup>

### b) Equal Partial Saturation of All Components

Let us generalize the results of Sec. 5 to include the case when equal partial saturation of all the hfs

components of the paramagnetic resonance takes place (see Fig. 2).

In the stationary case we have

$$\frac{N(m)}{N(m')} = \frac{W(m) + We^{\delta}}{W(m) + We^{-\delta}}, \quad (8.1)$$

where  $W(m)$  is the probability of transition (per unit time) between two states with nuclear-spin projections equal to  $m$ , caused by the interaction with an alternating field of suitable frequency;  $We^{\delta}$  and  $We^{-\delta}$  are the probabilities of vertical relaxation transitions  $m' \rightarrow m$  and  $m \rightarrow m'$ . Considering that, by definition, all the resonances are equally saturated, we obtain readily

$$\frac{N(m)}{W(m) + We^{\delta}} = \frac{N(m')}{W(m) + We^{-\delta}} = \text{const},$$

where the constant is independent of  $m$ . Next, since the hyperfine interaction establishes the equilibrium between the levels  $m + 1$  and  $m'$ , we obtain

$$\frac{N(m+1)}{N(m')} = \frac{W(m+1) + We^{\delta}}{W(m) + We^{-\delta}} = e^{2\delta}, \quad (8.2)$$

for  $m = \mathfrak{I} - 1, \mathfrak{I} - 2, \dots, -\mathfrak{I}$ . From this we get

$$W(m) = qe^{2m\delta}, \quad (8.3)$$

where  $q$  is independent of  $m$ .

We introduce the saturation parameter  $s$ , defined as the same for all resonances.  $s$  is defined by

$$N(m) - N(m') = (1-s)[N^0(m) - N^0(m')] = (1-s) \frac{N}{2\mathfrak{I}+1} \tanh \delta. \quad (8.4)$$

It is easy to obtain the following relation between  $q$  and  $s$ :

$$2 \frac{1-s}{s} q = (2\mathfrak{I}+1) W (e^{\delta} + e^{-\delta}) \frac{\sinh \delta}{\sinh (2\mathfrak{I}+1)\delta}. \quad (8.5)$$

Next, we readily obtain expressions for  $f_k$ , which characterize the degree of orientation of the nuclei. We find

$$f_h(s) = s f_h(s=1), \quad (8.6)$$

where the quantities  $f_k(s=1)$  were calculated in Sec. 5 [see (5.6) and (5.7)].

Let us note the following interesting circumstance. If we neglect the quantity  $\gamma_n$  and assume that only hyperfine relaxation of nuclear spin takes place, then when  $s = 1$  the result is found to be the same for all substances, namely: we find that the effective gyromagnetic ratio of the nucleus is  $\gamma_e$ . However, if  $s < 1$ , the dependence of  $f_k$  on  $s$  is different [see (6.30), (7.20), and (8.6)].\*

To conclude this subsection, we must note, however, that the case of equal partial saturation of all the components of the hyperfine structure is somewhat artificial, in view of the need of satisfying condition (8.3). Great interest therefore attaches to the saturation of one of the hfs components.

\*However, if  $\delta \ll 1$ , the result will again be the same, namely:  $\gamma_{\text{eff}} = s\gamma_e$ .

### c) Saturation of One of the Hfs Components

Assume that the resonance corresponding to the transition between states with nuclear spin projections equal to  $\mu$  is completely saturated. We then obtain in the stationary case for the populations of the states shown in Fig. 2

$$\begin{array}{cccccccc} L & L & L & L & Le^{-2\delta} & \dots & Le^{-2\delta} & Le^{-2\delta} + \frac{1}{2} \\ Le^{2\delta} & Le^{2\delta} & \dots & Le^{2\delta} & L & L & \dots & L & L & -\frac{1}{2} \end{array}$$

$$m = \dot{I} \quad \dot{I} - 1 \quad \dots \quad \mu + 1 \quad \mu \quad \mu - 1 \quad \dots \quad -\dot{I} + 1 \quad -\dot{I}$$

where L is determined by the normalization condition. It is easy to calculate the quantities

$$f_1(\mu) = \frac{1}{i} \frac{2\mu + \frac{1}{2} [\dot{I}(\dot{I}+1) - \mu(\mu+1)](1+e^{2\delta}) - \frac{1}{2} [\dot{I}(\dot{I}+1) - \mu(\mu-1)](1+e^{-2\delta})}{2 + (\dot{I}-\mu)(1+e^{2\delta}) + (\dot{I}+\mu)(1+e^{-2\delta})}, \quad (8.7)$$

$$f_2(\mu) = \frac{3}{i(2\dot{I}-1)} \frac{2 \left[ \mu^2 - \frac{1}{3} \dot{I}(\dot{I}+1) \right] + \frac{1}{6} [\dot{I}(\dot{I}+1) - \mu(\mu+1)](2\mu+1)(1+e^{2\delta}) - \frac{1}{6} [\dot{I}(\dot{I}+1) - \mu(\mu-1)](2\mu-1)(1+e^{-2\delta})}{2 + (\dot{I}-\mu)(1+e^{2\delta}) + (\dot{I}+\mu)(1+e^{-2\delta})}. \quad (8.8)$$

If the resonance saturation is incomplete, we have

$$f_k[s(\mu)] = s(\mu) f_k[s(\mu) = 1], \quad (8.9)$$

and the saturation parameter is given by

$$s(\mu) = \frac{[2 + (\dot{I}-\mu)(1+e^{2\delta}) + (\dot{I}+\mu)(1+e^{-2\delta})] W(\mu)}{[2 + (\dot{I}-\mu)(1+e^{2\delta}) + (\dot{I}+\mu)(1+e^{-2\delta})] W(\mu) + (2\dot{I}+1) W(e^\delta + e^{-\delta})}. \quad (8.10)$$

From the foregoing results it follows that when  $\delta$  is large it is most convenient to saturate the transition corresponding to  $\mu = \dot{I} - 1$ ; in this case  $f_1 = f_2 = 1$  for  $\delta \gg 1$  and complete saturation. The physical reason for this is readily understood. Actually, in this case, owing to the singularities of the hyperfine transitions, only the level  $m = \dot{I}$ ,  $M = -\frac{1}{2}$  will be populated.

### d) Role of Non-Contact Terms

Let us consider, for the case of a nuclear spin equal to  $\frac{1}{2}$ , the effect due to the participation of the flip-flip and horizontal transitions in the nuclear magnetic relaxation. The level scheme is as shown in Fig. 5. For the probabilities of the relaxation transitions we can write<sup>38</sup>

$$\left. \begin{array}{l} W(aa') = W(bb') = W e^{-\delta}, \quad W(a'a) = W(b'b) = W e^{\delta}, \\ W(ab') = \lambda W e^{-\delta}, \quad W(b'a) = \lambda W e^{\delta}, \\ W(ba') = \lambda_1 W e^{-\delta}, \quad W(a'b) = \lambda_1 W e^{\delta}, \\ W(ab) = W(ba) = W(a'b') = W(b'a') = \lambda_2 W, \end{array} \right\} (8.11)$$

where  $\lambda$ ,  $\lambda_1$ ,  $\lambda_2$ , and W are certain functions of the temperature and of the external field.

$$\begin{array}{cc} \frac{a'}{m} & \frac{b'}{+1/2} \\ \frac{a}{+1/2} & \frac{b}{-1/2} \end{array} \begin{array}{c} M \\ +1/2 \\ -1/2 \end{array}$$

FIG. 5

With complete saturation of both resonances, we readily obtain [compare with (7.17)]

$$\frac{N(a)}{N(b)} = \frac{\lambda e^\delta + \lambda_1 e^{-\delta} + 2\lambda_2}{\lambda e^{-\delta} + \lambda_1 e^{\delta} + 2\lambda_2}, \quad (8.12)$$

$$f_1 = \frac{(\lambda - \lambda_1) \sinh \delta}{(\lambda + \lambda_1) \cosh \delta + 2\lambda_2}. \quad (8.13)$$

### e) Determination of $f_k$

Let us consider the possible experimental determination of the quantities  $f_k$ . It is desirable to employ here methods which are not connected with the results obtained above.

Consider the case  $\dot{I} = \frac{3}{2}$  (Fig. 6). We readily obtain

$$f_1 = \frac{1}{3N} \{ 3[N(a) - N(b)] + 3[N(a') - N(b')] + 4[N(b) - N(c)] + 4[N(b') - N(c')] + 3[N(c) - N(d)] + 3[N(c') - N(d')] \}, \quad (8.14)$$

$$f_2 = \frac{1}{N} \{ [N(a) - N(b)] + [N(a') - N(b')] - [N(c) - N(d)] - [N(c') - N(d')] \}. \quad (8.15)$$

$$\begin{array}{cccc} \frac{a'}{m} & \frac{b'}{+1/2} & \frac{c'}{-1/2} & \frac{d'}{-3/2} \\ \frac{a}{+3/2} & \frac{b}{+1/2} & \frac{c}{-1/2} & \frac{d}{-3/2} \end{array} \begin{array}{c} M \\ +1/2 \\ -1/2 \end{array}$$

FIG. 6

If we measure experimentally, for example, the signal of nuclear resonance  $a \leftrightarrow b$ , we can determine its magnitude  $N(a) - N(b)$ . Thus, the values of  $f_k$  can be determined by measuring the signals of all the nuclear resonances.

We note that some of the differences  $N(a) - N(b)$ ,  $N(a') - N(b')$ , ... should increase strongly if at least one of the hfs components of the paramagnetic resonance is saturated, even in the case of small  $\delta$ . Thus, measurement of nuclear resonance, even at not

very low temperatures, can afford a verification of the foregoing theoretical results.

Actually, the situation is much more complicated. According to (4.2) the energies of all the nuclear resonance transitions ( $\Delta M = 0$ ,  $\Delta m = \pm 1$ ) coincide accurate to terms proportional to  $A$  and  $B$ , and have a value  $K/2$ . In the next approximation there will be a difference in terms of order  $B^2/g\beta H$ ,  $P$ , and  $g\gamma\beta H$ . On the other hand, in the case of paramagnetic salts, the width of the individual component of nuclear resonance will be sufficiently large.<sup>59,60</sup> Therefore, in order for the individual components of nuclear resonance not to overlap, experiments must be carried out at a relative weak external field, which, on the other hand, reduces the obtained polarization. This difficulty disappears in the case of doped silicon, for in this case the width of the nuclear resonance will not be so large.

Next, according to references 59 and 60, experiments on nuclear resonance in paramagnetic salts will apparently be successful only at helium temperatures, and not for all paramagnetic salts at that. The difficulty of observing nuclear resonance is due to its great width.

It is seen from (8.14) and (8.15) that when one of the paramagnetic resonance components is saturated, we cannot determine  $f_k$  directly by measuring the resonance signals of the remaining components. However, such measurements can be made to determine the contributions of different mechanisms to the nuclear relaxation. For example, it is easy to verify that in the case  $I = 3/2$  and complete saturation of the resonance  $b \rightarrow b'$

$$N(a) - N(a') = \frac{N(e^{2\delta} - 1)}{5 + e^{2\delta} + 2e^{-2\delta}},$$

if the nuclear relaxation is completely due to contact interaction, whereas in the absence of saturation we have

$$N^0(a) - N^0(a') = \frac{N}{4} \tanh \delta.$$

Thus, provided only  $\delta$  is of order of unity or greater, the signal of the resonance  $a \leftrightarrow a'$  should increase substantially in the case of total saturation of the resonance  $b \leftrightarrow b'$ . In particular, if  $\delta \gg 1$ , the resonance  $a \leftrightarrow a'$  should increase by a factor of four. Any deviation from this result should be due to the contributions made by other mechanisms of nuclear spin relaxation.

In the case of polarization of radioactive nuclei, the values of  $f_k$  can be determined from the angular distribution of the  $\beta$  radiation. The values of  $f_k$  with even  $k$  can be determined more simply, from the angular distribution of the  $\gamma$  radiation.

There are also other methods with which to determine  $f_k$  and estimate the contributions made by different relaxations. We shall discuss these in the next subsection of this section and in Section 11.

## f) Comparison with Experiment

Experiments on the Overhauser effect with paramagnetic salts have not yet been performed. The reason is that too high a microwave power is necessary to saturate the paramagnetic resonance, in view of the small relaxation time of the electron spin. We deal not merely with difficulties in obtaining high microwave power, but with the difficulty of dissipating the considerable heat liberated at low temperatures.

On the other hand, in silicon or germanium with pentavalent or trivalent impurities, the electron-spin relaxation times are considerably greater, because the orbital fraction in the magnetic moment of the electron (or hole) is exceedingly small, and therefore the electron spin is very weakly coupled to the lattice. At large relaxation times, on the other hand, relatively small microwave power is necessary to saturate the resonance. The experiments are easier to carry out in this case in silicon, in view of the higher ionization energy of the impurity (see Sec. 2).

In 1957–1959 several groups of physicists experimented on the Overhauser effect in silicon doped with phosphorus, arsenic, or antimony. Most of these investigations were devoted to the nonstationary Overhauser effect, and will be described in Sec. 11. Pipkin and Culvahouse, on the other hand, investigated the stationary Overhauser effect along with the nonstationary effects.

Let us discuss first the relaxation in silicon containing a pentavalent or trivalent impurity. These relaxation times have been investigated experimentally in work on the nonstationary Overhauser effect (see Sec. 11). The problem was analyzed theoretically in the paper by Pines, Bardeen, and Slichter.<sup>61</sup> The authors of this paper calculate the time of vertical and flip-flop relaxation. The numerical values of the relaxation time and also comparison with theory will be given in Sec. 11. We note here merely that these times are sufficiently long at helium temperatures (several minutes and more).

Experiments carried out by Pipkin and Culvahouse<sup>62,63</sup> consisted of the following. The authors took a sample of silicon doped with arsenic or antimony, some impurity atoms being radioactive. One of the hfs components of paramagnetic resonance, connected with the radioactive nuclei, was saturated. The degree of orientation of the nuclei was measured from the angular anisotropy of the  $\gamma$  radiation. These experiments were carried out in a field of 8500 oersteds at 1.3° K. In the case of As<sup>76</sup>, no effect was observed, a fact attributed by the authors to the excessive time of nuclear magnetic relaxation. In the case of Sb<sup>122</sup> the effect was observed. The Sb<sup>122</sup> nucleus has a spin of  $2/3$ . The level picture is shown in Fig. 7 (neglecting the spin-spin interaction energy). The anisotropy of  $\gamma$  radiation upon saturation of the resonance was ob-

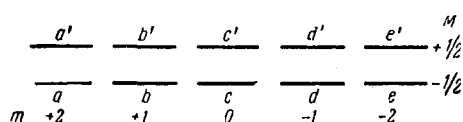


FIG. 7

served and measured. The authors then simultaneously saturated the two transitions  $c \leftrightarrow c'$  and  $b \leftrightarrow c$  and measured the time dependence of the anisotropy of the  $\gamma$  radiation. The anisotropy of  $\gamma$  radiation first increased with time, owing to the polarization of the nuclei upon saturation of the  $c \leftrightarrow c'$  transition, and then diminished because of the partial depolarization upon saturation of the  $b \leftrightarrow c$  transition. The time variation of the anisotropy makes it possible to determine the relaxation times. These experiments also made it possible to determine the magnetic moment of the  $\text{Sb}^{122}$  nucleus and its hfs constant.

### g) Overhauser Effect in Weak Magnetic Field

Kittel<sup>64</sup> and Abragam<sup>35</sup> considered the Overhauser effect in the absence of an external magnetic field. One can speak of an Overhauser effect on the splitting of the fine structure (which takes place if the effective spin of the electron shell of the paramagnetic ion is more than  $\frac{1}{2}$ ) or on the splitting due to anisotropic hyperfine structure.

According to Abragam,<sup>35</sup> when resonance is saturated in the absence of an external magnetic field, we obtain only aligned nuclei (i.e.,  $f_1 = 0$  and  $f_2 \neq 0$ ). Actually, if no external magnetic field is applied, there will be no preferred direction for the mean value of the nuclear spin vector.

In other words, in the absence of an external magnetic field the two transitions, which are obtainable from each other by interchanging the signs of  $M$  and  $m$  (the role of the quantization axis in the absence of a magnetic field is assumed by the symmetry axis of the intercrystalline electric field), have the same frequency. Therefore these two transitions are simultaneously saturated, indeed causing the lack of polarization.

If we apply a weak external field (weak in comparison with the fine or hfs splitting) but sufficient to separate these two transitions from each other, then saturation of one of these gives rise to a considerable nuclear polarization.

More details on the Overhauser effect in weak field are found in reference 65.

## 9. OVERHAUSER EFFECT IN ALKALI-HALIDE CRYSTALS AND ALKALI-AMMONIA SOLUTIONS

It was indicated in Sec. 2 that according to modern concepts the F center is a vacancy of the chlorine ion (to be specific, we again consider the KCl case), which has captured an electron. The wave function of

the electron of the F center has a maximum on the potassium nuclei closest to the vacancy. The electron of the F center experiences both contact and dipole-dipole interaction with each nucleus of the lattice (both with the potassium nuclei and with the chlorine nuclei). The contact interaction diminishes exponentially with increasing distance from the center of the vacancy, whereas the dipole-dipole interaction diminishes much more slowly, namely, as the cube of the distance. On the other hand, we have seen in Sec. 7 that whereas the contact interaction leads in the case of saturation of the electron resonance to a positive nuclear polarization, the dipole-dipole interaction does not lead to their polarization in the case of a diamagnetic solid with paramagnetic impurities.

In the KCl crystal we have many F centers, whose concentration is, however, much less than the concentration of the regular atoms. It can be assumed that each F center acts on the nuclear spins contained within a sphere centered about this F center of volume equal to the volume of the crystal, divided by the number of F centers in the crystal. The foregoing arguments show that with full saturation of the resonance of the F center in the central part of the sphere, the nuclear polarization will be positive and equal to  $B_j(2i\delta)$ . With increasing distance from the F center, the nuclear polarization will diminish and tend to zero, since the relative contribution of the dipole-dipole interaction to the relaxation of the nuclear spin will increase, as will the contribution of the interactions not connected with the spin of the F-center electron. It follows therefore that the average equilibrium polarization of the nuclei should increase with increasing F-center concentration.

In a rigorous analysis of this phenomenon, account must be taken of the role that can be played by the diffusion of nuclear spin.<sup>36</sup>

The question of the Overhauser effect in alkali-halide crystals with F centers was considered in greater detail by Korringa.<sup>66</sup> Instead of the spin of the individual nucleus, the author introduces the total spin of the nuclei of a given coordination sphere. The Overhauser effect is considered as an orientation of this overall spin due to its interaction with the spin of the F electron.

Experiments on the Overhauser effect with alkali-halide crystals have not yet been performed.

The alkali-ammonia solutions have certain similarity to alkali-halide crystals containing F centers. A theory of alkali-ammonia solutions was developed by Kaplan and Kittel,<sup>67</sup> who proposed a model that agrees with all the experiments. According to this model, the alkali-ammonia solutions contain vacancies, and the volume of each vacancy fluctuates between two and four times the volume of each ammonia molecule. These vacancies capture the valence electrons of the alkali metal. The electron captured by such a vacancy experiences a magnetic interaction with the protons of



the ammonia molecules surrounding the vacancy. Therefore, an Overhauser effect should take place on these protons.

Experiments have been set up by Carver and Slichter on a solution of sodium in ammonium anhydride.<sup>30</sup> The electron resonance line was found to be quite narrow (approximately 20 millioersted wide) and can therefore be readily saturated. The external field was taken to be 11.7 oersteds. The corresponding resonances of the electron and nuclear frequencies are 37.7 Mcs and 50 kcs respectively. The experiments were carried out at room temperature.

The authors measured the dependence of the amplification of the nuclear-resonance signal on the amplitude of the field that saturates the electron resonance. The measurements were carried out with three samples with sodium concentrations 0.01 N, 0.37 N, and 0.9 N, respectively. The  $1/A$  vs  $1/H_1^2$  plot was found to be a straight line in all three cases [see (6.42)]. Furthermore, as expected, it was found that in the case of sufficient saturation the effect increases with increasing sodium concentration. For a sample with a sodium concentration of 0.9 N at  $H_1 = 0.1$  oersted, the amplification of the nuclear resistance was 500, very close to the maximum possible amplification in contact interaction.

#### 10. OVERHAUSER EFFECT FROM THE POINT OF VIEW OF GENERAL PRINCIPLES OF STATISTICAL PHYSICS AND THERMODYNAMICS

Kittel has shown<sup>64</sup> that the Overhauser effect can be explained from the point of view of general principles of statistical physics.

It is well known that the canonical distribution gives the distribution of probabilities of the quantum states of the subsystem A, which comprises a small part of a large closed system A + B, as a function of the energy of the reservoir B.

We shall take A to mean a system of nuclear and electron spins, and B the aggregate of the remaining degrees of freedom of the specimen. For example, B is the lattice in the case of a paramagnetic salt, and the lattice and the translational degrees of freedom of the conduction electron in case of a metal; in the case of a diamagnetic liquid with paramagnetic impurities B comprises the degrees of freedom connected with the Brownian motion of the molecules of the liquid. We confine ourselves to the case of nuclear spin  $1/2$ .

We analyze the case when the relaxation of the nuclei is due only to flip-flop transitions. Assume that no saturating alternating field is applied to the system. In the transition  $(+, -) \rightarrow (-, +)$  the energy of the system A changes by  $-2(\beta + \beta_n)H$ . In view of the conservation of energy, the change in the energy of the system B will at this state be  $2(\beta + \beta_n)H$ . We know that the relaxation of the electron spin is much faster than that of the nuclear spin. Therefore the first stage

will be followed by a second one, namely the electron spin transition  $- \rightarrow +$ , caused by its interaction with the lattice. At this stage the change in the energy of the system A will be  $2\beta H$ , and the change in the energy of the system B will be  $-2\beta H$ . As a result we obtain the transition  $(+, -) \rightarrow (+, +)$ . An examination of the second stage is necessary, because we are interested in the distribution of the nuclei over the spin states, and we must therefore consider a process in which only the direction of the nuclear spin changes. The overall change in the energy of the system B is  $2\beta_n H$ . The change in the energy of the reservoir causes a change in the volume of the phase space accessible to it, and we obtain for the distribution of nuclei over the two spin states

$$\frac{n_+}{n_-} = \exp \left[ \frac{2\beta_n H}{kT} \right].$$

Assume that an alternating field producing total saturation of the electron resonance is now applied. The first stage will be the same as in the case considered above. As to the second stage, it is produced in this case not by relaxation but by the alternating field, and therefore the energy of the reservoir does not change. Thus, the overall change in the energy of the system B will be  $2(\beta + \beta_n)H$ , and we obtain

$$\frac{n_+}{n_-} = \exp \left[ \frac{2(\beta + \beta_n)H}{kT} \right], \quad (10.1)$$

i.e., the effective magnetic moment of the nucleus will be  $\beta + \beta_n$ .

A very interesting question is that of the temperature in the Overhauser effect. We introduce three temperatures, namely: the lattice temperature T (in the case of the metal it is equal to the temperature connected with the translational motion of the degrees of freedom of the conduction electrons), the Zeeman temperature of the electrons  $T_e$ , and the Zeeman temperature of the nuclei  $T_n$ . By Zeeman temperature is meant the temperature describing the distribution over the levels corresponding to the different spin directions.

In the case of complete statistical equilibrium, these three temperatures are the same.  $T_e$  increases with saturation of electron resonance. If, in particular, the saturation is complete,  $T_e$  becomes infinite.

On the other hand, the Overhauser effect takes place if a noticeable fraction of the nuclear relaxation is due to the magnetic interaction between the nuclei and the electrons. If the strongest interaction experienced by the nuclear spins is their interaction with the electron spins, one would expect at first glance the Zeeman temperature of the nuclei to vary with the Zeeman temperature of the electrons. According to the Overhauser effect, however, the result is just the opposite: the temperature  $T_n$  decreases (in some cases it even becomes negative).

Various points of view have been expressed on this

topic. Van Vleck<sup>68</sup> considered the Overhauser effect for the case when the nuclear spin has only hyperfine relaxation and obtained for the stationary case the result

$$\frac{1}{T_n} = \frac{1}{T} + \frac{\gamma_e}{\gamma_n} \left( \frac{1}{T} - \frac{1}{T_e} \right). \quad (10.2)$$

In the case of complete saturation of the electron resonance  $T_e = \infty$  and we obtain

$$T_n = \frac{\gamma_n}{\gamma_n + \gamma_e} T, \quad (10.3)$$

which corresponds to an effective nuclear gyromagnetic ratio  $\gamma_e + \gamma_n$ .

Deslay and Barker<sup>69</sup> believe that only one temperature, namely the lattice temperature, should be introduced, and that different chemical potentials must instead be assigned to the electrons, as well as to nuclei with different spin directions.

It is stated in the paper by Slichter<sup>70</sup> that in the presence of a rotating saturating field one cannot introduce the Zeeman electron temperature in the laboratory system. Changing, however, to a system which rotates with Larmor frequency about the  $z$  axis of the laboratory system, makes it possible to introduce into this system the electron Zeeman temperature, which equals the lattice temperature (the change to the rotating system gives rise to an additional effective field, which cancels out the main field, and thus the Hamiltonian will not contain the Zeeman energy of the electron in the rotating system of coordinates). However, as shown by Slichter, in the rotating system of coordinates the nucleus will have an effective gyromagnetic ratio  $\gamma_e + \gamma_n$ .

Let us note, finally, the paper by Abragam and Proctor,<sup>71</sup> devoted to a detailed analysis of the concept of spin temperature. We shall not discuss this work, however, since it is not directly connected with the Overhauser effect.

It is more or less accepted at present that one cannot introduce the Zeeman electron temperature in the presence of a saturating field. Brovotto and Cini<sup>72</sup> derived the Overhauser effect with the aid of the law of effective masses. Let us repeat this derivation for the case of nuclear spin of  $1/2$ , and in the presence of only the hyperfine nuclear spin relaxation. We consider the direct and inverse transitions

$$(+, -) \longleftrightarrow (-, +).$$

In the stationary state, according to the law of effective masses, we obtain

$$\frac{N_+ n_+}{N_- n_-} = K, \quad (10.4)$$

where the equilibrium constant  $K$  is determined by the Vant' Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta U}{kT^2}. \quad (10.5)$$

$\Delta U$  represents the change in the energy of the system in the transition  $(+, -) \rightarrow (-, +)$

$$\Delta U = -2(\beta + \beta_n)H = -\hbar(\gamma_n + \gamma_e)H. \quad (10.6)$$

Integration of (10.5) yields (we assume that  $K = 1$  when  $T = \infty$ )

$$\ln K = \frac{\hbar(\gamma_n + \gamma_e)H}{kT},$$

and thus we obtain

$$\frac{n_+}{n_-} = \frac{N_+}{N_-} \exp \left[ \frac{\hbar(\gamma_n + \gamma_e)H}{kT} \right]. \quad (10.7)$$

With total saturation, in particular,  $N_+ = N_-$  and we obtain the well known result that the effective gyromagnetic ratio of the nucleus is  $\gamma_n + \gamma_e$ . A generalization to the presence of other spin nuclear-spin relaxation mechanisms is given in references 73 and 74.

Brovotto and Ferroni<sup>75</sup> derived the Overhauser effect by calculating the so-called grand distribution function.

We call attention also to references 74, 76, and 77, in which the Overhauser effect is considered from the point of view of the principle of minimum entropy formation.

## 11. NONSTATIONARY METHODS

### a) Saturation of the Forbidden Resonance (Jeffries Method)

Let the sample be a paramagnetic salt or silicon with pentavalent or trivalent impurities. In Sec. 4 we considered both the ordinary paramagnetic resonance and the forbidden paramagnetic resonance. The method now considered<sup>76</sup> is based on the saturation of the forbidden transition when the time of the vertical relaxation is much shorter than the times of all other relaxations. This condition is always satisfied in the case of paramagnetic salts. It is also satisfied for certain impurities in silicon, for example,  $P^{31}$ ,  $As^{76}$ , or  $Sb^{122}$ .

Let us turn to Fig. 2. Assume that one of the transitions  $\Delta M = -\Delta m = \pm 1$  is completely saturated, in particular, the transition  $\mu \longleftrightarrow \mu - 1'$  (see Sec. 5 for notation), where  $\mu$  can assume the values  $\dot{I}, \dot{I} - 1, \dots, -\dot{I} + 1$ . Figure 8 shows three pairs of levels from Fig. 2, corresponding to nuclear-spin projections  $\mu + 1, \mu$ , and  $\mu - 1$ .

$$\begin{array}{ccc} \frac{\mu+1}{\mu+1} & \frac{\mu}{\mu} & \frac{\mu-1'}{\mu-1'} \\ \hline \frac{\mu+1}{\mu+1} & \frac{\mu}{\mu} & \frac{\mu-1'}{\mu-1'} \end{array}$$

FIG. 8

We denote by  $W(\mu)$  the probability of the transition  $\mu \longleftrightarrow \mu - 1'$  per unit time under the influence of the alternating field. In the present problem we have three parameters with dimensions of time, namely  $T_r = 1/W(\mu)$ , the time of vertical relaxation  $T_e = 1/2W \times \cosh \delta$ , and the time of nuclear relaxation  $T_n$ . Let us consider the case

$$T_r \ll T_e \ll T_n.$$

In this case the alternating field equalizes, with a relaxation time of order  $T_r$ , the populations of the levels  $\mu$  and  $\mu - 1'$ , while the populations of the remaining levels remain unchanged. Next, with a relaxation time of order  $T_e$ , equilibrium is established between the levels  $\mu$  and  $\mu'$  and also between the levels  $\mu - 1$  and  $\mu - 1'$ . Finally, the complete stationary state is established with a relaxation time of order  $T_n$ . We denote the orientation parameters corresponding to these three stages by the indices  $r$ ,  $e$ , and  $n$  respectively.

In the first stage we have

$$N(\mu) = N(\mu - 1') = \frac{N}{2(2j+1)},$$

and the populations of the remaining states are the same as in total equilibrium in the absence of an alternating field.

In the second stage we have the following equations for determining the populations of the states

$$N(\mu) = N(\mu - 1'),$$

$$\frac{N(\mu)}{N(\mu')} = \frac{N(\mu-1)}{N(\mu-1')} = e^{2\delta},$$

$$N(\mu) + N(\mu') + N(\mu - 1) + N(\mu - 1') = \frac{2N}{2j+1}.$$

We can also write out the equations that must be satisfied by the populations in the third stage.

It is easy to obtain\*

$$f_1^r = -\frac{1}{2j(2j+1)} \tanh \delta, \quad (11.1)$$

$$f_2^r = -\frac{3(2\mu-1)}{2j(2j+1)(2j-1)} \tanh \delta, \quad (11.2)$$

$$f_1^e = -\frac{1}{j(2j+1)} \tanh \delta, \quad (11.3)$$

$$f_2^e = -\frac{3(2\mu-1)}{j(2j+1)(2j-1)} \tanh \delta, \quad (11.4)$$

$$f_1^n = -\frac{j(j+1) - \mu(\mu-1)}{j[(j+1-\mu)e^{-\delta} + (j+\mu)e^{\delta}]} \sinh \delta, \quad (11.5)$$

$$f_2^n = -\frac{[j(j+1) - \mu(\mu-1)](2\mu-1)}{j[(j+1-\mu)e^{-\delta} + (j+\mu)e^{\delta}](2j-1)} \sinh \delta. \quad (11.6)$$

We can also show that for any  $k$

$$f_k^e = 2f_k^n. \quad (11.7)$$

Let us analyze the physical meaning of the results. The fact that  $f_1$  is negative is readily understood. Actually, the alternating field will cause more  $\mu \rightarrow \mu - 1'$  transitions than  $\mu - 1' \rightarrow \mu$  transitions, for prior to saturation the population of the state  $\mu$  exceeds the population of the state  $\mu - 1'$ .

Comparison of (11.1), (11.3), and (11.5) yields

$$|f_1^n| < |f_1^e| < |f_1^r|, \quad (11.8)$$

which is also easy to understand. After the populations of the states  $\mu$  and  $\mu - 1'$  become equalized, the vertical relaxation produces the transitions  $\mu' \rightarrow \mu$  and  $\mu - 1' \rightarrow \mu - 1$ . As a result, the alternating field will produce additional transitions  $\mu \rightarrow \mu - 1'$ . When nuclear relaxation enters into play, transitions will take place from the left levels of Fig. 2 to the right levels. This causes an increase in the populations of the states with small  $m$ .

If the condition  $T_r \ll T_e$  is not satisfied, Eqs. (11.1) and (11.2) become meaningless, since the equilibrium over the alternating field and over the vertical relaxation will be established simultaneously. On the other hand, Eqs. (11.3) - (11.6) retain their meaning.

If the condition  $T_e \ll T_n$  is not satisfied, Eqs. (11.3) and (11.4) also become meaningless, for in this case the equilibrium is established simultaneously over the vertical and nuclear relaxations.

As regards (11.5) and (11.6), they remain in force in all cases, and furthermore, if the saturation of the transitions  $\mu \rightarrow \mu - 1'$  is incomplete (which will take place if  $T_r \sim T_n$ ), a factor  $s(\mu)$  appears in their right halves, equal to the degree of the resonance saturation.<sup>79</sup>

At first glance it would appear more convenient to have  $T_n$  as small as possible. This is not so, however, for in rapid nuclear relaxation it is difficult to saturate the forbidden transition.

It is easy to show next that if the forbidden transition  $\mu \leftrightarrow \mu + 1'$  is saturated, then the minus sign of formulas (11.1) - (11.4) must be replaced by a plus sign, and in addition, the factor  $2\mu - 1$  must be replaced by  $2\mu + 1$ . The formulas for  $f_1^n$  and  $f_2^n$  become much more complicated, since the alternating field produces transitions  $\Delta M = \Delta m = \pm 1$ , while the nuclear relaxation connected with the transitions  $\Delta M = -\Delta m = \pm 1$ .

The first experiments on the Jeffries method were set up by Abraham, Kedzie, and Jeffries.<sup>81</sup> The sample used by these authors was the paramagnetic salt  $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{D}_2\text{O}$ , in which some of the magnesium atoms were replaced by cobalt atoms (both stable and radioactive isotopes). The ratio of the number of atoms of magnesium,  $\text{Co}^{59}$  and  $\text{Co}^{60}$  was  $10^4:50:1$ . The experiments were carried out at  $1.6^\circ \text{K}$ . The frequency of the saturating field was 9300 Mcs. The authors saturated one of the hfs components of the forbidden resonance of  $\text{Co}^{60}$  and measured the angular anisotropy of the  $\gamma$  radiation of these nuclei.

Very brilliant experiments on the application of the Jeffries method to silicon doped with arsenic or antimony were set up by Pipkin and Culvahouse.<sup>72,63,82,83</sup> The authors measured the intensity of  $\gamma$  radiation of the  $\text{As}^{76}$  or  $\text{Sb}^{122}$  nuclei in the direction of the external field and perpendicular to it. Upon saturation of one of the hfs components of the forbidden paramagnetic resonance of the radioactive nucleus, these intensities stop being equal and become furthermore functions of the time, corresponding to an increase in the para-

\*The expressions for  $f_1^n$  and  $f_2^n$  were derived in reference 79 for a nuclear relaxation due to the contact interaction. The remaining expressions were obtained in reference 80, and are independent of the mechanism of nuclear relaxation.

meters  $f_k$  by a factor of two when equilibrium is established in the vertical transitions. The value of the external field at which the forbidden paramagnetic resonance takes place\* at a fixed frequency of the saturating alternating field makes it possible to determine the hyperfine structure constant of the radioactive nucleus. Using this, we can determine the magnetic moment of the radioactive nucleus, if the magnetic moment and the hyperfine structure constant of the stable isotope of the given element are known.

Next, measurement of the time dependence of the angular anisotropy makes it possible to determine the relaxation times. The numerical values of  $T_n$  and  $T_e$  obtained by these authors are listed in subsection d) of the present section along with the values of  $T_n$  and  $T_e$  for stable isotope impurities.

We note also the theoretical paper by Odenhal,<sup>84</sup> who considers the polarization of nuclei in paramagnetic salts with saturation of forbidden transitions due to quadrupole interactions.

### b) Method of Double Resonance (Feher Method)

The method of double resonance was proposed by Feher. This method was found to be quite effective for the investigation of fine details in the structure of paramagnetic resonance of impurities in solids (see, for example, reference 85). We shall deal only with the use of the method of double resonance to obtain polarized nuclei.<sup>86</sup>

In Sec. 3 we have considered briefly the problem of adiabatically fast passage through resonance. We have seen that if the sweep through resonance is fast enough the result is an inversion of two corresponding levels, i.e., an interchange of their populations. We shall henceforth denote the inverted pair of levels  $i$  and  $k$  by the symbol  $[i, k]$ .

Let us turn to Fig. 2 (or Fig. 8). Let the pair of levels  $[\mu, \mu']$  be inverted first. For this purpose it is necessary to apply to the specimen a microwave field with fixed frequency and, by rapidly varying the magnitude of the main field (or, to the contrary, fixing the value of the main field and rapidly changing the frequency of the microwave field), pass through the resonance corresponding to the transition between levels  $\mu$  and  $\mu'$ . It is clear that this inversion does not change the degree of polarization of the nuclei.

We next invert one of the following four pairs of levels:  $[\mu, \mu - 1]$ ,  $[\mu, \mu + 1]$ ,  $[\mu', \mu - 1']$  or  $[\mu', \mu + 1']$ . As a result, considerable polarization of the nuclei is produced.

Actually, at first the populations of the levels are given by (5.1). After inverting the pair of levels  $[\mu, \mu']$  we obtain

$$N(\mu) = \frac{N}{2j+1} \frac{e^{-\delta}}{e^{\delta} + e^{-\delta}}, \quad N(\mu') = \frac{N}{2j+1} \frac{e^{\delta}}{e^{\delta} + e^{-\delta}},$$

If we next invert, for example, the pair of levels  $[\mu', \mu - 1']$ , we obtain

$$N(\mu) = N(\mu') = \frac{N}{2j+1} \frac{e^{-\delta}}{e^{\delta} + e^{-\delta}},$$

$$N(\mu - 1) = N(\mu - 1') = \frac{N}{2j+1} \frac{e^{\delta}}{e^{\delta} + e^{-\delta}}.$$

The remaining populations are again given by (5.1). The final result is equivalent to an interchange of the populations of the levels  $\mu$  and  $\mu - 1'$ . Such a sequence of two inversions causes an increase in the number of nuclei with spin projections equal to  $\mu - 1$ , and a reduction in the number of nuclei with spin projections equal to  $\mu$ . In this case we obtain therefore negative polarization of the nuclei ( $f_1 < 0$ ), regardless of the sign of the magnetic moment of the nucleus.

Let us introduce the final expressions for  $f_1$  and  $f_2$  for the four possible cases:<sup>80</sup>

$$f_1 = \pm \frac{1}{i(2i+1)} \tanh \delta, \quad (11.9)$$

$$f_2 = \pm \frac{3(2\mu-1)}{i(2i+1)(2i-1)} \tanh \delta, \quad (11.10)$$

where the upper sign corresponds to inversion of the pair  $[\mu, \mu - 1]$  after the pair  $[\mu, \mu']$ , and the lower respectively the pair  $[\mu', \mu - 1']$  after the pair  $[\mu, \mu']$ . Next,

$$f_1 = \mp \frac{1}{i(2i+1)} \tanh \delta, \quad (11.11)$$

$$f_2 = \mp \frac{3(2\mu+1)}{i(2i+1)(2i-1)} \tanh \delta, \quad (11.12)$$

where the upper sign corresponds to inversion of the pair  $[\mu, \mu + 1]$  after the pair  $[\mu, \mu']$ , and the lower to the pair  $[\mu', \mu + 1']$  after the pair  $[\mu, \mu']$ .

We note that (11.9) – (11.12) are valid when the time interval between two successive inversions is much less than the time of vertical relaxation  $T_e$ . In the opposite case we obtain a smaller degree of orientation, since prior to the second inversion the vertical relaxation has a chance to reestablish partially the equilibrium between the inverted levels.

The question arises as to how long the time in which we obtain polarization of the nuclei will continue. Let us consider the most frequent case  $T_e \ll T_n$ . In the aforementioned case of inversion of the pairs  $[\mu, \mu']$  and  $[\mu', \mu - 1']$  with a relaxation time on the order of  $T_e$ , vertical relaxation transitions will take place between the levels  $\mu$  and  $\mu'$ , and also between the levels  $\mu - 1$  and  $\mu - 1'$ , since the populations of these levels are not in equilibrium with each other. After establishment of equilibrium over the vertical transitions, we obtain

$$N(\mu) = N(\mu - 1') = \frac{N}{2j+1} \frac{2}{(e^{\delta} + e^{-\delta})^2},$$

$$N(\mu') = \frac{N}{2j+1} \frac{2e^{-2\delta}}{(e^{\delta} + e^{-\delta})^2}, \quad N(\mu - 1) = \frac{N}{2j+1} \frac{2e^{2\delta}}{(e^{\delta} + e^{-\delta})^2}.$$

\*The presence of the resonance itself is determined from the occurrence of the angular anisotropy of the  $\gamma$  radiation.

These values of the populations coincide exactly with the populations obtained in total saturation of forbidden resonance  $\mu \longleftrightarrow \mu - 1'$  (after establishment of the equilibrium over the vertical transitions).

In vertical relaxation, however, the projection of the nuclear spin does not change. Therefore the nuclear polarization obtained by the Feher method will attenuate with a relaxation time on the order of the time of nuclear magnetic relaxation.

Comparison of the results obtained in the present and in the preceding subsections of this section shows that the same values of  $f_k$  are obtained by the Feher method and in the second stage of the corresponding cases of the Jeffries method. For example, upon inversion of the two pairs  $[\mu, \mu']$  and  $[\mu', \mu - 1']$  we obtain the same result as upon saturation of the forbidden transition  $\mu \longleftrightarrow \mu - 1'$ .

For realizability of the Feher method, it is very important that the energies of the transitions  $\mu \longleftrightarrow \mu - 1$ ,  $\mu \longleftrightarrow \mu + 1$ , and  $\mu' \longleftrightarrow \mu - 1'$  not be the same. Actually, the energies of these transitions differ by amounts on the order of  $B^2/g\beta H$ ,  $g_j\beta H$ , and  $P$ .

The foregoing arguments show that two rapid passages can be replaced by a single one, namely the inversion of a pair of levels the transition between which corresponds to forbidden resonance. For example, instead of inverting the pairs  $[\mu, \mu']$  and  $[\mu', \mu - 1']$ , we can invert the pair  $[\mu, \mu - 1']$ .

Later on, Feher proposed a modification of the double-resonance method, more convenient for observation of fine details in the paramagnetic resonance spectrum. It is first proposed to saturate the allowed transition  $\mu \longleftrightarrow \mu'$ . In this case the paramagnetic resonance signal diminishes because of the reduction of the excess  $N(\mu) - N(\mu')$ . It is then proposed either to saturate\* or to invert one of the horizontal pairs of levels (see Fig. 8). It is clear that in this case the signal of paramagnetic resonance  $\mu - \mu'$  increases. Thus, from the radio frequency that intensifies the microwave resonance we can determine the energy differences between the levels  $\mu$  and  $\mu - 1$ , etc., so that the quantities  $g_j$ ,  $P$ ,  $A$ , and  $B$  can be determined.

Let us consider the use of these modifications of the Feher method to obtain polarized nuclei.

It is easy to see that the values of  $f_k$  obtained with total saturation of the transition  $\mu \longleftrightarrow \mu'$  and the subsequent inversion of one of the pairs  $[\mu, \mu + 1]$ ,  $[\mu, \mu - 1]$ ,  $[\mu', \mu - 1']$  or  $[\mu', \mu + 1']$  are one half the values of  $f_k$  given by (11.9) - (11.12). In other words, the values of  $f_k$  will coincide with the values of  $f_k$  in the first stage of the corresponding cases of the Jeffries method.

We note that after inversion, vertical transitions, as well as vertical relaxation transitions, will take place under the influence of the saturating field. These

transitions, however, do not change the degree of orientation of the nuclei. We obtain thus, a nuclear polarization which tends, with a relaxation time of order  $T_n$ , to its stationary value [see (8.7) and (8.8)].

It is also easy to see that the removal of the saturating field after inversion will not change the polarization of the nuclei (it is assumed that  $T_e \ll T_n$ ).

Nuclear polarization is obtained also by saturation of one of the vertical and one of the horizontal transitions. For more details see reference 80.

The first experiments on the verification of these methods were made by Feher and Gere.<sup>88</sup> The sample used was silicon containing  $3 \times 10^{16}$  atoms of phosphorus per cubic centimeter. The experiments were carried out at 1.2° K and in a field of approximately 3000 oersteds. Under these conditions the relaxation time of the electron spin is sufficiently long.

Since the spin of  $P^{31}$  is  $1/2$ , the level scheme is as shown in Fig. 5 (we neglect in this figure, however, the spin-spin interaction energy).

Let us carry out in succession two adiabatically fast passages through resonance, corresponding to a transition between the levels  $a$  and  $a'$ . If the time interval between two passages is considerably less than  $T_e$ , the level populations will not have time to change between the passages. Therefore the signal obtained in the second passage will be equal in magnitude but opposite in polarity to the signal of the first passage. If, however, we carry out the inversion of the pair  $[a, b]$  between two inversions of the pair  $[a, a']$ , then the signal should disappear in the second inversion of the pair  $[a, a']$ .

Experiments have confirmed these predictions. However, in the second inversion of the pair  $[a, a']$  the signal was not strictly equal to zero, since the time between the two passages was merely one-third of  $T_e$ .

Further experiments on the application of the Feher method were carried out by Pipkin and Culvahouse<sup>62,63,82,83</sup> on arsenic doped silicon at 1.25° K in a field of 8000 oersteds.

In one series of experiments, the angular distribution of the  $\gamma$  radiation of  $As^{76}$  nuclei was measured. One of the pairs  $[\mu, \mu']$  was inverted, following by the inversion of either pair  $[\mu, \mu + 1]$  or  $[\mu, \mu - 1]$ . Comparison of the obtained angular distribution with the angular distribution obtained by the Jeffries method made it possible for the authors to determine the sign of the magnetic moment of the  $As^{76}$  nucleus. From the angular distribution itself it is possible, independent of the Jeffries method, to determine the absolute value of the magnetic moment.

In experiments with  $As^{75}$ , saturation was produced in the transition  $\mu \longleftrightarrow \mu'$ . This was followed by inversion of one of the pairs  $[\mu, \mu + 1]$  or  $[\mu, \mu - 1]$ , and the change in the resonance  $\mu \rightarrow \mu'$  was used to determine the hyperfine structure constant and gyromagnetic ratio of the  $As^{75}$  nucleus.

\*Simultaneous saturation of the electron and nuclear transitions was proposed before Feher by Kastler.<sup>87</sup>

### c) The Experiments of Abragam and Combrisson

Abragam and his co-workers carried out many experiments with silicon doped with phosphorus or arsenic.

Let us discuss first the experiments of Abragam and Combrisson,<sup>89,90</sup> in which the nonstationary phenomena in the Overhauser effect were investigated in a sample of silicon doped with  $10^{17}$  atoms of arsenic per cubic centimeter. The experiments were made at 2° K in a field of 3000 oersteds.

Since  $\text{As}^{75}$  has spin  $\frac{3}{2}$ , the level scheme is shown in Fig. 6. We assume that we can neglect all the relaxations, except the vertical and the flip-flop relaxations. Furthermore, we can write for the probabilities of the relaxation transitions per unit time

$$\left. \begin{aligned} W(a'a) &= W(b'b) = W(c'c) = W(d'd) = We^\delta, \\ W(aa') &= W(bb') = W(cc') = W(dd') = We^{-\delta}, \\ W(b'a) &= W(d'c) = \lambda We^\delta, \quad W(ab') = W(cd') = \lambda We^{-\delta} \\ W(c'b) &= \frac{4}{3} \lambda We^\delta \quad W(bc') = \frac{4}{3} \lambda We^{-\delta}, \end{aligned} \right\} \quad (11.13)$$

where  $W$  and  $\gamma$  are certain functions of the temperature in the field. The fact that  $W(c'b)$  is  $\frac{4}{3}$  times greater than  $W(b'a)$  follows from the expressions for the nondiagonal matrix elements of the spin operator, equal to  $\frac{3}{2}$ .

Usually two relaxation times are introduced, one relative to the vertical transition,  $T_e$ , and one relative to the flip-flop transitions  $T_x$ , given by the formulas

$$T_e = \frac{1}{2W \cosh \delta}, \quad (11.14)$$

$$T_x = \frac{T_e}{\lambda} = \frac{1}{2\lambda W \cosh \delta}. \quad (11.15)$$

In the case of arbitrary  $\lambda$ ,  $\lambda$  is the ratio of the probability of the extreme flip-flop transition, i.e., the transition  $I \rightarrow I - 1'$ , and the probability of the vertical transition [see, for example, (11.13)].

Assume that first the equilibrium is established in the absence of an external field. Then

$$\begin{aligned} N(a) &= N(a') = N(b) = N(b') \\ &= N(c) = N(c') = N(d) = N(d') = \frac{N}{8}. \end{aligned}$$

We then apply the main external field  $H$ . Then, confining ourselves to time intervals  $t \ll W^{-1}$ , we readily obtain

$$\left. \begin{aligned} N(a) - N(a') &= W \sinh \delta \frac{N}{2} \left( 1 + \frac{1}{2} \lambda \right) t, \\ N(b) - N(b') &= W \sinh \delta \frac{N}{2} \left( 1 + \frac{7}{6} \lambda \right) t. \end{aligned} \right\} \quad (11.16)$$

We denote by  $E(t)$  and  $M(t)$  the signals of the resonances  $a \leftrightarrow a'$  and  $b \leftrightarrow b'$  respectively. Since the resonance signal is proportional to the difference in the populations of the corresponding levels, we obtain

$$\frac{E(t)}{M(t)} = \frac{6+3\lambda}{6+7\lambda}. \quad (11.17)$$

This formula is valid if  $Wt \ll 1$ . It is easy to see, furthermore, that the signals of resonances  $c \leftrightarrow c'$  and  $d \leftrightarrow d'$  should equal respectively the signals of resonances  $b \leftrightarrow b'$  and  $a \leftrightarrow a'$ .

A suitable experiment was set up. It was found that at small  $t$  the two extreme signals (i.e., signals  $a \leftrightarrow a'$  and  $d \leftrightarrow d'$ ) are smaller than the two middle signals ( $b \leftrightarrow b'$  and  $c \leftrightarrow c'$ ). With  $t$  on the order of two or three minutes and less, the ratio  $E(t)/M(t)$  is independent of  $t$  and is approximately equal to 0.6. This yields  $\lambda \cong 2$  (for  $T = 2^\circ \text{K}$  and  $H = 3000$  oersteds).

For times considerably in excess of  $W^{-1}$ , equilibrium is established and we obtain

$$N(a) - N(a') = N(b) - N(b') = \frac{N}{4} \tanh \delta. \quad (11.18)$$

The four signals become equal in intensity. For the ratio of the signals of the resonance  $a \leftrightarrow a'$  at small and large  $t$  we obtain

$$\frac{E(t)}{E(\infty)} = W \cosh \delta (2 + \lambda) t. \quad (11.19)$$

In the experiments of Abragam and Combrisson,  $E(t)$  was measured for  $t$  equal to two minutes. The stationary signal was next measured, i.e., the value of  $E(\infty)$ . The value of  $\delta$  was approximately 0.1. Using the foregoing value of  $\lambda$ , the authors obtained from the last expression  $W^{-1} = 20$  minutes.

Additional investigations have shown that  $W$  depends little on the external field. On the other hand, the dependence on the temperature was found to be strong. Namely, for the same specimen,  $W^{-1}$  was found to be of the order of one minute at  $T = 4^\circ \text{K}$  and the order of one second for  $T = 8^\circ \text{K}$ .

We see that at low temperatures in silicon doped with arsenic ( $\text{As}^{75}$ ) the flip-flop relaxation is more probable than the vertical relaxation. Abragam and Combrisson,<sup>90</sup> and also Pines, Bardeen, and Slichter<sup>61</sup> have shown that in this case, upon application of an external field, the degree of nuclear polarization will not vary monotonically in time from zero to  $B\bar{i}(2\bar{I}\delta_n)$  (this proceeds with a relaxation time of the order of  $T_x$ ), and then diminish to an equilibrium value (with a relaxation time on the order of  $T_e$ ).

Let us discuss still another interesting effect, investigated by Abragam and Combrisson<sup>90,91,92</sup> (see also the paper by Abragam and Proctor<sup>71</sup>). Although these experiments were carried out successfully with silicon doped with arsenic, we shall consider, for the sake of simplicity, silicon doped with phosphorus (this case is simpler, since  $\text{P}^{31}$  has spin  $\frac{1}{2}$ ). We assume that the temperature is so low, that the impurity atoms are not ionized.

We deal with a system consisting of two spins,  $S$  and  $\bar{I}$ , with values  $\frac{1}{2}$ , in an external field and connected by a contact interaction. The Hamiltonian of this system is of the form

$$\mathcal{H} = g\beta HS_z - g_i\beta H\dot{I}_z + A\dot{S}\dot{I}, \quad (11.20)$$

In the case of a strong field ( $g\beta H \ll A$ ) the energy levels are of the form

$$E_{Mm} = Mg\beta H - mg_i\beta H + AMm, \quad (11.21)$$

and each state has a definite  $M$  and  $m$ .

In the case of a weak field ( $g\beta H \ll A$ ) the vectors  $\mathbf{S}$  and  $\dot{\mathbf{I}}$  add up to form a total spin

$$\mathbf{F} = \mathbf{S} + \dot{\mathbf{I}}, \quad (11.22)$$

which is then quantized in the external field.

For energy levels in the absence of an external field we have

$$E_F = \frac{A}{2} \left[ F(F+1) - \frac{3}{2} \right]. \quad (11.23)$$

Thus, in the absence of a field we obtain two levels: the triply degenerate level with  $F = 1$  and energy  $A/4$ , and the simple level with  $F = 0$  and energy  $-3A/4$ .

In the general case of an arbitrary field, the problem was considered by Breit and Rabi. For the energy levels we obtain (see, for example, reference 93)

$$E(M+m, \pm) = -\frac{1}{4}A - g_i\beta H(M+m) \pm \frac{1}{2}A\sqrt{1 + 2x(M+m) + x^2}, \quad (11.24)$$

where

$$x = \frac{(g+g_i)\beta H}{A}. \quad (11.25)$$

Here, if  $M+m = 0$ , both signs must be taken in front of the radical, and if  $M+m = \pm 1$ , only the plus sign is taken.

Thus, we obtain four states with energies

$$\left. \begin{aligned} E(a') &= \frac{1}{2}(g-g_i)\beta H + \frac{1}{4}A, \\ E(b) &= -\frac{1}{2}(g-g_i)\beta H + \frac{1}{4}A, \\ E(b') &= -\frac{1}{4}A + \frac{1}{2}\sqrt{A^2 + (g+g_i)^2(\beta H)^2}, \\ E(a) &= -\frac{1}{4}A - \frac{1}{2}\sqrt{A^2 + (g+g_i)^2(\beta H)^2}. \end{aligned} \right\} \quad (11.26)$$

Since the operator  $S_z + \dot{I}_z$  commutes with the Hamiltonian (11.20),  $M+m$  will always be a good quantum number. In a strong field,  $M$  and  $m$  themselves are approximately good quantum numbers, and in a weak field it is  $F$  that is an approximately good quantum number.

The case  $M+m = 1$  is realized only in one way:  $M = m = 1/2$ . Analogously, the case  $M+m = -1$  is realized only in one way,  $M = m = -1/2$ . Therefore the states  $a'$  and  $b$  for arbitrary value of an external field are pure states in  $M$  and  $m$ . In particular,\*

$$a' = (+, +), \quad b = (-, -). \quad (11.27)$$

On the other hand, the states  $a$  and  $b$  are super-

\*As before,  $(+, -)$  denotes, for example, the wave function of the state with  $M = +1/2$  and  $m = -1/2$ .

positions of the states  $(+, -)$  and  $(-, +)$ . In particular, in a strong field we have approximately

$$a = (-, +), \quad b' = (+, -). \quad (11.28)$$

On the other hand, in a weak field we have

$$\left. \begin{aligned} a &= \frac{1}{\sqrt{2}} [(-, +) \mp (+, -)], \\ b' &= \frac{1}{\sqrt{2}} [(-, +) \pm (+, -)], \end{aligned} \right\} \quad (11.29)$$

where the upper signs must be taken if  $A > 0$  and the lower ones if  $A < 0$ .

Next, in the case of a weak field, for  $A > 0$ , the states  $a'$ ,  $b'$ , and  $b$  correspond to  $F = 1$ , and  $a$  corresponds to  $F = 0$ . If  $A < 0$ ,  $F = 1$  corresponds to  $a'$ ,  $a$ , and  $b$ , while  $F = 0$  corresponds to  $b'$ .

The energy levels are shown as functions of the external field in Fig. 9 for  $A > 0$  and in Fig. 10 for  $A < 0$ .

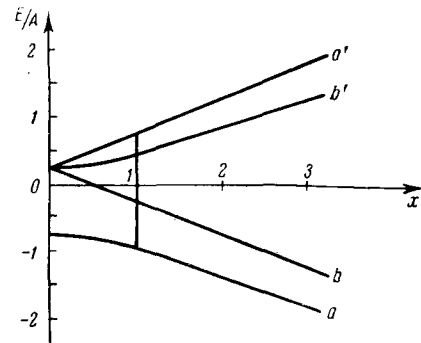


FIG. 9

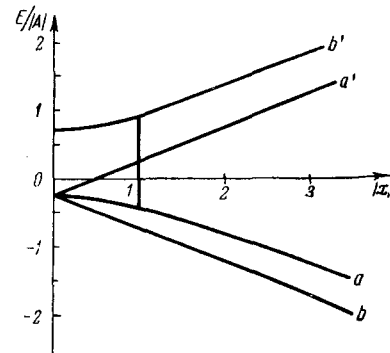


FIG. 10

After these preliminary remarks regarding a system consisting of two spins of value  $1/2$ , let us proceed with the Abragam-Combrisson method.

Let equilibrium first be established in a strong field. If we neglect the energy of the spin-spin interaction and the nuclear Zeeman energy in the Boltzmann factors for a strong field, we obtain for the populations

$$\left. \begin{aligned} N(a') &= N(b') = \frac{N}{2} \frac{e^{-\delta}}{e^{\delta} + e^{-\delta}}, \\ N(a) &= N(b) = \frac{N}{2} \frac{e^{\delta}}{e^{\delta} + e^{-\delta}}. \end{aligned} \right\} \quad (11.30)$$

We now reduce the external field to a value which is considerably less than  $A/g\beta$ . If the time during which exchange is effected is considerably less than the relaxation time (either  $T_e$  or  $T_n$ ), there will be no transitions, i.e., the process will be adiabatic (for more details regarding the adiabatic nature, see reference 71). If, for example, the system was in state  $a$ , it remains in state  $a$  after the field is increased.

Therefore, after a weak field is reached, the populations of the four levels will be given, as before, by (11.30). But in a weak field the states  $a$  and  $b'$  are not pure states in the projections of the nuclear spin  $m$ . The mean value of  $m$  in these states is zero. This gives rise to a considerable polarization of the nuclei. It is easy to obtain

$$f_1 = -\frac{1}{2} \tanh \delta, \quad (11.31)$$

and it is important that the  $\delta$  contained therein includes a strong initial field.

The state obtained is, naturally, not in equilibrium and the polarization will attenuate with a relaxation time on the order of  $T_e$  and  $T_n$ . If, after reducing the field, we again increase and return it to the initial state, the nuclear polarization will again be zero (provided the duration of the entire process is considerably less than the relaxation times).

Actually, however, the situation is more complicated and more interesting.

We assume that the relaxation times  $T_e$  and  $T_n$  are sufficiently large and that all the processes have been effected within a time considerably shorter than  $T_e$  and  $T_n$ . In this case the system which we consider will be isolated from the lattice, and it can be subject only to transitions in which the spin-system energy does not change. It is enough to look at Figs. 9 and 10 to verify that in the case of strong fields all transitions will be forbidden, and therefore in strong fields the populations will not change with changing field. But if the external field is  $H^* = A/(g + g_i) \beta = 42$  oersted, corresponding to a value of unity for the parameter  $x$  (for the sake of being specific, we consider the case  $A > 0$ ), the three levels  $b'$ ,  $b$ , and  $a$  become equidistant. In this case the energy of the spin system does not change if the two transitions

$$b \rightarrow a \text{ or } b \rightarrow b',$$

proceed simultaneously, and therefore such transitions can occur under the influence of external interactions in the spin system. When the system passes through the value  $H^*$  as the field is changed, an internal equilibrium corresponding to a certain spin temperature is established between the three levels  $b'$ ,  $b$ , and  $a$  (provided the passage is slow compared with the internal spin-spin relaxation). We can readily write down the equations for the populations that should be obtained after establishment of this internal equilibrium

$$\left. \begin{aligned} \frac{N(b')}{N(b)} &= \frac{N(b)}{N(a)}, \\ N(b') + N(b) + N(a) &= N - \frac{N}{2} \frac{e^{-\delta}}{e^{\delta} + e^{-\delta}}, \\ N(a) - N(b') &= \frac{N}{2} \tanh \delta. \end{aligned} \right\} \quad (11.32)$$

We confine ourselves to an analysis of the case of small  $\delta$ . Then the system (11.32) becomes

$$\left. \begin{aligned} N(b') + N(a) &= 2N(b), \\ N(a) + N(b) + N(b') &= \frac{3}{4} N \left( 1 + \frac{1}{3} \delta \right), \\ N(a) - N(b') &= \frac{N}{2} \delta. \end{aligned} \right\} \quad (11.33)$$

The solution yields

$$\left. \begin{aligned} N(a') &= \frac{N}{4} (1 - \delta), & N(b') &= \frac{N}{4} \left( 1 - \frac{2}{3} \delta \right), \\ N(b) &= \frac{N}{4} \left( 1 + \frac{1}{3} \delta \right), & N(a) &= \frac{N}{4} \left( 1 + \frac{4}{3} \delta \right). \end{aligned} \right\} \quad (11.34)$$

For the corresponding nuclear polarization we obtain

$$f_1 = -\frac{1}{3} \delta, \quad (11.35)$$

while at small  $\delta$  we obtain from (11.31)  $f_1 = -\frac{1}{2} \delta$ .

If we increase the field and turn to strong fields, we obtain

$$f_1 = \frac{1}{6} \delta. \quad (11.36)$$

All these predictions of the theory can be verified experimentally in the following manner. First, after equilibrium is established in a strong field, the signals of resonances  $a \leftrightarrow a'$  and  $b \leftrightarrow b'$  are equal to each other. If we reduce the field to a value less than  $H^*$  and return to strong fields, we should have according to (11.34)

$$N(a) - N(a') = \frac{7}{12} N\delta, \quad N(b) - N(b') = \frac{1}{4} N\delta,$$

and therefore the ratio of the signals of the resonances  $a \leftrightarrow a'$  and  $b \leftrightarrow b'$  should be  $\frac{7}{3}$ .

On the other hand, if the field is reduced to a value greater than  $H^*$ , and a return made to strong fields afterwards, the process should be reversible, in particular, the resonant signals  $a \leftrightarrow a'$  and  $b \leftrightarrow b'$  should remain equal.

Figure 9 shows that at certain values of the field, considerably less than  $H^*$ , the levels  $a'$ ,  $b'$ , and  $b$  become equidistant, and therefore in such a field an additional redistribution takes place, which will in particular influence the resonance signals observed after returning to the strong field.

It was impossible to verify these facts with silicon doped with phosphorus, because the relaxation times are not sufficiently long. These facts were investigated with silicon doped with arsenic ( $As^{75}$ ) by observing the changes in the resonance signals. For details see reference 90.

On the other hand, it was impossible to observe anisotropy of the  $\gamma$  radiation in an application of the



Abragam-Combrisson method to a specimen of silicon doped with radioactive arsenic.<sup>62</sup>

#### d) Magnetic Relaxation in Silicon with Pentavalent Impurity

We present a table of experimental data on the values of  $T_e$  and  $T_X$  in silicon doped with arsenic. The table is taken from reference 83.

|     | Im-<br>purity    | Con-<br>cen-<br>tra-<br>tion | $T$  | $\nu_e$ | $A$  | $T_X$     | $T_e$ |
|-----|------------------|------------------------------|------|---------|------|-----------|-------|
| A-C | As <sup>75</sup> | $10^{17}$                    | 2    | 9,000   | 196  | 10        | 20    |
| F   | As <sup>75</sup> | $3.5 \cdot 10^{16}$          | 1.2  | 9,000   | 196  | 40        | 80    |
| P-C | As <sup>75</sup> | $2.8 \cdot 10^{16}$          | 1.3  | 24,000  | 196  | 4.7       | 6.5   |
| P-C | As <sup>76</sup> | $3 \cdot 10^{10}$            | 1.25 | 24,000  | 93.7 | $\geq 75$ | 4     |

A-C, F, and P-C denote respectively Abragam-Combrisson, Feher, and Pipkin-Culvahouse,  $\nu_e$  is the electron resonant frequency in Mcs, the hfs constant  $A$  is also in Mcs,  $T_X$  and  $T_e$  are in minutes, the concentration is in  $\text{cm}^{-3}$ , and the temperature  $T$  is in degrees Kelvin.

Theoretically the question of magnetic relaxation in silicon containing pentavalent or trivalent impurities was considered by Pines, Bardeen, and Slichter<sup>61</sup> (see also reference 94). The authors note that the longer relaxation times are due to the following circumstance. The electron is bound with the impurity ion in such a way, that it reacts adiabatically to changes in external conditions. This causes a strong decrease in the matrix elements connected with the change in the spin direction. A calculation was made for the relaxation time  $T_X$  for transitions produced by hyperfine interactions between the electron and the spin of the impurity nucleus. In some cases the value obtained for  $T_X$  agrees with the experimental data. For example, calculation yields for As<sup>75</sup> impurity at  $T = 1.2^\circ \text{K}$  and  $\nu_e = 9000$  Mcs a value  $T_X = 56$  minutes, whereas the tabulated experimental value is  $T_X = 40$  minutes. We note, however, that this theory is unable to explain the excessive value of  $T_X$  obtained for the As<sup>76</sup> impurity.

A calculation was later performed for the relaxation time  $T_e$ . Transitions were considered, caused by the modulation of the spin-orbit and hyperfine interaction of the electron with the spin of the Si<sup>29</sup> nuclei (the modulation is due to the lattice vibrations). The theoretical values obtained for  $T_e$  are considerably higher than those experimentally measured. Nor is there any agreement concerning the dependence of  $T_e$  on  $T$  or  $H$ . One must note furthermore that the empirical values of  $T_e$  depend greatly on the impurity concentration.

Experiments have been recently performed on the dependence of the relaxation time in silicon doped with phosphorus on the temperature, external field, and impurity concentration. In particular, Honig and Stupp<sup>95</sup> measured the dependence of  $T_e$  on the field in the in-

terval 3.5 – 10 kilooersted for temperatures 1.27° K and 2.06° K (the phosphorus concentration was  $1.4 \times 10^{16} \text{ cm}^{-3}$ ).

Feher and Gere<sup>96</sup> measured the dependence of different relaxation times in phosphorus doped silicon on the temperature (in the interval 1.25° K – 4.2° K), on the external field (in the interval 3.2 – 8 kilooersted), and on the impurity concentration. It was found that at a phosphorus concentration less than  $10^{16} \text{ atoms/cm}^3$ ,  $T_e$  is independent of the concentration; at greater concentrations  $T_e$  diminishes rapidly with increasing concentration. We denote that according to experiment made on silicon doped with P<sup>31</sup>,  $T_e$  is much less than  $T_X$ .

The experimental values of  $T_e$  disagree likewise with the theory of Bardeen, Pines, and Slichter in the case of silicon doped with phosphorus. Thus, the problem of magnetic relaxation of silicon with donor impurity is at present in an unsatisfactory state.

Let us note, finally, the interesting fact observed by Feher and Fletcher<sup>97</sup> (for more details see reference 96). It was found that when a crystal is illuminated, the time of relaxation of  $T_e$  diminishes rapidly. This reduction in  $T_e$  is attributed to the fact that upon illumination additional free electrons are produced in the silicon, and these cause additional relaxation of the electron spin.

## 12. CONCLUSION

From the point of view of applications to nuclear physics and to the physics of elementary particles, the greatest interest attaches to the production of samples containing polarized protons. In Sec. 7 we have considered a method of induced dynamic polarization, which makes it possible to obtain polarized protons.

From the point of view of obtaining polarized protons, a recent work by Jen, Foner, Cochran, and Bowers<sup>93</sup> is also of interest. This work is devoted to an investigation of paramagnetic resonance by atomic hydrogen that intrudes in the lattice of solid hydrogen. Of considerable interest is to obtain the Overhauser effect or the effect of induced dynamic polarization of nuclei in such specimens.

In connection with the possibility of using targets with polarized protons, mention should be made of the theoretical paper by Capps.<sup>98</sup> He considers the processes

$$\pi^- + p \rightarrow K^0 + \Lambda, \quad K^- + p \rightarrow \pi^0 + \Lambda$$

(and also processes obtained by replacing the  $\Lambda$  hyperon with a  $\Sigma$  hyperon) in the case of polarized protons. It was shown that measurement of the angular distribution of the pions (obtained from the decay of the hyperons) relative to the direction of the polarization of the protons makes it possible to determine uniquely the relative parity of the  $K$  meson and hyperon.

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