INVESTIGATION OF THE ELECTRON STRUCTURE OF METALS WITH THE AID OF NUCLEAR MAGNETIC RESONANCE

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1. INTRODUCTION

1. Preliminary remarks. Nuclear magnetic resonance (n.m.r.), discovered in 1945 simultaneously and independently [1,2] by two groups of American physicists, immediately attracted considerable attention since it is a powerful method for the study of the internal microscopic structure of various objects. In particular, a large number of papers was devoted to the study of n.m.r. in metals and alloys. Such investigations are first of all of interest because they enable us to obtain information on the electronic structure of metals. Indeed, owing to the interaction between the electrons and the nuclear spins the nuclear resonance absorption line becomes sensitive to quantities characteristic of electrons in a metal. This circumstance makes it possible to study their behavior by means of nuclear magnetic resonance.

In the present review we wish to give an idea of the nature of the papers devoted to the study of the electronic structure of metals with the aid of n.m.r., and of the results obtained in these papers. In order not to lengthen this article excessively we shall not touch upon the numerous papers devoted to the study of alloys which are of interest in themselves.

2. The phenomenon of nuclear magnetic resonance consists, as is well known, of the following. A sample containing nuclei of magnetic moment different from zero is placed in a fairly high magnetic field H which we take in our subsequent discussion to be along the z axis. This gives rise to a system of equidistant Zeeman energy levels separated by $\Delta E = \hbar \gamma H$ where γ is the nuclear gyromagnetic ratio. A weak alternating field H_t of frequency ω is then applied in a direction perpendicular to the direction of the field H. We shall in subsequent discussion take this field to define the x axis. This field induces transitions between the Zeeman levels accompanied by absorption and emission of energy; the phenomenon of resonance consists of the fact that the probability of such transitions increases sharply when the condition $\omega = \omega_0 = \gamma H$ is satisfied. For the majority of nuclei subjected to the usual fields in the kilogauss range this resonance frequency lies in the very convenient radio-frequency band.

The resonance manifests itself in two physical phenomena which are used for recording it. First, as we have already noted, energy will be emitted in the form of electromagnetic radiation of frequency ω as a result of a transition from a higher to a lower energy level. The magnetic vector of this radiation will be circularly polarized in the xy plane, and this leads to the appearance in this plane of an alternating magnetic field in directions in which no field existed previously, for example along the y axis. This phenomenon is sometimes called nuclear induction. Second, if the variable field H_t is not very large, then the number of transitions per unit time corresponding to absorption of energy will always be greater than the number of transitions corresponding to emission of energy, and the sample will absorb energy from the electric field. This occurs because the system of nuclear spins interacts with its surroundings, for example with the crystalline lattice, and sooner or later attains thermal equilibrium with the lattice. As a result of this, the lower Zeeman levels become more heavily populated than the higher ones, and if the variable field H_t does not lead to an appreciable change in these equilibrium populations, then the number of transitions from the lower levels into higher ones will exceed the number of inverse transitions, since the probability of the direct and the inverse transitions are the same. This phenomenon is sometimes called magnetic resonance absorption.

3. Relaxation times. If the nuclear spins did not interact with one another nor with their surroundings, then the resonance condition would be determined only by the external field H and would be satisfied only in an infinitely narrow frequency interval. The existence of various kinds of interactions leads to the fact that the resonance condition ceases to be so rigid; instead of one resonance frequency a range of frequencies appears, i.e., a resonance line is produced whose shape and position is determined by such interactions. Since the energy difference between the Zeeman levels of nuclear spins corresponding to the usual intensities of the magnetic field H is very small, even very weak interactions existing between the nuclei and their surroundings in solids produce an appreciable effect on the appearance and position of a resonance line. This circumstance makes nuclear resonance, as we have already mentioned, a powerful method for the investigation of microscopic local fields and of interactions existing in the sample under investigation.

It is clear that any local magnetic field H_l which is constant in time will simply be added to the constant external field H and will lead to a shift of the resonance frequency. If this local field is different at

different points of the sample then it will also lead to a corresponding broadening of the line. Magnetic fields of this kind may be due, for example, to the orientation of electron spins along the field in metals and in paramagnetic substances, or due to the spontaneous magnetization in ferro- and antiferromagnetic substances. In an equally simple manner we can take into account the interaction of the nuclear quadrupole moment with a local electric field produced by the crystalline lattice. That part of the interaction which is independent of the time leads to a displacement of the Zeeman levels and as a result splits the resonance line.

It is considerably more difficult to determine the manner in which the shape and the position of the line will be affected by interactions which cannot be described by means of static local fields. In his fundamental paper [3] Bloch proposed to characterize such interactions by means of two relaxation times: T_1 and T_2. The relaxation time T_1 describes the interaction of the spin system with its surroundings, for example with lattice vibrations, with paramagnetic impurities, with conduction electrons in a metal etc. This relaxation time essentially describes the rate of establishment of thermal equilibrium between the spin system and its surroundings. It is called the spin-lattice relaxation time. The relaxation time T_2 describes interactions existing within the spin system. It characterizes the widths of the Zeeman energy levels, i.e., in the final analysis the widths of the resonance line. It is often called the spin-spin relaxation time.

Bloch showed the manner in which the phenomenon of nuclear magnetic resonance can be described with the aid of these two parameters in agreement with experimental facts. His approach is based on the analysis of the behavior of the macroscopic nuclear magnetization $<M>$ in the presence of external fields H and H_1 and of random internal interactions characterized by the relaxation times T_1 and T_2. Classical equations of motion are introduced for the vector $<M>$ which are related in the usual manner to the quantum mechanical picture of the phenomenon which was introduced above. They show that under the action of the variable field H_1 a rotating magnetic moment appears in the xy plane whose magnitude takes on its maximum value when the resonance condition $\omega = \omega_0$ is satisfied. On solving these equations we can obtain an expression for the dynamic nuclear complex susceptibility $\chi(\omega) = \chi' - i\chi''$, which characterizes the magnetic moment appearing in the xy plane. In the practically important case of slow passage through resonance

$$\chi' = \frac{1}{2}\chi_0\omega_0 T_2 \frac{(\omega_0-\omega)T_2}{1+(\omega_0-\omega)^2 T_2^2+\frac{1}{4}\gamma^2 H_1^2 T_1 T_2},$$

$$\chi'' = \frac{1}{2}\chi_0\omega_0 T_2 \frac{1}{1+(\omega_0-\omega)^2 T_2^2+\frac{1}{4}\gamma^2 H_1^2 T_1 T_2},$$

(1)

where χ_0 is the static nuclear susceptibility. The real part of the dynamic nuclear susceptibility χ' determines the component of the magnetization rotating in the xy plane in phase with the oscillating field H_1. The imaginary part of the susceptibility χ'' determines the component of the magnetization rotating in the xy plane with a phase shift of 90° with respect to the field H_1. This component describes the effect of resonance absorption.

The Bloch approach also enables us to obtain a very graphic picture of the behavior of a spin system under nonstationary conditions, for example under the action of short radio frequency pulses, or in the case of a rapid change in the constant magnetic field. If the variable field H_1 of resonance frequency acts on a spin system placed in a constant field H, for a time $\Delta t \ll T_1$, T_2, it simply deflects the macroscopic nuclear magnetization from the direction of the z axis by an angle $\theta = \frac{1}{2}\gamma H_1\Delta t$, and, after the end of the pulse, free precession of the macroscopic nuclear magnetic moment occurs about the direction of the constant external field. This precession will be damped: the z component of the nuclear magnetic moment will grow towards its equilibrium value exponentially with a characteristic time T_1, while the transverse rotating component of the magnetic moment will diminish exponentially with a characteristic time T_2. If the duration of the pulse Δt is such that $\frac{1}{2}\gamma H_1\Delta t = \pi/2$, then such a pulse is called a 90-degree pulse, and it gives rise to the greatest nuclear induction signal; if $\frac{1}{2}\gamma H_1\Delta t = \pi$, then this is a 180-degree pulse which gives rise to a reversal of the magnetic moment. A similar reversal of the magnetic moment is obtained as a result of a rapid variation of the constant magnetic field, when the resonance region is traversed during a time $\Delta t \ll T_1$, T_2.

4. The moments of an absorption line. The shape of an absorption line described by expression (1) is called the Lorentz shape. It has been shown that the description of the resonance by formula (1) reproduces quite well the situation existing in liquids. It has turned out to be possible to develop a microscopic theory for the evaluation of T_1 and T_2 which has turned out to be in very good agreement with the experimental facts [4].

In solids, as a rule, the shape of an absorption line differs considerably from the Lorentz shape. It does not appear to be possible to calculate the line shape in general form since the corresponding calculations are very complex. Van Vleck [5], therefore, proposed to characterize the line shape in this case by means of its moments. If the line is described by the normalized function $g(\omega)$, i.e. $\int_0^\infty g(\omega)d\omega = 1$, then its n-th moment with respect to some point ω' is given by

$$\overline{\Delta\omega^n} = \overline{(\omega-\omega')^n} = \int_0^\infty (\omega-\omega')^n g(\omega)\,d\omega.$$

Van Vleck has shown how the moments of an absorption line can be calculated if the complete Hamiltonian of the spin system is known. His calculations are based on the so-called adiabatic approximation in which all the terms in the spin Hamiltonian are neglected which do not commute with the z component M_z of the total magnetic moment of the system. Such terms lead to the appearance of small satellite absorption lines at frequencies different from the Larmor frequency. The physical meaning of neglecting such nonsecular terms amounts to assuming that the satellite lines to which these terms give rise are sufficiently far removed from the main line and can be well resolved experimentally. In this approximation all the odd moments vanish, and Van Vleck has calculated the second and the fourth moments for spin systems coupled by dipole-dipole and exchange interactions.

The dipole-dipole interaction between the spin I_i and the spin I_k is described by the operator

$$\mathscr{H}_{ik}^{d} = \hbar^2 \gamma^2 r_{ik}^{-3} \{ I_i I_k - 3 r_{ik}^{-2} (I_i r_{ik})(I_k r_{ik}) \},$$

where r_{ik} is the distance between the spins. The exchange interaction may have different origins and is characterized by the constant A_{ik}

$$\mathscr{H}_{ik}^{e} = A_{ik} I_i I_k.$$

It turns out that the second moment of the absorption line is determined only by the dipole-dipole interaction and that its value with respect to the frequency ω_0 is given by the expression

$$\overline{\Delta\omega^2} = \frac{3}{4} \frac{I(I+1)}{N\hbar^2} \sum_{i,k=1}^{N} (\gamma^2 \hbar^2 r_{ik}^{-3})^2 (3\gamma_{ik}^2 - 1)^2. \tag{2}$$

Here N is the total number of nuclei in the system, γ_{ik} is the cosine of the angle between the vector r_{ik} and the direction of the field H. The exchange interaction in this case determines only the finer features of the absorption line, since it enters only into higher-order moments.

Van Vleck also discussed the case when the sample contains spins of two different kinds*. In order for the adiabatic approximation to be valid in this case it is necessary for the difference between the energies of the Zeeman levels of the spins of different kinds to be much larger compared to the energy of the exchange interaction between them. In this case terms due to the dipole-dipole and exchange interactions between spins of different kinds appear in the expression for the second moment, and it becomes equal to

$$\overline{\Delta\omega^2} = \frac{3}{4} \frac{I(I+1)}{N\hbar^2} \sum_{i,k} (\gamma^2 \hbar^2 r_{ik}^{-3})^2 (3\gamma_{ik}^2 - 1)^2 + \frac{1}{3} \frac{I'(I'+1)}{N\hbar^2}$$

$$\times \sum_{i,k'} (\gamma\gamma' \hbar^2 r_{ik'}^{-3})^2 (3\gamma_{ik'}^2 - 1)^2 + \frac{I'(I'+1)}{3N\hbar^2} \sum_{ik'} A_{ik'}^2. \tag{3}$$

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*We have in mind that spins of different kinds differ from one another by the value of their gyromagnetic ratio.

The primed quantities in this expression refer to spins of the second kind; N denotes the number of unprimed spins.

Van Vleck's expression for the second moment (2) and the corresponding formula for the fourth moment were subjected to special experimental check [6,7] in the case of the F^{19} resonance in CaF_2. These expressions turned out to be in excellent agreement with experimental results thus providing evidence that the adiabatic approximation describes sufficiently well the system of nuclear spins in a rigid lattice.

The next step in the theory of the line shape of magnetic resonance absorption was taken by Kubo and Tomita[8]. They have developed a perturbation theory which, in principle, enables us to obtain in any specific case an expression for the shape of the resonance line with any desired degree of accuracy. However, due to the complexity of the resultant expressions practical calculations, if they are at all possible, are very difficult. Therefore, the authors introduce a series of simplifying assumptions which lead to the final expressions for the line shapes being of a rather qualitative character. However, it is important that the method developed by them makes it possible to calculate moments taking into account nonsecular terms in the Hamiltonian which are neglected in Van Vleck's theory and which in a number of cases play an important role.

2. SPECIFIC FEATURES OF NUCLEAR MAGNETIC RESONANCE IN METALS

1. The experimental difficulties which arise in the study of n.m.r. in metals are basically associated with the fact that the variable field H_1 penetrates into the sample only to a depth of the order of the skin-layer. If the dimensions of the sample are large in comparison to the skin depth, this leads to two unpleasant effects. First, the working volume occupied by the substance is reduced; secondly, the resonance absorption will be determined not only by the imaginary part χ'' of the dynamic nuclear susceptibility, but also by its real part χ'. Indeed, the quantity χ' determines the thickness of the skin-depth; as χ' increases the thickness of the skin-depth is reduced and, everything else remaining equal, the absorption of energy in the sample is diminished. Experimentally the effect of finite skin depth is manifest by the shape of the absorption line becoming distorted. The paper of Chapman, Rhodes and Seymour [9] is devoted to a detailed theoretical and experimental analysis of this problem.

In order to get around these difficulties one ordinarily uses samples either in the form of fine metallic powders with particle size smaller than the skin-depth, or, less frequently, in the form of thin foils insulated from one another. In this way one succeeds in avoiding an appreciable reduction of the working volume of the sample and in obtaining absorption

which is proportional only to the value of χ''.

However, the use of finely dispersed samples is unsatisfactory from other points of view. Firstly, it turns out to be impossible to study n.m.r. in single crystals*; secondly, it is never clear to what extent such finely dispersed samples are free of impurities and of distortions of the crystalline lattice. In particular, the fact that the influence of the value of χ' on the shape of the absorption line is often observed to be smaller than might be expected from the estimates made in [9-11] is probably basically related to the fact that the thickness of the skin-depth in the samples utilized differs from the thickness of the skin-depth in a large sample of the pure metal.

Investigation of large samples of metal with the aid of n.m.r. may turn out to be possible if we succeed in using other methods of inducing transitions between nuclear Zeeman levels which will make it unnecessary to place the sample in an alternating magnetic field. One such method was proposed by Al'tshuler [12,13] who pointed out the possibility of resonance absorption of ultrasound by a system of nuclear spins. Here the transitions between the nuclear Zeeman levels are induced by the interactions of the quadrupole moment of the nucleus with the varying electric field gradients which arise due to the oscillations of the crystalline lattice.

This method was utilized [14] for the observation of n.m.r. in single crystals of KI and KBr. It is, generally speaking, suitable only for nuclei of spin $I > \frac{1}{2}$; however, Kaner has pointed out† that in the case $I = \frac{1}{2}$ transitions can be induced by magnetic fields which will themselves arise due to the presence of variable electric fields.

2. The interaction between the spins of nuclei and of conduction electrons manifests itself in nuclear magnetic resonance in metals in three ways. Firstly, it gives the basic contribution to the value of the spin-lattice relaxation time T_1; secondly, it alters the effective magnetic field acting on the nucleus giving rise to the so-called Knight shift; thirdly, it determines the indirect interaction between nuclei.

Estimates show that the principal contribution to the interaction between the nuclear and the electronic spins is given by the Fermi contact term proportional to the scalar product of the spins. As is well known, it is this contact interaction that leads to the hyperfine splitting of s-terms in atoms. In fact, one can visualize the situation in the following manner: an electron in an s-state, i.e., having a wave function whose value differs from zero in the neighborhood of the nucleus, produces in the neighborhood of the nu-

cleus a magnetization $\mathbf{m} = 4\beta_0 \mid \psi_{\mathrm{k}}(0) \mid^2 \mathbf{S}$, where β_0 is the Bohr magneton, $\psi_{\mathrm{k}}(0)$ is the value of the electron wave function at the point where the nucleus is situated, $\mathbf{k}$ is the propagation vector characterizing the electron state in the metal. The origin of this formula is obvious: $2\beta_0 \mathbf{S}$ is the magnetic moment of the electron, while $2 \mid \psi_{\mathrm{k}}(0) \mid^2 dv$ is the probability of finding it in the element of volume dv near the nucleus. The field corresponding to this magnetization is $\Delta \mathbf{H} = 4\pi \mathbf{m}/3 = (16\pi/3)\beta_0 \mid \psi_{\mathrm{k}}(0) \mid^2 \mathbf{S}$, and the energy of interaction with the nuclear magnetic moment is

$$V = \frac{16\pi}{3} \beta_0 \gamma \hbar \mid \psi_k(0) \mid^2 \mathbf{IS} = a_k \mathbf{IS}. \tag{4}$$

If the state of the electron is not a pure s-state, then in addition to this isotropic part of the interaction there can also exist an anisotropic dipole-dipole part. This leads to an anisotropy of the Knight shift and to the so-called pseudodipolar interaction between the nuclei.

Cohen, Goodings, and Heine [15] have shown that conduction electrons can interact with nuclei not only directly, but also indirectly by giving rise to a polarization of the spins of the electrons situated in inner filled atomic shells. Generally speaking, a pair of electrons in a filled s-shell has identical wave functions and oppositely directed spins, and, therefore, the total energy of their contact interaction with the nucleus is equal to zero. However, if the sample contains a certain excess of conduction electrons with spins oriented in one direction, then due to the fact that the exchange interaction between the inner electrons and the conduction electrons depends on the relative orientation of their spins, the wave functions of the electrons of the filled s-shell will begin to differ from one another slightly, and an additional field arises at the nucleus.

This effect, apparently, plays no essential role in nontransition metals. However, transition metals show a number of anomalies which, at least partially, are probably related to this additional interaction. Therefore, we shall consider these two cases separately.

3. NUCLEAR MAGNETIC RESONANCE IN NONTRANSITION METALS

1. The relaxation time T_1. A systematic investigation of n.m.r. in metals began approximately in 1948 when Rollin and Hutton [16] measured for the first time the spin-lattice relaxation times for a number of metals. They have used the so-called direct method for the measurement of T_1. It consists of first applying to the sample a strong alternating field H_1 which completely equalizes the populations of the Zeeman levels and thus suppresses resonance absorption. After this the field H_1 is rapidly decreased, and the exponential growth of the nuclear resonance

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*Translator's Note. Such studies have been recently reported by Jones and Williams[106] and by P. L. Sagalyn and J. A. Hofmann, Phys. Rev. 127, 68 (1962).

†In a report at the conference on the radiospectroscopy of pure metals and alloys, Moscow, 1961.

signal is observed which is described just by the relaxation time T_1.

The theoretical formula for the relaxation time determined by the interaction between nuclei and conduction electrons was obtained by Heitler and Teller[17] as far back as 1936. A more rigorous derivation of this formula was later given by Korringa[18]. The relaxation time is evaluated simply as the reciprocal of the total transition probability of a nuclear spin from one level to another under the influence of the interaction with the electrons of the form (4). Korringa carried out the calculations in the Bloch approximation and showed that if the sample is situated in a magnetic field which is sufficiently strong in comparison with the spin-spin interactions, then the relaxation time is determined by the expression

$$\frac{1}{T_1} = \left(\frac{\pi k T}{\hbar}\right) \{\langle a_h \rangle_F v_0 \varrho\,(E_F)\}^2. \tag{5}$$

Here k is the Boltzmann constant, T is the absolute temperature, $<a_k>_F$ denotes the value of the hyperfine interaction constant averaged over the Fermi surface, v_0 is the atomic volume, $\rho(E_F)$ is the number of states per unit energy interval and per unit volume for an electron with a given value of the spin situated on the Fermi surface. For monovalent metals $v_0\rho(E_F) = 3/4\,E_F$ and the expression for T_1 assumes the form

$$\frac{1}{T_1} = \frac{9\pi k T}{16\hbar} \frac{\langle a_h \rangle_F^2}{E_F^2}. \tag{5'}$$

The hyperfine interaction constant can be calculated if we know the value of the electron wave function at the nuclear site. In order of magnitude $a_k \sim 0.1°$, $E_F \sim 10^{4°}$, and this yields $T_1 \sim 10^{-4}$–10^{-5} sec at room temperature.

Rollin and Hutton have shown that the values of T_1 obtained by them for aluminum and copper agree in order of magnitude with the theoretical values. Later the methods of measuring the spin-lattice relaxation time were considerably improved. Thus, Bloembergen[19] studied the dependence of T_1 on the temperature in metallic copper utilizing the so-called saturation method. This method consists of measuring the dependence of the magnitude of the resonance absorption signal on the amplitude of the alternating field H_1. Since the magnitude of the signal is proportional to χ'', then by using the Bloch expressions for the dynamic nuclear susceptibility (1) it is possible from these measurements to determine the value of the product $T_1 T_2$. The value of T_2 is in turn determined from the width of the absorption line.

By the same method the relaxation times have been measured in aluminum, in lithium[20] and in cadmium[21]. Such measurements apparently yield more or less accurate data on the temperature dependence of the relaxation time T_1, but the absolute values of T_1 are not obtained very reliably by this method.

Holcomb and Norberg[22] have made measurements of T_1 in alkali metals by means of the pulse technique. Later similar measurements were carried out for aluminum[23] and copper[24]. The method of measurement in this case consists of subjecting the sample to the action of two radio frequency pulses of resonance frequency separated by a time interval τ. The first pulse, a 180-degree pulse (sometimes a 90-degree pulse is utilized here instead), serves for inverting the macroscopic nuclear magnetization, while a second 90-degree pulse enables us from the magnitude of the resultant nuclear induction signal to measure the value of the magnetic moment which is produced at the time τ. As a result of spin-lattice relaxation the magnitude of the magnetic moment which is directed immediately after the 180-degree pulse oppositely to the field decreases exponentially with increasing time and the index of the exponent determines the quantity T_1.

Redfield[10] has measured the relaxation times in copper and in aluminum in the helium temperature region by using the method proposed by Chiarotti et al[25]. In this method the constant magnetic field is modulated near the resonance value in such a way that in each passage through resonance the magnetic moment is reversed due to the rapid passage. If the time between two successive passages, which, in the final analysis, is determined by the frequency of the modulating field, is comparable with the value of T_1, then the equilibrium value of the nuclear polarization does not have time to become established, and the magnitude of the nuclear resonance signal diminishes. By observing the dependence of the value of the signal on the frequency of modulation it is possible to determine the spin-lattice relaxation time T_1.

All these measurements have confirmed the theoretically predicted dependence of the spin-lattice relaxation time on the temperature over a wide temperature range. Moreover, the theoretical values of the relaxation times,* as may be seen from Table I, are very nearly equal to the experimentally obtained values. It is noteworthy that the theoretical relaxation times are always lower than the experimental ones. This convincingly demonstrates that the interaction with the conduction electrons indeed gives the principal contribution to the spin-lattice relaxation in metals, since the presence of other relaxation mechanisms would lead to the result that the experimentally observed relaxation times would be smaller than the theoretical ones. Pines[28] has shown that taking into account the correlation between the conduction electrons increases the theoretical relaxation times and improves the agreement between theory and experiment.

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*The theoretical values of T_1 are usually calculated not directly in accordance with formula (5), but from the measured Knight shift and formula (8); cf. below.

Table I. Theoretical and experimental relaxation times

Iso-tope	T_1T, sec·deg	Ref-eren-ces	T_1T_{th}, sec·deg	Iso-tope	T_1T, sec·deg	Ref-eren-ces	T_1T_{th}, sec·deg
Li⁶	290	22	195	Cu⁶³	1.27	27	0.7
Li⁷	44.6	22	27		1.28	24	
	44.2	27		Rb⁸⁵	0.81	22	0.65
Na²³	4.77	22	3.1	Rb⁸⁷	0.08	22	0.06
	5.1	27		Sn¹¹⁹	0.054	23	0.038
Al²⁷	1.6	26	1.5				
	1.8	27					

Expression (5) for the spin-lattice relaxation time in metals was obtained by Korringa, as has been noted already, on the assumption that the external magnetic field in which the sample is situated is large, so that the Zeeman energy is much larger than the energy of the dipole-dipole interaction between the spins. The theory for the spin-lattice relaxation in metals in arbitrary fields has been given by Hebel and Slichter[26] and by Anderson and Redfield [27]. Their calculations are based on the assumption that the spin system can always be described by a certain temperature which is either equal to, or not equal to, the lattice temperature. From this point of view the process of relaxation of nuclear spins is the process of the spin system and the lattice attaining a common temperature. In such an approach it is not necessary to know the energy spectrum of the spin system in order to calculate the spin-lattice relaxation time, and the calculations can be carried out to the end. It turns out that the relaxation time T_1 depends on the field in the following manner

$$T_1(H) = T_1(\infty) \frac{H^2 + (10/3)\overline{\Delta H^2}}{H^2 + \delta(10/3)\overline{\Delta H^2}} \qquad (6)$$

where $\overline{\Delta H^2}$ is the value of the second moment of the absorption line determined by Van Vleck's expression (2), and $\delta \approx 2$.

The same authors have also measured the dependence of the relaxation time T_1 on the field in Li, Na, Al, Cu. For the measurement of T_1 in weak fields they have utilized the following experimental method. The n.m.r. signal was observed twice in the strong magnetic field, while in the interval between these observations the magnetic field was rapidly reduced to the desired value and during a certain time interval τ relaxation of nuclear spins took place in a given weak field. The magnitude of the signal in the second measurement, made after the magnetic field had been increased once again, diminished exponentially with increasing time τ; thus, it was possible to determine the relaxation time T_1. It was demonstrated that the observed field dependence $T_1(H)$ is satisfactorily described by expression (6), and the relaxation time in zero field is indeed about half the relaxation time in strong fields.

The same method of measurement was also utilized by Hebel and Slichter[26] and by Masuda and Redfield

[29] to measure the spin-lattice relaxation time in aluminum in the superconducting state. As is well known, the small penetration depth of the magnetic field introduces great difficulties into the study of n.m.r. in superconductors. The measurement of the relaxation time in zero field enables us to avoid this difficulty, because in this case the measurements themselves are made on the metal in the normal state which arises due to the presence of the higher magnetic field. But the relaxation occurs in the superconducting state in zero field. It was found that the spin-lattice relaxation time at first diminishes considerably on going over to the superconducting state and then increases again as 1/T.* It was possible to describe this behavior quantitatively with the aid of the Bardeen, Cooper and Schrieffer theory.

2. Knight shift. In the early papers on n.m.r. in metals the investigators overlooked the fundamental fact that the resonance frequency in a metallic sample always differs from the resonance frequency of the same nucleus in a nonmetallic compound. This effect was discovered by Knight[31] in 1949 and has received the name of the Knight shift. Knight investigated n.m.r. in metallic lithium, sodium, aluminum, copper and gallium and established that the resonance line in the metal is always shifted in the direction of higher frequencies (in a given field) and that this displacement is proportional to the external field, increases with increasing atomic number and is practically independent of the temperature. In Fig. 1, reproduced from Knight's paper, we can see the manner in which the resonance frequency of Cu⁶³ in metallic copper is displaced with respect to the resonance frequency in CuCl.

The relative change in frequency amounts to approximately 0.1% in light metals and attains the value
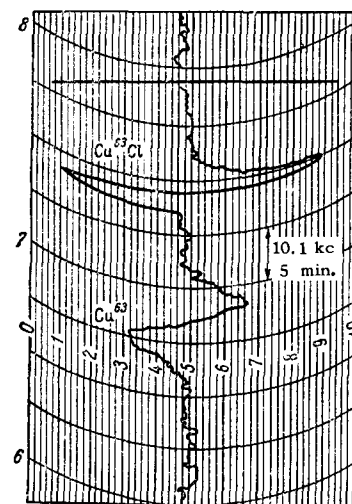

FIG. 1. Record of the derivatives of the absorption lines of Cu⁶³ demonstrating the shift of the resonance frequency in the metal.

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*Similar results were also obtained by Hammond and Knight[30] who measured T_1 in superconducting Ga by means of nuclear quadrupole resonance.

of 1—2% in heavier metals. Such large shifts cannot be explained simply as being due to the paramagnetism of the conduction electrons, since in such a case the shift should be of the order of $10^{-4}\%$. Townes et al [32] have given the correct explanation of this effect by taking into account the fact that the electrons are distributed in the metal not uniformly, but have a greater probability of being found near a nucleus. This is taken into account in formula (4) by the fact that the quantity $|\psi_k(0)|^2$ occurs in it. This localization leads to the fact that the local field in the neighborhood of the nucleus is greatly increased, and this gives rise to the observed line shift. In the Bloch approximation the formula for the Knight shift has the form

$$K = \frac{\Delta\omega}{\omega} = \frac{\beta_0}{\gamma h}\langle a_k\rangle_F \varrho(E_F)v_0 = \frac{8\pi}{3}\chi_p v_0\langle|\psi_h(0)|^2\rangle_F, \qquad (7)$$

where $\chi_\rho = 2\beta_0^2\rho(E_F)$ is the electronic paramagnetic susceptibility. If we again use the approximate relation $v_0\rho(E_F) = 3/4\,E_F$ which is valid for monovalent metals, we obtain

$$K = \frac{3}{4}\frac{\beta_0}{\gamma h}\frac{\langle a_k\rangle_F}{E_F}. \qquad (7')$$

This yields $K \sim 1\%$ for $a_k \sim 0.1°$ and $E_F \sim 10^{4°}$.

A comparison of formulas (5) and (7) shows that a universal relation exists between the relaxation time and the Knight shift:

$$T_1 K^2 = \frac{h}{\pi k T}\left(\frac{\beta_0}{\gamma h}\right)^2. \qquad (8)$$

This relation was obtained by Korringa[18] and, as we have already stated, it is this relation which is ordinarily used for the theoretical evaluation of the spin-lattice relaxation time.

A very large number of papers has been devoted to the measurement of the Knight shift. In Table II we have given the values of the Knight shift in nontransition metals that have been measured up to the present time. Such measurements are of interest because, as can be seen from formula (7), the value of the shift contains such characteristic properties of the electrons as the density of states at the Fermi surface and, through a_k, the value of the electron wave function at the nucleus. Since the density of electron states at the Fermi surface can be obtained from data on electron specific heat or on susceptibility, the Knight shift, therefore, enables us to measure directly the hyperfine interaction constant, and, consequently, the value of the electron wave function in a metal.* It can, therefore, serve as a sensitive criterion of the correctness of calculations devoted

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*It can be seen from formula (5) that the same information about a metal can also be obtained from measurements of the relaxation time T_1. However, it is possible to measure the relative displacement $\Delta\omega/\omega$ to five decimal places, while it is possible to measure T_1 only with comparatively limited accuracy, and, therefore, measurements of the Knight shift naturally yield more reliable data.

Table II. Knight shifts in nontransition metals

Isotope	K	Reference	Isotope	K	Reference
Li⁶	0.0263	33	Cd¹¹¹	0.43	21
Li⁷	0.0261	33	Cd¹¹³	0.43	21
Be⁹	<0.001	34	In¹¹⁵	0.80*	37
Na²³	0.112	33	Sn¹¹⁷	0.701	38
Al²⁷	0.161	33	Sn¹¹⁹	0.709	38
K³⁹	0.248	35	Cs¹³³	1.49	33
Cu⁶³	0.232	33	Ba¹³⁵	0.403	39
Cu⁶⁵	0.235	33	Ba¹³⁷	0.403	39
Ga⁶⁹	0.449*	33	Hg¹⁹⁹	2.46	40
Ga⁷¹	0.449*	33	Tl²⁰³	1.55	41
Rb⁸⁵	0.650	33	Tl²⁰⁵	1.55	41
Rb⁸⁷	0.653	33	Pb²⁰⁷	1.24	41
Ag¹⁰⁷	0.520	36	Bi²⁰⁹	1.40*	37
Ag¹⁰⁹	0.524	36			

*Nuclear resonance has been observed only in the liquid state.

to the evaluation of the electron wave function in a metal.

Until now such calculations have been carried out only for the alkali metals and for beryllium. In Table III the experimental values of the quantity $P_F = \langle|\psi_k(0)|^2\rangle_F$ obtained from measurements of the Knight shift in these metals are compared with theoretical values obtained by various authors. In this table are also given experimental and theoretical values of the quantity $\xi = \langle|\psi_k(0)|^2\rangle_F/|\psi_a(0)|^2$, where ψ_a is the wave function of the electron in a free atom. It is assumed that the inaccuracies in the calculations associated with leaving certain features out of account will equally affect the values of both $\psi_k(0)$, and $\psi_a(0)$, and that, therefore, the comparison of measured and calculated values of this ratio may turn out to be in a certain sense more instructive than a direct comparison of the wave functions.

Table III. Experimental and theoretical values of the quantities P_F and ξ

(a_0 — Bohr radius)

Metal	Experiment			Theory		
	$P_F \cdot a_0^3$	ξ	Reference	$P_F \cdot a_0^3$	ξ	Reference
Li	0.10±0.05	0.43±0.02	42	0.11	0.49	43
				0.11	0.455	42*
Na	0.53±0.05	0.705±0.07	42	0.664	0.79	42*
				0.555	0.81	44
				0.566	0.825	45
K	0.95	0.855	35	0.91	—	35
	—	0.905	49	—	0.82	49
				0.862	1.16	46
Rb	2.32	0.993	42	1.76	0.81	42*
				2.162	1.10	47
Cs	4.39	1.13	42	2.47	0.832	42*
				2.89	1.1	48
Be	0.1	—	34	0.43	—	34
				1.03	0.6	50

*Calculations of Brooks quoted in [42].

Calculations in the case of alkali metals have been carried out by different authors who have utilized for this purpose one or another modification of the Wigner-Seitz cell method[51]. In the case of Li and Na for which sufficiently reliable experimental data on electronic susceptibility are available [52] the calculated values of P_F agree with the measured ones within approximately 10%. In the case of K, Rb, and Cs one has to use the theoretical values of the electronic susceptibility calculated by Pines[78] since no reliable experimental data are available. For K the agreement between the value of P_F "measured" by this method and the theoretical value is still very good, but in the case of Rb and Cs it is much worse, and this may be explained both by the inaccuracies in the calculations of the wave function, and by the inaccuracies in the calculation of the electronic susceptibility. Calculations for beryllium [34,50] were carried out by the method of orthogonalized plane waves [53]. These calculations disagree strongly with experiment.

As we have noted already, Cohen et al [15] have shown that conduction electrons will contribute to the Knight shift not only directly, but also indirectly by giving rise to the polarization of the spins of the electrons situated in the inner s-shells of the atom. Taking this circumstance into account leads to a reduction of the experimental value of P_F by approximately 20% in Li, by 5% in Na[15] and by approximately 10% in K[35], which makes the agreement with the theoretical values of the wave function somewhat worse in the case of these metals. It is of interest to note that if the correction due to the inner electrons has the same sign both for Rb and Cs then in this case the agreement between theory and experiment will be slightly improved.

Some authors have utilized data on the Knight shift in order to obtain more detailed information on the nature of the electron states at the Fermi surface. Thus, Jones and Schiff [54] have concluded that the electron wave function at the Fermi surface in sodium is predominantly an s-type function while in lithium it is basically a p-type function. An analysis of the same kind has been carried out for cadmium by Masuda[21]. However, it is clear that such calculations should be regarded rather as an illustration of the possibilities that exist in this direction, since the very great simpliciations in the calculations make the quantitative results obtained unreliable.

Benedeck and Kushida [42] undertook careful measurements of the dependence of the Knight shift in alkali metals on the pressure. This effect is very small: as the pressure is varied from 0 to 10^4 kg/cm² the Na resonance line characterized by a frequency of the order of 7 Mc is displaced by 135 cps, while the Li resonance frequency of the order of 10 Mc is displaced by only 35 cps; nevertheless, it was possible to measure this effect. Since the compressibili-

ties of these metals are well known, such measurements enable us to obtain information on the dependence of the product $\chi_p P_F$ on the volume. On the other hand, there are theoretical data for the quantities $\partial \chi_p/\partial V$ [28] and $\partial P_F/\partial V$ [42 44], which turn out to be in sensible agreement with experiment.

Moreover, these measurements enabled us to determine that the previously observed also very small temperature dependence of the Knight shift in alkali metals [33] cannot be explained only by the changes in volume due to thermal expansion. This effect by itself turns out to be insufficient, and from this it follows that there exists an explicit dependence of the Knight shift on the temperature. Benedeck and Kushida assume that such a dependence is due to the fact that the quantity P_F depends on the volume nonlinearly, and, that therefore, random fluctuations of volume due to the thermal vibrations of the lattice give a non vanishing contribution ($\partial^2 P_F/\partial V^2$) ΔV^2 to the quantity P_F calculated for a rigid lattice.

A number of papers was devoted to the investigation of the Knight shift in liquid metals [31,37,38]. Of interest here also is the circumstance that in passing from the solid to the liquid state the Knight shift practically does not change. It might appear that this provides evidence for the fact that in a liquid metal a considerable degree of short range order is preserved, and that the electronic structure is almost unaltered. But, on the other hand, there exists a number of metals-In, Ga and Bi,-in which no n.m.r. is observed at all in the solid state,* since the resonance line is very greatly broadened by the interaction of the quadrupole moment of the nucleus with the electric field gradient of the lattice. But in the liquid state it is possible to observe the resonance line in these metals, and this apparently provides evidence for the fact that the short range order is essentially altered. No satisfactory explanation of these effects has been given so far.

Interesting work has been carried out on the measurement of the Knight shift in superconductors. As we have noted previously, a serious difficulty here is the fact that the magnetic field penetrates into the sample only to a distance of $\sim 10^{-6}$ cm, and, therefore, very finely dispersed samples are needed for such work. Reif [40] has used for this purpose samples of colloidal mercury. Androes and Knight [55] prepared a sample by sputtering onto a cold backing thin films of tin interspersed with insulating material. As should be expected, the magnitude of the Knight shift is reduced as the metal goes over into the superconducting state, since the number of normal electrons is diminished. In accordance with the theory of [56,57] the shift ought to tend to zero as T → 0. But instead

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*Translator's note. Recently observations were made in In by Barnes et al, Phys. Rev. Letters 9, 255 (1962).

of this, the experimentally observed limiting (as T → 0) value of the Knight shift amounts to approximately 0.6—0.7 of the magnitude of the shift in the normal state. Moreover, in a recently published brief note [58] Noer and Knight report that within experimental error (~10%) the Knight shift in vanadium does not change at all either in the course of a transition into the superconducting state (the transition temperature is 5.1% K), or in the course of a further reduction of temperature down to 1.5°K. A number of authors[59,60-64,105] have attempted to explain this disagreement by taking into account in one form or another the specific properties of samples of very small size. But apparently this problem has not yet received its final solution.

As we have mentioned already, admixing of states with nonvanishing orbital angular momentum leads to the appearance of a dipole part of the hyperfine interaction and this makes the Knight shift anisotropic. This question was examined by Bloembergen [41] who showed that in the case of axial symmetry the anisotropic part of the Knight shift $\Delta\omega_a/\omega$ depends on the angle ϑ between the external field H and the axis of symmetry in the following manner:

$$\frac{\Delta\omega_a}{\omega} = \beta_0^2 v_0 \varrho \, (E_F) \, \langle q \rangle_F \, (3\cos^2\vartheta - 1) = \delta_a (3\cos^2\vartheta - 1). \quad (9)$$

Here $< q >_F$ denotes the average over the Fermi surface of the quantity

$$q = \int \psi_k^* \frac{3\cos^2\theta - 1}{r^3} \psi_k \, dv,$$

where θ is the angle between the radius vector $\mathbf{r}$ and the axis of symmetry, ψ_k is the wave function for the electron of momentum $\hbar k$, and the integration is carried out over the whole volume. The quantity $< q >_F$ characterizes the anisotropy in the distribution of the electronic charge around the nucleus.

In a polycrystalline sample, owing to the different orientation of individual crystallites with respect to the external field, the anisotropic Knight shift leads to an additional spread in the resonance frequencies, i.e., it broadens the line. On the other hand, if for the sake of simplicity we imagine the case of an axially symmetric Knight shift, then it is clear that the number of crystallites whose axis of symmetry coincides with the direction of the external field will be smaller than the number of crystallites whose axes are perpendicular to the direction of the external field, since it is possible to realize this second possibility in a much larger number of ways. This leads to an asymmetry in the absorption line.

An anisotropy in the Knight shift was found in tin [41], cadmium [21] and thallium [65]. For example, in Fig. 2 we have shown the shape of the absorption line in metallic tin in a strong field.

It is possible to measure the magnitude of the anisotropy of the Knight shift $(\Delta\omega_\parallel - \Delta\omega_\perp)/\omega_0 = 3\delta_a$ either by analyzing the shape of the absorption line
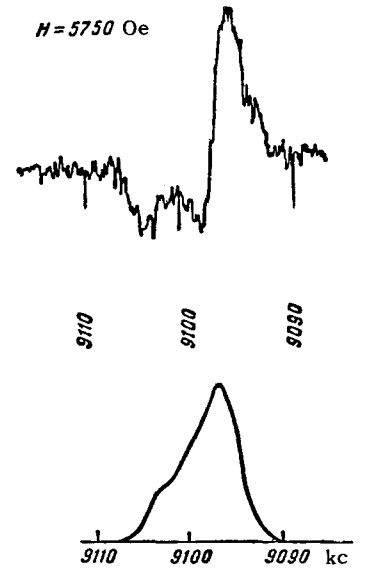

FIG. 2. Shape of the resonance line of Sn^{119} in metallic tin in a strong field. Above — record of the derivative of the absorption line; below — integrated line shape.

[41], or by observing the dependence of the magnitude of the second moment of the absorption line on the intensity of the applied field [11,65] (cf., the first note added in proof at the end of the article). It can be easily shown that the contribution made by the anisotropy of the Knight shift to the second moment is given in the case of axial symmetry by

$$\overline{\Delta\omega_a^2} = \frac{3}{4} \delta_a^2 \gamma^2 H^2;$$

and by measuring the dependence of $\overline{\Delta\omega^2}$ on H^2 we can obtain the value of δ_a. A measurement of the anisotropy of the Knight shift enables us to obtain more detailed information on the nature of the distribution of the electronic charge in the neighborhood of the nucleus. Thus, in tin and in cadmium the quantity $< q >_F$ turns out to be positive, and this tells us that the density of the electronic charge along the c axis is greater than in the plane perpendicular to this axis. In thallium, apparently, the opposite situation exists.

In conclusion we would like to note a recent paper by Blumberg, Eisinger, and Klein [66] the aim of which was to find out the extent to which the magnitude of the isotropic Knight shift is actually determined only by the contact interaction between the nucleus and the conduction electron in the s-state. These authors measured with a great degree of accuracy the magnitudes of the Knight shift for the two rubidium isotopes Rb^{85} and Rb^{87}, and compared the quantity $\Delta = K^{85}/K^{87} - 1$ obtained in this manner with the value of the anomaly in the hyperfine interaction $\Delta(S_{\frac{1}{2}}) = \nu_{hf}^{85}/\nu_{hf}^{87} - 1$ obtained from measurements of the hyperfine splitting in the ground state $5sS_{\frac{1}{2}}$ of the Rb^{85} and Rb^{87} atoms. It is clear that if the hyperfine interaction responsible for the appearance of the Knght shift in a metal is determined only by electrons in an s-state, then these two quantities must agree. Measure-

ments have shown that this actually occurs with a high degree of accuracy.

3. Indirect interaction between nuclear spins. In 1954 Ruderman and Kittel[67] drew attention to the fact that the width of nuclear magnetic resonance lines in a number of metals is observed to be greater than it ought to be if it were entirely due to the dipole-dipole interaction between nuclei. In order to explain this anomalous broadening they proposed a mechanism of indirect interaction between nuclei due to the conduction electrons. This interaction arises because an electron on the Fermi surface interacts with a pair of nuclear magnetic moments and thereby establishes between them an indirect coupling that depends on the mutual orientation of the nuclear spins. Ruderman and Kittel have shown that if in the hyperfine interaction only the contact term (4) is taken into account, then in the Bloch approximation the interaction between the nuclear spins I_i and I_k has the form

$$\mathscr{H}_{ik} = A_{ik} I_i I_k, \qquad (10)$$

i.e., it is an interaction of exchange type. Therefore, if several kinds of spins with non-vanishing magnetic moments are present in the sample this interaction will broaden the line producing a contribution to the second moment described by the last term of formula (3).

The value of the constant A_{ik} depends on the specific properties of electrons in a metal. Ruderman and Kittel have calculated its form for the case when the electron energy is a quadratic function of its momentum: $E = \hbar^2 k^2/2m^*$, where m^* is the effective mass. In this case we have

$$A_{ik} = -\frac{\langle a_k \rangle_F^2 \, \varrho \, (E_F) \, v_0^2}{16\pi k_F r_{ik}^4} \, [2k_F r_{ik} \cos 2k_F r_{ik} - \sin 2k_F r_{ik}]. \qquad (11)$$

The method of averaging the constant a_k over the Fermi surface in this expression may, generally speaking, not coincide with the method of averaging utilized in (7), and, therefore, these averaged values may differ somewhat from each other.

The fact that the value of the interaction between nuclei in a metal can be considerable has been convincingly shown by Bloembergen and Rowland [65]. These authors measured the width of the nuclear magnetic resonance line in metallic thallium which has two stable isotopes possessing magnetic moments. They carried out measurements utilizing samples of different isotopic composition and have shown that the line width for one isotope increases greatly as the concentration of the other isotope is increased. The existence of an appreciable indirect interaction was also found in metallic Ag [67], Cd [21] and Sn [11].

In a metal in which there are two kinds of nuclear spins an interaction of the form (10) must in addition to broadening the lines also lead to another curious effect. Since this interaction conserves the total spin angular momentum it must bring together the reso-

nance lines of individual isotopes and must lead to their total coalescence in weak fields, when the difference between the Zeeman energies of the different isotopes become smaller than the energy of the indirect exchange interaction. This occurs because in weak fields the nuclear spins of the different isotopes coupled by a relatively strong interaction of the form (10) behave as a single entity and must give one common resonance line. In strong fields the coupling between the spins is broken and each isotope gives rise to its own resonance line. It turns out to be possible to observe this effect, analogous to a certain extent to the Paschen-Back effect, in metallic thallium [68]. In Fig. 3 it is shown how the lines of the two thallium isotopes, Tl^{203} and Tl^{205} coalesce as the magnetic field is reduced.

As can be seen from formula (11), a measurement of the constant A gives, in principle, information about the magnitude of the hyperfine interaction in a metal and about the density of electron states at the Fermi surface. Since the quantities a_k and $\rho(E_F)$ appear in (11) in a different combination than in the expression for the Knight shift, then by combining data on the Knight shift with those on the constant A it ought to be possible to determine these two quantities simultaneously. However, the very great simplifying approximations made in deriving formula (11) do not permit us to regard too seriously the results obtained in this manner. As a matter of fact, this remark can be taken to refer to almost all the material presented in this section. At the present time the microscopic electron theory of metals lags far behind in comparison with the experimental possibilities that are available in this direction.

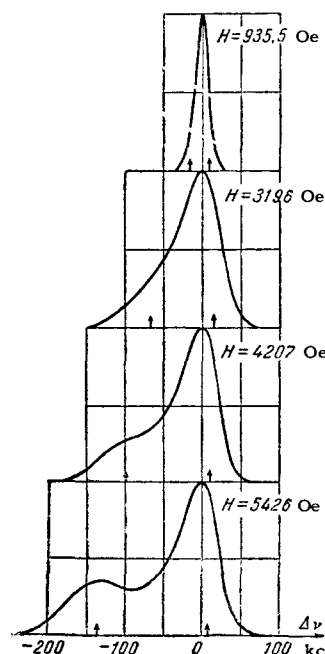If the distribution of the conduction electrons about

FIG. 3. Coalescence of the absorption lines of Tl^{203} and Tl^{205} in metallic thallium with decreasing magnetic field under the influence of the indirect exchange interaction between nuclear spins.

the nucleus is not spherically symmetric, and the electronic wave function contains an admixture of p-, d- etc., states, then the dipole part arising in the hyperfine interaction will also lead to an indirect interaction between the nuclei. This question has been considered by Bloembergen [65] who has shown that such an interaction, which he calls pseudodipole, can be represented in the form

$$\mathcal{H}_{ik} = B_{ik} \{ \mathbf{I}_i \mathbf{I}_k - 3r_{ik}^{-2} (\mathbf{I}_i r_{ik}) (\mathbf{I}_k r_{ik}) \}.$$

In principle, expressions can be obtained for the constant B of the same type as for the constant A, but explicit calculations are extremely complicated. The pseudodipolar interaction also leads to additional line broadening, and its contribution to the second moment is noticeable in metallic thallium [65,68]. Knowledge of the constant B enables us to estimate the extent to which the wave function of the electron at the Fermi surface deviates from a function of the s-type.

4. NUCLEAR MAGNETIC RESONANCE IN TRANSITION METALS

1. The study of nonferromagnetic transition metals by the n.m.r. method began quite a long time ago; nevertheless, up to the present time they have not yet been studied very well. The first measurements were made by Knight[69] in the case of vanadium and niobium soon after the discovery of the Knight shift. Several years later the Knight shifts for the two isotopes of molybdenum [70] were measured. Since the Knight shifts turned out to be of the expected magnitude, they did not attract close attention, and an exhaustive study of these metals was not undertaken.

Unexpected results began to be obtained in 1958 when Rowland[71] measured the Knight shift in platinum and found that it, firstly, depends fairly strongly on the temperature, and, secondly, most unexpectedly has a negative sign. This latter circumstance appeared to be so unlikely that Rowland himself tended to ascribe this result to an anomalously large positive chemical shift of the resonance frequency in that

platinum compound with respect to which the Knight shift was measured. However, subsequent work in transition metals showed that such an anomalous behavior of platinum is not exceptional. Thus, it became clear that the simple theory, due to Korringa, which took into account only the contact interaction between the conduction electrons and the nuclei, described fairly well a number of phenomena in nontransition metals, but was insufficient for describing the behavior of the transition metals.

Nuclear magnetic resonance has been observed so far in a total of ten transition metals, data with respect to which are collected in Table IV (cf. the second note at the end of the article). Of these, only five have been studied more or less in detail: scandium, vanadium, manganese, lanthanum and platinum.

Blumberg et al [72], who studied n.m.r. in metallic scandium and lanthanum, noted two facts which appeared to them to be anomalous. The first is the appreciable temperature dependence of the Knight shift: as the temperature varies from 295 to 1.7°K the Knight shift in both metals increases by approximately 15%; the second is the anomalously great increase in the Knight shift as the number of electrons in the unfilled d-shell increases from one to three. Thus, on going from $_{21}Sc^{45}$ with one electron in the 3d-shell to $_{23}V^{51}$ with three electrons in the 3d-shell the Knight shift increases from 0.24 to 0.55%. In going from $_{57}La^{139}$ with one electron in the 5d-shell to $_{73}Ta^{181}$ with three electrons in the 5d-shell the Knight shift increases from 0.63 to 1.1%. The authors consider that such an increase in the Knight shift is due to the increase in the polarization of the s-electrons due to the s—d-exchange interaction. The recently obtained information on the magnitude of the Knight shift in yttrium shows that a similar anomalous increase in the Knight shift is obtained in going over from $_{39}Y^{59}$ with one electron in the 4d-shell to $_{41}Nb^{61}$ with four electrons in the 4d-shell.

Butterworth [73] has arrived at an analogous conclusion with respect to the important role played by the exchange interaction between the conduction electrons in transition metals by studying the spin-lattice

Table IV. Transition metals in which nuclear magnetic resonance has been observed

Isotope	Structure of d-shell	K (%) at 295° K	Temperature dependence	Reference	T_1T, sec·deg	Reference
$_{21}Sc^{47}$	$3d^1$	0.24	Observed	72	0.6	72
$_{23}V^{51}$	$3d^3$	0.55	»	69	0.788	73
$_{25}Mn^{55}$	$3d^5$	—0.13	»	74	—	
$_{39}Y^{89}$	$4d^1$	0.337	Not studied	75	—	
$_{41}Nb^{93}$	$4d^4$	0.85	»	69	—	
$_{42}Mo^{95}$	$4d^5$	0.584	»	70	—	
$_{42}Mo^{97}$	$4d^5$	0.584	»	70	—	
$_{57}La^{139}$	$5d^1$	0.63	Observed	72	0.2	72
$_{73}Ta^{181}$	$5d^3$	1.1	Not studied	76	—	
$_{74}W^{183}$	$5d^4$	1.06	»	77	—	
$_{78}Pt^{195}$	$5d^8$	—3.52	Observed	71	$3.25 \cdot 10^{-2}$	108

relaxation in vanadium. He noted that if from the relaxation time T_1 measured by him he calculated the value of the Knight shift by utilizing Korringa's relation (8), then for K_V he obtained the value 0.22%, while the measured value of this quantity lies in the range 0.55—0.58%. The author notes that this is just the behavior that should be expected due to the s-d exchange interaction between electrons which will increase the polarization of the s-electrons practically without altering the value of the relaxation time.

However, it should be noted that Butterworth's arguments are not very compelling. Firstly, as we have noted earlier, Korringa's relation by itself always gives too low values for the product $T_1 T K^2$. On the other hand, while in the case of vanadium the value of the Knight shift calculated from the relaxation time T_1 is smaller by a factor 2.5 compared to the actual value, yet in the case of scandium this calculated value (0.27%) practically coincides with the measured value, and in the case of lanthanum the calculated Knight shift (0.81%) is even greater than the measured value.

It is possible that the s-d exchange interaction in fact does play an important role in transition metals, but the most curious fact observed here - the possibility of a negative Knight shift - requires for its explanation the introduction of other mechanisms for the interaction of the nucleus with the conduction electrons. At present it appears to be fairly evident [78,79,109] that the effect responsible for this phenomenon is the polarization of the spins of the electrons in the inner s-shell induced by the exchange interaction between these electrons and the conduction electrons.

Interesting measurements have been carried out by Blumberg et al [80] on a series of intermetallic compounds of the type V_3X, where X = As, Au, Co, Ga, Ge, Ir, Sb, Si, Pt, which all have the structure of β-tungsten. These authors measured the Knight shifts of both components in the temperature range from 20 to 300°K and have established that 1) in those compounds which are superconducting with a high transition temperature (> 1°K) the Knight shifts depend noticeably on the temperature, and 2) in these compounds K_V is always positive and decreases as the temperature is reduced, while K_X is always negative and increases in absolute value as the temperature is reduced.

Clogston and Jaccarino [81] have proposed a simple explanation of the observed behavior of the Knight shifts. They assume that one contribution to the Knight shift in vanadium, a positive one, is given by the 4s-electrons, while a second contribution, a negative one, is made by the 3d-electrons which give rise to the exchange polarization of electrons situated in the inner s-shell. Further, the measurements of Williams and Sherwood [82] show that the susceptibility of those compounds of the V_3X type for which an ap-

preciable temperature dependence of the Knight shifts is observed also depends on the temperature, increasing as the temperature is lowered. Clogston and Jaccarino assume that since the susceptibility of the s-electrons does not depend on the temperature, this means that as the temperature is reduced the susceptibility of the d-electrons increases. This leads to the fact that the negative contribution of the d-electrons to the Knight shift in vanadium increases as the temperature is reduced, and the total Knight shift diminishes. On the other hand, an assumption is made that the 4s-electrons of the X-component form a narrow filled band which lies considerably below the Fermi surface and, therefore, give no contribution to the Knight shift. Thus, the only contribution to the Knight shift of the second component is obtained as a result of the exchange polarization of the inner electrons of the X-component. This contribution is negative, and increases in absolute value as the temperature is reduced, since the corresponding susceptibility increases.

Similar measurements were made [83] for a series of intermetallic compounds of the type Al_2X, where X is a rare earth metal. The Knight shift of aluminum in these compounds also depends appreciably on the temperature, in such a way that if the f-shell of the rare earth element is less than half-full, then $K_{Al} > 0$ in such compounds and $K_{Al} < 0$ in the remaining cases.

Jaccarino [84] explained the observed effects by assuming that in the intermetallic compounds under consideration a strong exchange interaction exists between the spins of the electrons of the f-shell and the spins of the conduction electrons. This leads to the result that the conduction electrons begin to experience an additional magnetic field which gives rise to additional magnetization of the conduction electrons and thus gives a contribution to the Knight shift. The magnitude of this field is proportional to the susceptibility of the f-electrons, and since it is known that this susceptibility depends on the temperature, then the temperature dependence of the Knight shift can be understood. Further, it is known that in shells which are less than half-full the average total spin angular momentum is oriented antiparallel to the total angular momentum of the shell, i.e., against the external field, while in shells which are more than half-full the average total spin angular momentum is oriented parallel to the conserved total angular momentum, i.e., along the field. Therefore, the additional field acting on the conduction electrons will have opposite signs in these two cases, and this explains the opposite signs in the Knight shifts.

2. Nuclear magnetic resonance in ferromagnetic metals was first observed by Gossard and Portis [85] in 1959. These authors observed a very strong nuclear absorption signal in finely powdered metallic cobalt which has a cubic face-centered structure.

Measurements were carried out at room temperature in zero field at a frequency of 213.1 Mc, which corresponds to a field of 213.4 kilogauss acting on the Co^{59} nucleus.

It turned out that the n.m.r. in ferromagnetic cobalt exhibits a series of unexpected features to a detailed examination of which the next paper by Portis and Gossard [86] is devoted. Firstly, the nuclear resonance absorption signal, as can be seen from Fig. 4, has the form of a dispersion curve; secondly, its intensity is by approximately five orders of magnitude greater than could be expected from a knowledge of the nuclear magnetic susceptibility and the value of the alternating field H_1 applied to the sample; thirdly, application to the sample of a constant external field practically produces no shift of the resonance frequency, but sharply decreases the signal intensity so that in fields of ~ 5 kilogauss resonance is no longer observed.
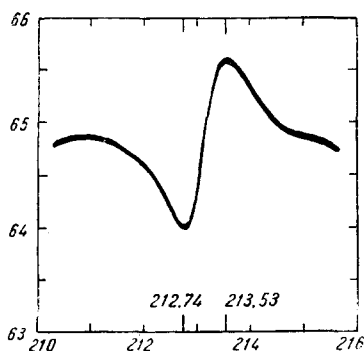
FIG. 4. The shape of the absorption line of Co^{59} in metallic cobalt with a cubic face-centered lattice.

In order to explain these anomalies Portis and Gossard have advanced the hypothesis that the contribution to the observed resonance line is made only by those nuclei which are situated within domain walls, while all the other nuclei practically take no part in resonance. A domain wall is situated at the boundary of two domains, so that within it in going over from one domain to the other one the spontaneous magnetic moment changes its direction. Under the influence of the alternating field H_1 the boundaries between the domains begin to be displaced, and the magnetic field which acts on the nuclei situated within domain walls begins to vary slightly in direction since a given nucleus turns out to occupy different positions in the domain wall. This is equivalent to the situation in which the nuclei within the domain walls begin to be acted upon by an oscillating magnetic field perpendicular to the magnetization. The magnitude of this field turns out to be approximately 10^3 times greater than the magnitude of the field H_1, and this leads to the observed increase in the intensity of the n.m.r. signal. Further, the principal losses in the sample are associated with the movement of the domain walls, and the resonance absorption of energy by the system of nuclear spins is not felt against this background. How-

ever, the real part of the dynamic nuclear susceptibility alters the total susceptibility of the sample at resonance, and this leads to the result that the losses due to the movement of the domain walls are altered. This change in the losses is recorded by the output device which thus responds not to the imaginary but to the real part of the dynamic nuclear susceptibility. It is now clear that since the multidomain structure of the sample disappears when a strong external field is imposed, the domain walls also disappear and as a result of this the nuclear resonance signal disappears.

Soon after the appearance of the first papers of Portis and Gossard nuclear resonance was observed in hexagonal cobalt [87-89], and also in two other ferromagnetic metals, iron [90-92] and nickel [93]. The principal quantity which is determined from the study of n.m.r. in ferromagnetic substances is the value of the internal field acting on the nucleus. We give in Table V appropriate values of these fields at room temperature.

Table V

Nucleus	H_{eff} at 300° K, kOe	Reference	Sign of field	Reference
Fe^{57}	330.5	90	—	95
	330.5	91		
Co^{59} cub	213.4	85	—	96, 97
	213.4	88		
Co^{59} hex	222.4	87		
	222.4	88		
Ni^{61}	170	93	—	98

The first calculations of the magnitude of the effective field acting on nuclei in ferromagnetic substances were carried out by Marshall [94] who pointed out that there are several sources making contributions to this field. A part of the field arises as a result of the contact interaction of the nucleus with the 4s-conduction electrons, a second part is due to the admixture of the 4s-state to the wave function of the 3d-electrons, a third part arises due to the interaction of the nucleus with the incompletely quenched orbital motion of the electrons and, finally, the last contribution is given by the exchange polarization of the electrons of the inner s-shells. The first three mechanisms give an effective field directed parallel to the total magnetization, while the last interaction yields an effective field of opposite sign. Marshall gave an approximate estimate of all these contributions and concluded that the effective field acting on nuclei in hexagonal cobalt is equal to +220 kilogauss. This value agreed well with the data which were obtained from measurements of nuclear specific heat and which were known to Marshall; however, it is now clear that it has no relation to reality, since in actual fact the effective field acting on nuclei in hexagonal cobalt is equal to −220 kilogauss.

A more thorough calculation of the effective magnetic fields acting on nuclei in ferromagnetic substances was carried out by Watson and Freeman [98] who showed that the principal contribution to the magnitude of the field is due to the exchange polarization of the inner electrons. However, these authors did not succeed in obtaining satisfactory agreement between calculated and measured values of the effective internal field existing in ferromagnetic substances: the calculated absolute values turned out to be several times smaller than the measured ones. The authors think that a way out of this situation can possibly be found by taking into account the fact that the positive contribution from the contact interaction with the conduction electrons, as was recently pointed out by Anderson and Clogston [99], is almost completely compensated by the negative contribution arising as a result of the covalent mixture of the s- and d-states.

Jaccarino [100] and Portis and Gossard [86] have measured the dependence of the resonance frequency in cubic cobalt on the temperature. Similar measurements were also carried out for iron [92]. Since the resonance frequency is proportional to the spontaneous magnetization, $\nu = AM$, it was thought that such measurements would enable us to verify the predictions of the theory of ferromagnetism with respect to the temperature dependence of the spontaneous moments. Although agreement between theory and experiment with respect to this point turned out to be quite good, these measurements hardly have much meaning, since it is clear that the constant A itself can depend on the temperature both implicitly (due to the changes in volume), and explicitly (cf., the analogous situation in the nontransition metals, Sec. 3, item 2). By measuring the dependence of the resonance frequency of Fe^{57} in iron on the pressure and by comparing these data with the known dependence on the pressure of the spontaneous magnetization Benedeck and Armstrong [101] have shown that the constant A indeed varies noticeably with the temperature.

Weger, Hahn, and Portis [97] undertook measurements of relaxation times in ferromagnetic metals. They carried out their measurements by means of the pulse technique, and they showed that the reestablishment of the equilibrium value of the nuclear magnetization does not take place according to a simple exponential law. This signifies that, apparently, there exists not one but several different spin-lattice relaxation times. Simanek and Šroubek [102] have explained this result by assuming that the principal mechanism for the spin-lattice relaxation of nuclear spins in a ferromagnetic substance is determined by the fluctuation oscillations of the domain walls about their equilibrium position. The random motion of the domain walls gives rise to fluctuations of the direction of the magnetic field acting on the nuclei within the domain walls, and this leads to relaxation transitions of nuclear spins. The probabilities of such

transitions will, evidently, be determined by parameters which describe the random oscillations of the domain walls, and since these parameters can be different at different points of the sample, the distribution of relaxation times observed experimentally can now be understood. Numerical estimates of the relaxation times made by Simanek and Šroubek have shown that their theory is in satisfactory agreement with experiment. A similar relaxation mechanism has also been proposed by Buishvili and Giorgadze [103].

An attempt to give a theoretical estimate of the relaxation time for nuclear spins in a ferromagnetic substance was also made by Winter [104].

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Translated by G. Volkoff