Conduction-electron paramagnetic resonance in metals

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An account is given of the principal results of the theoretical and experimental investigations of the paramagnetic resonance absorption due to conduction electrons in metals. The physical principles of the phenomenon and the features which distinguish it from electron paramagnetic resonance in insulators are considered, and modern data on the resonance line shape and on the g factor are given briefly. A considerable part of the review is devoted to an account of the different mechanisms of spin relaxation of electrons in metals. In particular, a detailed survey is given of the results of recently performed theoretical and experimental studies of the problem of impurity relaxation in solid and liquid metals. In the final part of the article, the data available in the literature on the influence of surface effects on the spin resonance absorption are critically analyzed (these data are partly contradictory), and the question of the possibility of observing spin resonance in superconductors is briefly considered.

CONTENTS

1. INTRODUCTION

Metals are one of the classical objects in which it is theoretically possible to observe the paramagnetic resonance absorption effect discovered by Zavoĭskiĭ[1]. However, unlike paramagnetic insulators, the study of which in the course of the last two decades has given an enormous amount of information on the principal energy states of paramagnetic ions in the crystals, conduction-electron paramagnetic resonance (CEPR) in metals is still a field that has been comparatively little studied. To a considerable extent, this is due to difficulties in observing the effect by means of the standard technique, these difficulties being associated mainly with the small penetration depth of the high-frequency field into the metal, and, as a rule, the extremely short spin-lattice relaxation times of the conduction electrons (CE).

At the same time, extensive studies of metals by the CEPR method along with electron and nuclear magnetic resonance at the localized spins gives the possibility of obtaining information on the fine details of the interaction of the electron spin system with the lattice (the spin-orbit and hyperfine interactions, exchange with spin moments localized in the metal lattice, effects associated with electron-electron correlation, the interaction of the CE with defects, etc.). The study of CEPR in superconductors appears promising. To a definite extent, the development of this work is associated with progress in the experimental technique of detecting the resonance signals. In this respect, a great step forward is the technique based on the phenomenon of "selective transparency of metals" under spin-resonance conditions, which was predicted theoretically by Azbel', Cerasimenko and Lifshitz[2] and experimentally observed comparatively recently[3,4].

In this paper a brief account is given of the principal results of investigations of CEPR in metals, with no pretense of chronological order. We consciously omit

questions concerning selective spin transparency and nuclear polarization by the CEPR method, about which special reviews[5,6] have already been published.

2. THE CEPR LINESHAPE

a) Physical aspects of the theory. The finite depth of penetration of the alternating magnetic field into a conductor and the high mobility of the electrons determine the characteristic features of the observed shape of the CEPR signal. In fact, unlike paramagnetic insulators, in which the varying part of the magnetization is determined by the magnitude of the applied oscillating field, in metals, because of the skin effect, there is also dependence of the local values of this field on the magnetization. Therefore, whereas in insulators the shape of the detected EPR line is determined entirely by the imaginary part $\chi''(\omega)$ of the dynamic susceptibility (when the radiospectrometer is tuned to the absorption signal), in metals it will also contain an admixture of the dispersion $\chi'(\omega)$. We stress that this simultaneous dependence of the resonance signal on both components of the dynamic susceptibility $\chi = \chi' - i\chi''$ is of a fundamental character and not an instrumental effect[7]. It is characteristic for any type of magnetic resonance in a metal, e.g., for electron paramagnetic resonance at localized spins and for nuclear magnetic resonance.

The CEPR signal will also be deformed as a consequence of the rapid motion of the CE, which, within the skin-depth, experience the action of a radio-frequency field of varying amplitude and phase. We shall consider the qualitative pattern of the behavior of the CE in a bulk sample of metal placed in a constant magnetic field H_0 and a field H_1 oscillating with angular frequency ω, under the conditions that $H_0 \perp H_1$, $H_1 \ll H_0$, and the values of H_0 and ω are close to resonance:

$$\hbar\omega = g\beta H_0, \qquad (2.1)$$

where β is the Bohr magneton, and the g-factor has a value close to the value $g_0 = 2.00220$ for free electrons. As is usual, we shall treat the orbital motion of the electrons quasi-classically. This is valid in any case when the condition $\tau \gg 1/\omega > \tau_R$ is fulfilled, where τ and τ_R are the spin-lattice relaxation time and the "transport" relaxation time of the CE respectively.

Then, if we denote the probability of finding an electron at point $\mathbf{r}$ at time t by $F(\mathbf{r}, t)$, we can assume that, for time intervals $t \gg \tau_R$, $F(\mathbf{r}, t)$ satisfies the classical diffusion equation[8]

$$\partial F/\partial t = D \Delta F \qquad (2.2)$$

with the boundary condition

$$(\mathbf{n} \, \mathrm{grad} \, F) = 0;$$

here $D = v_F \Lambda/3$ is the diffusion coefficient, v_F is the Fermi velocity of the electron, Λ is the mean free path, and $\mathbf{n}$ is a unit vector normal to the surface and pointing into the metal.

For a CE to pass through the skin depth, on average a time

$$t_D = \delta^2/2D, \qquad (2.3)$$

is required, where δ is the classical skin depth. In this time, the amplitude and phase of the oscillating magnetic field change by a factor of approximately e. Consequently, the radio-frequency field acting on the CE will not have

a fixed frequency ω, but in accordance with the well-known relation for intervals of frequency and time $\Delta\omega\Delta t \approx 2\pi$, will have a whole band of frequencies, of width $\Delta\omega \approx 2\pi/t_D$. For reasonable values of the quantities occurring in (2.3) ($\delta \approx 10^{-4}$ cm, $v_F \approx 10^8$ cm/sec, $\tau_R \approx 10^{-14}$ sec), in the standard frequency range $\omega \approx 10^{11}$ Hz we obtain $\Delta\omega \approx 10^{11}$ Hz. Thus, it would seem that the absorption should not have a resonance character.

In reality, diffusion of the CE leads to change of the intensity and shape of the resonance line, leaving the width of the CEPR signal practically unchanged. This nontrivial physical result can be illustrated qualitatively with the following spectral example. The condition $\tau \gg t_D$ is normally fulfilled in a metal, and there is a high probability that, in the time τ, the electron will find itself in the skin depth at least twice, being subjected each time to the action of a field pulse of average duration t_D. For simplicity, we shall assume that two consecutive video pulses, of duration t_D and separated by a time interval T, act on the CE (in reality, of course, a CE in the metal experiences the action of radio pulses, and T can take arbitrary values within the interval τ). According to the retardation theorem[9], the resulting complex Fourier spectrum $S(\Omega)$ can be written in the form

$$S(\Omega) = s(\Omega)(1 + e^{-i\Omega T}),$$

where $s(\Omega)$ is the complex Fourier spectrum of a single pulse. The corresponding real spectrum is equal to

$$\Phi(\Omega) = |S(\Omega)| = 2|s(\Omega)||\cos(\Omega T/2)|. \qquad (2.4)$$

Thus, the spectrum of the field from two staggered video pulses acting on the CE coincides with the spectrum $|s(\Omega)|$ of a single pulse with width $\approx 1/t_D$, modulated by the factor $|\cos(\Omega T/2)|$, and, consequently, consists of a series of peaks with width $\approx 1/T$ with a central maximum at $\Omega = 0$ (which corresponds to the resonance frequency ω for the radio pulse). Averaging (2.4) over the time interval from zero to τ leads, clearly, to an increase of the central peak and suppression of the amplitudes of the harmonics at other frequencies. Ramsey's well-known method of two oscillating fields, for magnetic resonance in molecular beams, is based on an analogous physical effect.[10]

Thus, the spectrum of the field acting on an "average" electron consists of a weak maximum ("background"), with width of order $1/t_D$, and a narrow intense peak at frequency ω, with width determined by the spin-lattice relaxation time τ; therefore, the absorption should have a resonance character.

b) Dyson's theory. A theory of the CEPR lineshape with allowance for the effect of diffusion of the CE within the skin depth was developed in the classical work of Dyson[8]. Lying at the basis of his calculations are three simplifying conditions: 1) the free-electron model is valid, 2) the constant magnetic field H_0 is directed perpendicularly to the metal surface ($H_0 \parallel n$), 3) the conditions of the normal skin effect are fulfilled ($\Lambda \ll \delta$). The principal results of Dyson's theory will be obtained below by a sufficiently simple and compact method, using the Bloch-Torrey equation with a diffusion term[11]; this method was first applied to CE by Kaplan[12].

Let the metal, which occupies the half-space $z \geq 0$, be situated in crossed magnetic fields H_0 and H_1 (H_x, H_y) (cf. Sec. 2a), and, in addition, let the Dyson conditions enumerated above be fulfilled. To determine the

B. M. Khabibullin and E. G. Kharakhash'yan

shape and intensity of the CEPR absorption line, it is necessary to calculate the paramagnetic contribution to the surface impedance Z of the metal[13] close to the resonance conditions (2.1); this reduces to solving consistently the Bloch and Maxwell equations:

$$\frac{\partial M}{\partial t} = \gamma \, [M \times H] - \frac{M}{T_2} + D\Delta M,$$
$$\text{rot } E = -\frac{1}{c}\left(\frac{\partial H}{\partial t} + 4\pi \frac{\partial M}{\partial t}\right),$$
$$\text{rot } H = \frac{4\pi\sigma}{c} E = \frac{4\pi}{c} j;$$
(2.5)

here $H = (H_x, H_y, H_0)$, M is the magnetization of the metal, T_2 is the relaxation time of the transverse component of the magnetization, γ is the gyromagnetic ratio, σ is the electrical conductivity, and j is the current density.

Assuming that the x- and y-components of H, E and M vary inside the metal like $\exp(i\omega t - kz)$ and changing to the variables $H^- = H_x - iH_y$ and, correspondingly, to E^- and M^-, we transform the system (2.5) to the form

$$\left[\alpha - i\left(1 - \tfrac{1}{2}\delta_M^2 k^2\right)\right] M^- + \beta H^- = 0,$$
$$4\pi M^- + \left(1 + \tfrac{1}{2}i\delta^2 k^2\right) H^- = 0,$$
(2.6)

where $\alpha = (\omega - \omega_0)T_2$, $\omega_0 = \gamma H_0$, $\beta = \chi_0 \omega_0 T_2$, and χ_0 is the static magnetic susceptibility; $\delta^2 = c^2/2\pi\sigma\omega$; δ_M is the "magnetic skin depth," equal to the distance over which an "average" electron diffuses in the time T_2 while conserving its spin direction ($\delta_M^2 = 2DT_2$).

Taking into account the continuity of the tangential components of H on passing through the surface z = 0, we obtain the first boundary condition:

1) H^- is continuous.　　　　　　　　(2.7a)

Integration of the Bloch equation over the volume of an infinitesimally thin disk at the metal surface gives the second boundary condition:

2)　　　　　　$(\text{n grad } M^-) = 0.$　　　(2.7b)

The physical basis of (2.7b) is the assumption that surface relaxation is absent.

From the condition that the system (2.5) have a nontrivial solution, we obtain for k the equation

$$k^4 - a_1 k^2 + a_2 = 0,$$

the coefficients of which are equal to

$$a_1 = \frac{2i}{\delta^2} + \frac{2(1+i\alpha)}{\delta_M^2}, \quad a_2 = \frac{4i(1 + i\alpha - i4\pi\beta)}{(\delta\delta_M)^2}.$$

The two roots k_1^2 and k_2^2 of this equation (only those values of these roots that have positive real parts have physical meaning) inside the metal correspond to two solutions: an electromagnetic wave that is strongly damped over the depth δ, and a weakly damped wave of small intensity, with a characteristic penetration depth δ_M, the existence of which was first pointed out by Azbel', Gerasimenko and Lifshitz[2].

The energy of the high-frequency field absorbed in the metal, averaged over the period of the vibrations, is equal to the real part of the complex Poynting vector:

$$S = \frac{c}{4\pi}|H_0^-|^2 \text{Re } Z = \left(\frac{c}{4\pi}\right)^2 \frac{|H_0^-|^2}{2\sigma} \text{Re } X,$$
(2.8)

where X equals $(4\pi\sigma/ic)E_0^-/H_0^-$, and E_0^- and H_0^- are equal respectively to E^- and H^- at the metal surface.

Solving (2.6) with the boundary conditions (2.7) gives

$$X = \frac{\sqrt{a_2}\sqrt{a_1 + 2\sqrt{a_2}}}{-2i\delta^{-2} + (a_1 + \sqrt{a_2})}.$$
(2.9)

In calculating the expression (2.9), it is convenient to expand it in powers of the small quantity β. We denote the numerator and denominator by $N(\beta)$ and $Q(\beta)$ respectively, and confine ourselves to two terms of the expansion. The first term clearly corresponds to the nonmagnetic losses in the metal and will be of no interest to us in the following. The paramagnetic contribution to the surface impedance is determined by the second term of the expansion:

$$Y = \frac{\beta}{Q(0)}\left(N'(0) - \frac{N(0)Q'(0)}{Q(0)}\right).$$
(2.10)

Calculating the polynomials N, N', Q and Q' from (2.8)—(2.10), we obtain for the magnetic losses

$$P = -\left(\frac{\omega H_1^2}{4}\delta\omega_0\chi_0 T_2\right)\frac{R^2}{2[R^4 + (R^2\alpha - 1)^2]^2}$$
$$\times \left\{[R^4 - (R^2\alpha - 1)^2]\left[\frac{2\xi}{R\sqrt{1+\alpha^2}} + R^2(\alpha+1) - 3\right] -\right.$$
$$\left. - 2R^2(R^2\alpha - 1)\left[\frac{2\eta}{R\sqrt{1+\alpha^2}} + R^2(\alpha-1) - 3\right]\right\},$$

where

$$R = \frac{\delta}{\delta_M} = \sqrt{\frac{t_D}{T_2}}, \quad \xi = (\text{sign }\alpha)\sqrt[3]{\left(\sqrt{\alpha^2+1}-1\right)^2},$$

$\eta = \sqrt{\sqrt{\alpha^2+1}+1}$, and H_1 is the amplitude of the high-frequency field.

The expression (2.11) describes the lineshape obtained by Dyson for the paramagnetic resonance absorption at the CE in unit surface of a bulk metal, when the dimensions of the sample are much greater than the skin-depth δ (cf.[14]).

a) For pure metals ($R \to 0$), the expression (2.11) is transformed into

$$P = -\left(\frac{\omega H_1}{4}\delta\omega_0\chi_0 T_2\right)\frac{R\xi}{\sqrt{1+\alpha^2}}.$$

b) In the case of slowly diffusing particles ($R \to \infty$),

$$P = \frac{1}{2}\left(\frac{\omega H_1}{4}\delta\omega_0\chi_0 T_2\right)\frac{1-\alpha}{1+\alpha^2}.$$

Figure 1 shows the theoretical CEPR absorption lineshape when the conditions a) and b) are fulfilled.

Dyson's theory has been subjected to a detailed experimental check in the work of Feher and Kip[14]. The results of their measurements, which were performed with bulk samples of lithium and sodium in a broad temperature range, are in good agreement with the corresponding formulas of the theory. Graphs convenient for practical use are given in[14] for the determination of g-factor values and linewidths ΔH from an observed absorption signal, along with dependences of the symmetry parameters of the CEPR line on the quantity R. The distortion of the resonance-signal shape for bulk metal samples as a function of the amplitude of modulation of the magnetic field and the effect of modulation broaden-
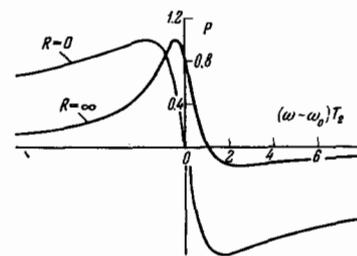

FIG. 1. Theoretical CEPR lineshape for pure metals (R → 0) and for the case of slowly diffusing particles (R → ∞).

ing of the CEPR line were considered in[15]. In[16], the lineshape was calculated for the case when the metallic samples are spherical.

c) CEPR lineshape in films. For metal films of thickness $d < 4\delta$, Dyson[8] showed that the paramagnetic resonance absorption curve has a Lorentzian shape and does not depend on the diffusion of the electrons. In a recent paper[17], a theory of the CEPR lineshape for metallic layers of arbitrary thickness was constructed with the use of the Bloch-Torrey equations, with the assumption of the symmetric boundary conditions encountered most often in experiment. In the asymptotic cases of large and small thicknesses, the expressions obtained coincide with the corresponding results of the Dyson theory. In the range of thicknesses of the order of the skin depth, the shape of the resonance signal turns out to be highly sensitive to the sample thickness and contains a significant admixture of the dispersion. For films of thickness $d < \delta_M$, the CEPR lineshape is described by the simple expression

$$P \approx A\frac{\alpha}{1+\alpha^3} + B\frac{1}{1+\alpha^2},$$

where the dependence of the parameters A and B on $d/2\delta$ is shown in Fig. 2. It is interesting that the symmetry of the line changes sign at the point $d = \pi\delta$. The experimental investigations[17,18] performed on lithium films are in quantitative agreement with the theoretical calculations.

d) Case of the anomalous skin effect. A theoretical expression for the magnetic losses in the regime of the anomalous skin effect, when $\Lambda \gtrsim \delta$, was first obtained by Kittel (cf.[14]) on the basis of the Dyson theory. Later, the problem of the paramagnetic absorption in metals for this case was treated by different methods, including with the use of the Bloch-Torrey equation, in the papers[19-21]. Omitting the details of the calculation, which is analogous to that performed in Sec. 2b,[1] we write down the general expression describing the CEPR lineshape for a bulk metal sample under the conditions of the anomalous skin-effect:

$$P \approx \frac{[2qZ_1Z_2 - p(Z_1^2 - Z_2^2)]}{\sqrt{1+\alpha^2}},$$

where

$$p = \sqrt{\sqrt{1+\alpha^2}+1}, \quad q = (\text{sign }\alpha)\sqrt{\sqrt{1+\alpha^2}-1},$$

and the surface impedance $Z = Z_1 + iZ_2$.

e) Dependence of the shape of the resonance signal on the angle of inclination of the constant magnetic field to the metal surface and on the electron dispersion law. The most general theory of paramagnetic resonance in metals under conditions of both the normal and the anomalous skin effect has been developed on the basis of the quantum kinetic equation for the statistical density
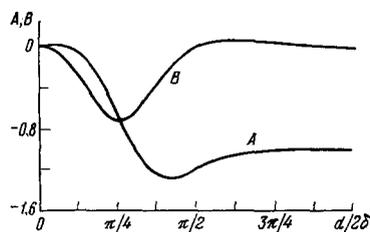

FIG. 2. Dependence of the lineshape parameters A and B on the film thickness d for films with $d < \delta_M$.

operator of the CE, with the spin taken into account, in[2,19,22]. A derivation of the Bloch-Torrey equation for the CE from the general kinetic equation and the equivalence of the methods of Dyson and Kaplan were treated in[23,24].

Azbel', Gerasimenko, and Lifshitz[2,19] obtained a general expression for the paramagnetic part of the impedance for metals with an arbitrary dispersion law $\epsilon(k)$ and for arbitrary magnitude and direction of the constant field H_0. We shall not give here the corresponding cumbersome formulas, the direct comparison of which with the experimental data is not a simple problem, but confine ourselves to a qualitative treatment of the simple physical arguments that explain the existence of the dependence of the CEPR lineshape on the dispersion law and on the direction of the magnetic field[19].

For a metal sample for which at least one of the geometric dimensions $d \ll \delta$, the probability of reorientation of a CE spin will not depend on the character of the motion of the electron, inasmuch as the electron is all the time in a field with the same amplitude and phase over the whole volume of the sample. Consequently, the particular form of the dispersion law and the angle of inclination of H_0 to the surface of the sample are unimportant.

In the case of a bulk metal, the radius r of the circular orbit of the electron in a strong magnetic field can be much smaller than the mean free path Λ. Under the conditions of the anomalous skin effect, the electron performs $n \approx \Lambda/r$ revolutions between successive collisions with the lattice. If the magnetic field is parallel to the metal surface, the electron returns n times into the skin depth, and thus spends n times more time in it than in the case when the constant field is perpendicular to the metal surface. The observed surface impedance will thus depend on the angle of inclination of H_0.

The specific form of the dispersion law $\epsilon(k)$ can have a substantial influence on the dependence of the impedance of the metal on the direction of H_0. Thus, for CE whose energy levels in momentum space are represented by open isoenergetic surfaces and, consequently, whose motion can be infinite in a plane perpendicular to H_0, such a dependence may be absent.

In[21,23], a calculation was performed of the dependence of the CEPR lineshape on the angle of inclination θ of the constant magnetic field to the surface of the sample for CE with a quadratic dispersion law. It was shown that, in this case, the lineshape is described by the appropriate expressions of Secs. 2b and 2d with allowance, however, for the fact that the diffusion coefficient D has the form

$$D(\theta) = \frac{v_F^2 \tau^*}{3(1+i\omega_0\tau^*)} \frac{(1+i\omega_0\tau^*)^2 + \omega_c^2\tau^{*2}\cos\left(\frac{\pi}{2}-\theta\right)}{(1+i\omega_0\tau^*)^2 + \omega_c^2\tau^{*2}};$$

ω_c is the cyclotron frequency, and $\tau^* = \tau_R(1 - i\omega\tau_R)^{-1}$.

Qualitative observations of the angular dependence of CEPR signals were made in[25] on a single-crystal sample of pure aluminum, and in[26] for samples of very pure potassium. At liquid-helium temperatures, under conditions characteristic for cyclotron resonance ($\omega_c\tau_R > 1$), the explicit dependence of the intensity of the signal on the angle of inclination of the field H_0 to the surface of the sample was observed. The intensity was a maximum at $\theta = 0$ and fell rapidly with increasing θ. This is in qualitative agreement with the theory. The

splitting of the CEPR line for a given θ into two components with intensities with different angular dependences was observed in[26] for extremely pure samples. Attempts to interpret this effect theoretically were undertaken in[21,27].

Recently, in[28], the possibility of studying the shape of the Fermi surface and the parameters of the electron Fermi liquid in a metal by the CEPR method was considered.

3. THE G-FACTOR

The relation between the resonance values of the constant magnetic field H_0 and frequency ω is determined, in accordance with (2.1), by the magnitude of the g-factor of the CE. For free electrons, $g_0 = 2.00229$[29]. The existence of internal interactions in a metal lead to a shift of the value of the g-factor from g_0.

A calculation of the theoretical values of $\Delta g = g - g_0$ for the alkali metals was performed in[29-35]. It was shown that Δg can be represented by the following formula[34]:

$$\Delta g(k) = \frac{2}{i}\int_{\Omega_0} \Psi^* \,[r\times\nabla]_z\, \Psi \,d\Omega + \frac{1}{mc^2}\int_{\Omega_0} \Psi^*\left(x\frac{\partial V_0}{\partial x}+y\frac{\partial V_0}{\partial y}\right)\Psi\,d\Omega$$

$$-\int_{S_0}\left\{u^*\,[r\times\nabla]_z\,\frac{\partial u}{\partial \nu}+2ik_\nu u^*\,[r\times\nabla]_z\,u-\frac{\partial u}{\partial k_y}\frac{\partial}{\partial \nu}(xu^*)+\frac{\partial u}{\partial k_x}\frac{\partial}{\partial \nu}(yu^*)\right\}dS$$

$$-\mathrm{Im}\int_{S_0}\left[\frac{k_y}{k_x}\frac{\partial \Psi^*}{\partial k_x}\frac{\partial}{\partial \nu}\frac{\partial \Psi}{\partial k_x}-\frac{k_x}{k_y}\frac{\partial \Psi^*}{\partial k_y}\frac{\partial}{\partial \nu}\frac{\partial \Psi}{\partial k_y}\right]dS. \tag{3.1}$$

where V_0 is the potential of the ion framework, ν is the component of the gradient normal to the surface of the unit cell, u is the periodic part in the Bloch wave function Ψ, Ω_0 and S_0 are respectively the volume and surface area of the unit cell, k is the CE wave-vector, and m is the CE effective mass.

The first term in (3.1) describes the contribution to Δg due to the orbital motion of the electron. The second term represents the correction to the z-component of the orbital magnetic moment which arises when the spin-orbit interaction is taken into account. The terms in the form of integrals over the surface S_0 arise when the motion of the CE in the lattice is taken into account[34].

It was noted recently, in[35], that in (3.1) it is necessary to take account also of the relativistic correction

$$\Delta g' = -\frac{\hbar^2}{m^2c^2}\int_{\Omega_0}\Psi^* \hat{k}^2\Psi\,d\Omega, \tag{3.2}$$

which, for CE moving with the Fermi velocity $\approx 10^8$ cm/sec, amounts to $\simeq 5\times10^{-5}$, which is within the limits of the experimentally attainable accuracy of the measurement of the g-factor.

In the calculation of the numerical values of Δg, it has been found that they are extremely sensitive to the choice of approximations in the determination of the CE wave functions. The errors inherent in each of the methods used (the method of quantum defects[31,33,34], and the method of orthogonalized plane waves[35]) do not permit us at the present time to calculate the shift Δg with an accuracy sufficient for a correct comparison with the corresponding experimental values. We therefore confine ourselves to giving, in Table I, only experimental values of Δg. The data marked by an asterisk in Table I were determined by the spin-transmissivity method. As can be seen, for potassium and rubidium they agree with the corresponding values of Δg obtained

by the standard method. For cesium, a discrepancy is observed. Inasmuch as a detailed analysis of the accuracy of the g-factor measurements is not given in the original papers[42,43], the observed discrepancy could be associated with underestimated values of the experimental errors.[2] Table I does not include the data from a number of papers in which the measurements of g are either qualitative in character[1,25,47] or cannot yet be considered to be sufficiently reliably established[48-51] (when there is one brief publication, or the data are contradictory).

4. SPIN RELAXATION IN PURE METALS

The important kinetic parameters characterizing the phenomenon of magnetic resonance absorption are the Bloch relaxation times T_1 and T_2 for the longitudinal (M_z) and transverse (M_x and M_y) components of the magnetization respectively[52]. Their values can be estimated from the following relations:

$$T_1^{-1} \approx H_x^2 + H_y^2, \quad T_2^{-1} \approx H_x^2 + H_y^2 + 2H_z^2,$$

which are a consequence of the commutation properties of the electron spin operators. In these relations, H_α ($\alpha = x, y, z$) are the fluctuations of the components of the effective magnetic field acting on the CE spin. Possible causes of these fluctuations are the lattice vibrations, the Coulomb or dipole-dipole interactions of the magnetic particles with each other, the varying magnetic fields induced by the orbital motion of the CE, and others.

If the characteristic time of the fluctuations of the magnetic fields $\tau_c < \omega^{-1}$, then, according to[53], $T_1 = T_2$. It follows from a consideration of the possible relaxation mechanisms in metals that, for the magnetic fields usually used in CEPR experiments ($H \lesssim 10^4$ G), this condition is fulfilled. In[54], it is shown by the general method of the quantum kinetic equation that for isotropic metals the transverse and longitudinal relaxation times coincide for $g\beta H < kT$.

Experimental confirmation of the equality $T_1 = T_2$ in metals was obtained by Carver and Slichter[55] by the method of stationary saturation of the CEPR line in lithium. Recently[56,57], the CEPR in lithium and sodium was investigated by a pulse method. An analysis of the free-precession and spin-echo signals gave $T_1 = T_2$, in complete agreement with the predictions of the theory. Thus, the spin-lattice relaxation time $\tau = T_1$ introduced in Sec. 2a can be determined directly in metals by measuring the width of the resonance signal:

$$\delta H = 2\hbar/\sqrt{3}\,T_1\mu_e,$$

where δH is the peak linewidth, and μ_e is the CE magnetic moment.

The time T_1, under the condition $\tau_R \ll T_1$, is calculated from the formula [29]

$$\frac{1}{T_1} = \frac{4}{(2\pi)^3} \left(\int \frac{\partial f_\beta(k)}{\partial E_k} dk \right)^{-1} \int \frac{\partial f_\beta(k)}{\partial E_k}$$

$$\times \{(1 - f_\alpha(k')) W_{k'\alpha, k\beta} + f_\alpha(k') W_{k\beta, k'\alpha}\} dk \, dk'; \qquad (4.1)$$

Here $W_{k'\alpha, k\beta}$ is the transition probability for scattering of an electron from a state with wave vector k and spin β to a state $k'\alpha$; $f(k)$ is the distribution function of the electrons.

To calculate the transition probabilities for k $k\beta \rightarrow k'\alpha$, it is necessary to consider the actual relaxation mechanisms. In pure metals, the main relaxation mechanism consists in the modulation of the magnitude of the Coulomb interaction V_0 [58] and of the spin-orbit interaction V [29,59] by the thermal vibrations. For the valence electrons, the spin-orbit interaction constant λ increases rapidly with increasing atomic number of the element, although a simple dependence has not been obtained. In heavy metals, the increase of λ leads to a large relaxation width of the CEPR line, and this makes it impossible to observe the resonance absorption by the usual methods.

The spin-orbit interaction can be regarded as the interaction of the spin moment of the electron with a certain effective magnetic field appearing as the result of the relative motion of the electron and the ions of the lattice framework. With this interaction taken into account, the Hamiltonian $\mathcal{H}_0$ of an electron in a periodic lattice is of the form

$$\mathcal{H}_0 = \frac{p^2}{2m} + V_0(r) + \frac{\hbar^2}{4m^2c^2} [\nabla V_0(r) \times k] \sigma, \qquad (4.2)$$

where $V_0(r)$ is the periodic lattice potential and σ is the Pauli spin operator.

By virtue of the invariance of the Hamiltonian $\mathcal{H}_0$ under a translation of the lattice, the eigenfunctions will have the Bloch form. However, generally speaking, inclusion of the spin-orbit interaction leads to the result that the eigenfunctions will not correspond to pure spin states $\chi_\pm$ with $\delta_z = 1$ or -1. In the general case, the CE wave function is written as follows:

$$\Psi_{k\uparrow} = \varphi_{k\uparrow}\chi_+ + \gamma_{k\downarrow} \chi_- = e^{ikr} u_{k\uparrow}(r),$$

where the arrow in the Bloch function indicates the spin state, e.g., the value of $\langle \Psi_{k\downarrow} | \sigma_z | \Psi_{k\downarrow} \rangle$ is positive. The quantity $\gamma_{k\downarrow}$ is proportional to the shift Δg of the g-factor of the electron.

For the spin-lattice mechanism considered, the interaction of the CE with the lattice vibrations is given as follows:

$$\hat{W}_q(t) = \Sigma_i u_q(i, t) \nabla_i \left\{ V_0(r, R_i) + \frac{\hbar^2}{4m^2c^2} [\nabla_r V_0(r, R_i) \times k] \sigma \right\}; \quad (4.3)$$

here R_i is the position vector of the i-th ion of the lattice, and $u_q(i, t)$ is the displacement of this ion from its equilibrium position in the lattice as a result of thermal vibrations characterized by wave vector q. The mixing of the spin states leads to the result that, in the matrix element $\langle \Psi_k | W_q | \Psi_{k'} \rangle = M_{k, k'}$, the terms representing the modulation of the Coulomb interaction by the thermal vibrations give a non-zero contribution proportional to Δg. Substitution of a matrix element with a power dependence on $q (M_{k,k+q} = \text{const} \cdot q^n)$ into the

expression (4.1) leads, at low temperatures (below the Debye temperature Θ), to the dependence

$$T_1^{-1} \approx T^{2n+1};$$

W_q is a Hermitian operator invariant with respect to time reversal $t \rightarrow -t$ and spatial inversion $r \rightarrow -r$. Using these symmetry properties of W_q, it can be shown [29,60] that, for metals with a structure possessing a center of inversion,

$$M_{k\downarrow, k'\uparrow} = AQ^2q^2,$$

where $q = |k - k'|$, $Q = |k + k'|$, and A is the interaction constant. Consequently, for such metals the temperature dependence of the spin-lattice relaxation time has the form

$$T_1^{-1} \approx T^5 \qquad (T < \Theta). \qquad (4.4)$$

For metals with a structure without a center of inversion, the matrix element is equal to AQq and, thus, $T_1^{-1} \approx T^3$.

At high temperatures, when the number of phonons with frequency ω is $n(\omega) \approx n(\omega) + 1 \approx kT/\hbar\omega$,

$$T_1^{-1} \approx T \qquad (\Theta < T). \qquad (4.5)$$

At the present time, sodium is the only metal for which studies of the temperature dependence of the relaxation time have been carried out in a sufficiently wide range of temperatures [14,40,61-64]. In the region $T > \Theta$, the linear dependence (4.5) of T_1^{-1} on temperature is observed:

$$T_1 T = 3 \cdot 10^{-6} \text{ sec} \cdot {}^\circ K.$$

Below the Debye temperature, the behavior of the experimentally measured times agrees with the temperature dependence (4.4). The numerical values of T_1 in the whole range of temperature are in satisfactory quantitative agreement with the corresponding values calculated from formula (4.1).

At very low temperatures, other relaxation mechanisms, treated by Overhauser [59], may turn out to be more effective:

1) The interaction of the CE magnetic moments with the magnetic and electric fields created by the thermal vibrations of the ion framework of the metal.

2) The magnetic dipole-dipole interaction of the electron spins.

3) The interaction of the electron spin with the magnetic field of the currents arising in the orbital motion of the CE.

4) The hyperfine interaction of the electrons with the nuclear spins.

For temperatures $T > 1^\circ K$, all these relaxation mechanisms give values of T_1 at least an order of magnitude longer than the experimentally observed values, and their contributions to T_1 have not yet been detected.

5. PARAMAGNETIC RELAXATION OF CONDUCTION ELECTRONS AT IMPURITIES

The important dependence of the absorption linewidth on the purity of the sample had been made clear in the early papers on CEPR. Thus, e.g., for metallic lithium the magnitude of the spin-orbit interaction is exceptionally small (for a free atom, $\lambda = 2.8 \times 10^5$ eV [29]), and

therefore the presence of impurities in the most insignificant quantities entirely determines the rate of spin relaxation[14].

A study of the effect of impurities on the spin relaxation times gives extremely interesting information on a number of questions. Measurement of the dependence of the relaxation linewidth on the impurity concentration makes it possible to determine the magnitude of the effective cross section for scattering with spin reorientation at impurities. From the dependence of the scattering cross section on the valence and atomic number of the impurity, it is possible to obtain information on the character of the screening of a charged impurity. In combination with experimental data on the effect of impurities on the electrical conductivity, it is possible to determine the role of the spin-orbit interaction in kinetic processes. From a study of the impurity contribution to the linewidth, information can be obtained, in principle, on the spectrum of the local vibrations and on the character of the diffusional motion of the impurity.

The systematic study of the influence of controlled impurities on the width of CEPR lines in metals was begun by Garif'yanov and co-workers[64,65-68]. In particular, in the case of impurities of group-IIB metals in lithium, which form primary solid solutions in the concentration range $c \leq 1$ at.%[69], it was shown that the linewidth increases linearly with increasing c (Fig. 3). On the basis of the simple theory of paramagnetic relaxation of Pines and Slichter[70], it follows from the results obtained that the spin-orbit interaction of the CE with an impurity atom in the metal does not differ in order of magnitude from its value for the free impurity atom.

Subsequently, the impurity contribution to the CEPR linewidth at room temperatures was studied in[71-73]. The most detailed results of experimental and theoretical investigations are given in[72], in which the effect of fourteen different metal impurities on the CEPR linewidth in Li and Na was studied. The authors started from the plausible assumption that all the metals studied form true solid solutions at sufficiently low concentrations. One of the interesting results obtained in[72] is the discovery of a maximum in the curve of the dependence of $\partial \delta H(c)/\partial c$ on the valence of the impurity.

In the interpretation of the experimental results, the impurity atoms are regarded as static defects in the first approximation. The probability of spin-flip scattering does not depend on temperature in the Born approximation, and therefore expression (4.1) for T_1 has the form

$$\frac{1}{T_1} = \frac{1}{8\pi\hbar} N_0 c \int |\langle \mathbf{k}_F'\alpha | \hat{V} | \mathbf{k}_F\beta \rangle|^2 \rho(E_F) d\Omega_h d\Omega_{h'}, \quad (5.1)$$

where N_0 is the number of atoms per unit volume and $\rho(E_F)$ is the density of electron states near the Fermi level. The interference terms, which occur with a factor c^2 in the expression for T_1, are omitted here. Under the assumption that the impurity-ion potential in the crystal deviates weakly from spherical symmetry[74], the spin-orbit interaction V in (4.2) can be represented in the form

$$V = \frac{\hbar}{4m^2c^2} [\nabla_r V_0(r) \times \mathbf{k}] \sigma = \lambda(r)\langle \mathbf{sl} \rangle, \quad (5.2)$$

where

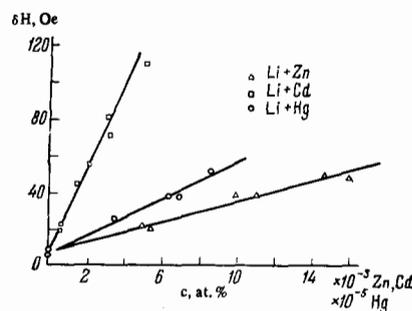$$\lambda(r) = \frac{\hbar^2}{2m^2c^2} \left(\frac{1}{r} \frac{\partial V_0}{\partial r} \right),$$

FIG. 3. Dependence of the absorption-line peak-width δH (between the points of maximum slope) on the atomic concentration c of Group-IIB metal impurities.

and l and s are the dimensionless angular-momentum operators.

In the calculation of the matrix element, the CE were described[72] by plane waves orthogonalized to the orbital wave-functions of the electrons localized at the impurity. The orthogonalization leads to the satisfaction of the Pauli principle and gives rise to oscillations of the CE wavefunction near the impurity, similar to the atomic-electron oscillations. For monovalent metals, as is well known[75], one plane wave gives a completely satisfactory approximation:

$$\varphi_\alpha(\mathbf{k}) = \exp(i\mathbf{k}_F\mathbf{r}) - \Sigma_{l\beta} a_{l\beta} \Psi_{l\beta}, \quad (5.3)$$

where $\Psi_{l\beta}$ is the wavefunction of the electrons localized at the impurity, and $a_{l\beta}$ is the overlap integral

$$a_{l\beta} = \int \Psi_{l\beta}^* \exp(i\mathbf{k}_F\mathbf{r}) dr.$$

As shown by the calculations performed in[72] using the Hartree-Fock wavefunctions for the atomic electrons of the impurity[76], the greatest contribution to the quantity T_1 arises from overlap with the p-orbital lying immediately below the valence state of the impurity.

An explanation of the resonance character of the dependence of δH on the valence of the impurity[72] was suggested in the paper[77], and somewhat later in[78]. By analogy with the theory of the resonance scattering of conduction-band d-electrons at an impurity, which is due to the existence of virtual bound states with energy approximately equal to the Fermi energy[79], in interpreting the curves of the experimental results the authors started from the assumption of the existence of a virtual bound-state level for the p-electrons. For scattering of electrons by a heavy impurity, the conditions for the applicability of simple perturbation theory may be violated. In this case, the scattering cross-section is calculated in the "tight-binding" scheme[80].

The results of numerical calculations of the values of the cross-section σ_{theor} for spin-flip scattering of CE by impurities[72] are given, together with σ_{exp}[64,72,73], in Table II. The scattering cross section σ is connected with the spin-lattice relaxation time by the relation

$$\sigma = (cN_0 v_F)^{-1}/T_1.$$

In the calculation of the values of σ_{theor}, the following approximations were used: the one-electron model for the description of the CE, first-order perturbation theory (the Born approximation), and neglect of the effects of screening of the spin-orbit interaction of the impurity atom. With allowance for these approximations,

    B. M. Khabibullin and E. G. Kharakhash'yan

Table II

Host metal	Impurity	z	σ_{exp} [64]	σ_{exp} [72]	σ_{exp} [73]	σ_{theor} [72]
Li	Mg	12		$(6.4\pm0.5)\cdot10^{-21}$	$(5.2\pm0.1)\cdot10^{-21}$	$9.2\cdot10^{-20}$
	Al	13		$(1.6\pm1.0)\cdot10^{-20}$		$4.9\cdot10^{-21}$
	Zn	30	$(7.2\pm0.7)\cdot10^{-19}$	$(6.8\pm0.6)\cdot10^{-19}$	$(6.2\pm0.1)\cdot10^{-19}$	$9.8\cdot10^{-20}$
	Ga	31		$(1.5\pm0.1)\cdot10^{-18}$		$5.2\cdot10^{-19}$
	Pd	46		$(2.0\pm0.3)\cdot10^{-18}$		$7.8\cdot10^{-18}$
	Ag	47		$(3.5\pm0.3)\cdot10^{-18}$	$(3.0\pm0\ 2)\cdot10^{-18}$	$3.0\cdot10^{-18}$
	Cd	48	$(5.7\pm0.5)\cdot10^{-18}$	$(7.5\pm0.7)\cdot10^{-18}$		$6.2\cdot10^{-18}$
	In	49	$(6.0\pm1.2)\cdot10^{-18}$	$(1.0\pm0.1)\cdot10^{-17}$		$1.7\cdot10^{-17}$
	Sn	50		$(2.2\pm0.3)\cdot10^{-18}$		$1.3\cdot10^{-16}$
	Pt	78		$(2.5\pm0.4)\cdot10^{-17}$		$6.5\cdot10^{-18}$
	Au	79		$(6.8\pm1.0)\cdot10^{-17}$		$3.6\cdot10^{-17}$
	Hg	80	$(1.2\pm0.2)\cdot10^{-16}$	$(1.1\pm0.1)\cdot10^{-16}$		$0.85\cdot10^{-16}$
	Tl	81		$(8.9\pm0.9)\cdot10^{-17}$		$2.2\cdot10^{-16}$
	Pb	82		$(1.6\pm0.3)\cdot10^{-17}$		$9.8\cdot10^{-16}$
Na	K	19	$(8\pm1)\cdot10^{-21}$ *)			
	Rb	37	$(1.2\pm0.3)\cdot10^{-19}$ *)			
	Cd	48		$(6.6\pm0.8)\cdot10^{-18}$		$2.5\cdot10^{-18}$
	In	49		$(2.3\pm0.3)\cdot10^{-17}$		$7.6\cdot10^{-18}$
	Sn	50		$(2.8\pm0.6)\cdot10^{-18}$		$8.2\cdot10^{-17}$
	Hg	80		$(9.6\pm1.5)\cdot10^{-17}$		$3.1\cdot10^{-17}$
	Tl	81	$(4.1\pm0.5)\cdot10^{-16}$ $(5.5\pm1)\cdot10^{-16}$ *)	$(2.7\pm0.3)\cdot10^{-16}$		$9.7\cdot10^{-17}$
	Pb	82		$(2.0\pm0.3)\cdot10^{-16}$		$7.1\cdot10^{16}$

*The values of σ were obtained for the liquid alloy at 100°C and depend on the temperature.

FIG. 4. Dependence of the peak linewidth on the temperature for pure Na [64]. ○ denotes points in the return after heating.

FIG. 5. Dependence of the peak linewidth on the temperature for a Na + Tl sample (c = 0.5 × 10⁻⁴ at.%) [82]. ○ denotes points in the return after heating.

the agreement between the quantities σ_{exp} and σ_{theor} in Table II must be regarded as satisfactory.

The temperature dependence of the impurity contribution to the CEPR linewidth in the alkali metals was studied in [64,81,82]. From the data obtained for alloys based on lithium and sodium, it follows that, up to temperatures $T \leq 300°K$, the impurity contribution to the relaxation width does not depend on the temperature. Thus, an analog of the Mathiessen rule for the electrical resistivity is valid for the CEPR width:

$$\delta H_{sol}(T, c) = \delta H_{lat}\ (T) + \delta H_{imp}\ (c). \qquad (5.4)$$

Figures 4 and 5 give typical dependences of δH on T for pure Na and for the system Na + Tl. For Na of high purity, a linear dependence of δH on T was observed up to the melting point T_{mp} of the metal. According to [64,81,82] the smooth increase of the linewidth in the interval $300°K < T < T_{mp}$ (analogous to the increase also observed in Li) is explained by the change in the solubility of the uncontrolled impurities contained in the alloy as the temperature is raised. We remark that the presence of rapid diffusional motion in lithium and sodium for $T > 250°K$ is confirmed by nuclear magnetic resonance data [83].

There exists another possible explanation of the dependence of the impurity contribution to the CEPR linewidth on temperature near T_{mp}; this explanation is associated with allowance for the thermal vibrations of the impurity atoms. According to the theory of vibrations of impurity atoms [84-86], the spectrum of the thermal vibrations of an impurity depends strongly on the ratio of the impurity mass M' to the mass M of an atom of the metal solvent. In the case of a heavy impurity $|\eta| > 1$ ($\eta = (M - M')/M$), the distribution function $f(\omega^2)$ of the squares of the frequencies in the spectrum of the impurity vibrations has a resonance character with a maximum in the region of frequencies $\omega_*^2 = \omega_0^2/3|\eta|$, where ω_0 is the Debye frequency, while in the frequency range $\omega < \omega_*$ the spectral density increases by a factor of M'/M compared with the spectral density in the ideal crystal. In the case of a sufficiently light impurity $\eta < 1$, practically the whole spectral density is concentrated at the discrete frequency $\omega_D^2 \approx 2\omega_0^2/5(1 - \eta)$. A number of papers [85-87] have recently appeared in which a series of experimental results (violation of the
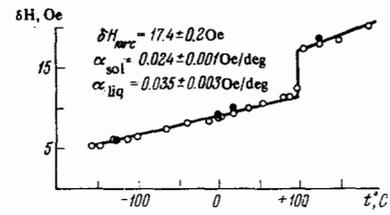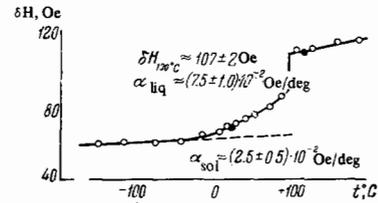
Mathiessen rules for the electrical resistivity in weak solutions, anomalies in the lattice thermal conductivity, and the infrared absorption spectrum) are explained by taking into account the vibrations of the impurity atoms.

A calculation of the effect of thermal vibrations of the impurity on the CEPR linewidth was given in [88]. The quantity T_{imp}^{-1} represents the sum of three terms:

$$\frac{1}{T_{imp}} = \frac{1}{T_1(1)} + \frac{1}{T_1(2)} + \frac{1}{T_1(3)}\ ;$$

$T_1(1)$, $T_1(2)$, and $T_1(3)$ describe the respective contributions to T_1^{-1} of the impurity scattering, the interference scattering and the scattering by the deformed vibrational spectrum of the ideal lattice. In all the experimental work enumerated above on the effect of impurities on the CEPR linewidth, the case $\eta < 0$ (heavy impurities) was realized. For $|\eta| > 1$ and $T \leq \Theta/2$, the ratio p of the part $T_1^{-1}(1)$ depending on the impurity vibrations to the part $T_1^{-1}(0)$ due to scattering by a stationary impurity does not depend on the temperature and is equal to

$$p \approx -\frac{9|\eta|}{4\pi}\ \frac{q_0^3}{\omega_0}\ \frac{\hbar}{M}\ ,$$

where q_0 is the momentum of a phonon with the Debye frequency. Physically, this result is explained by the fact that the decrease in the probability of elastic scattering (with spin-flip) with increasing temperature as a consequence of the Debye-Waller factor is compensated by the increase in the probability of inelastic scattering by phonons. For the alloy Na + Tl, estimates give p = −0.12.

In the region of high temperatures $T > \Theta/2$, the quantity p becomes equal to

$$p = -\frac{\hbar}{M}\ \frac{q_0^2}{8}\ \frac{\hbar}{kT}\ \frac{1}{1-\eta}\ ,$$

which leads to an increase of the linewidth with increasing temperature, in accordance with the law $a - b/T$ (a, b > 0).

For $T < \Theta$, the contribution from scattering by the deformed lattice spectrum is equal to

$$\frac{1}{T_1(3)} = \frac{1}{T_{lat}}(-2c\eta)[(I_4/I_5)-1],$$

where $I_n(n) = \Gamma(n)\zeta(n)$, $\zeta(n)$ is the Riemann zeta-function, $\Gamma(n) = (n - 1)!$, and T_{lat} is the relaxation time for

B. M. Khabibullin and E. G. Kharakhash'yan

scattering by thermal vibrations of the ideal lattice. In the paper[88], the temperature dependence of T_1 in the case of a light impurity ($\eta < 1$) has also been considered.

Thus, allowance for the thermal vibrations of heavy impurities gives a qualitatively correct description of the experimentally observed temperature dependence $\delta H(T)$.

6. CEPR IN LIQUID METALS

In the transition of a metal into the liquid state, a discontinuous increase of the resonance linewidth is usually observed. By analogy with the electrical conductivity, we can associate the jump at the melting point with the change in the character of the pair correlation function for the coordinates of the metal ions[89]. This qualitative explanation is also confirmed by data from measurements of the magnitude of the Knight shift[90], which indicate that the density of states of the CE at the Fermi surface $\rho(E_F)$ for a number of metals (Li, Na, Rb, Cs, Hg, Al, Sn) changes negligibly in the transition to the liquid state (these changes amount to 10^{-2} of $\rho(E_F)$).

The experimental and theoretical study of CEPR in liquid alkali metals are the subject of[39-41,62,64,81,82,91-93].

According to[81,82], the dependence of the CEPR linewidth on temperature and impurity concentration for alkali metals in the liquid state can be represented in the following form:

$$\delta H = AT + BTc + Dc + E. \qquad (6.1)$$

It follows from (6.1) that "Mathiessen's rule" is violated for the linewidth in a liquid metal: the impurity contribution to δH becomes temperature-dependent (see Fig. 5), with

$$\alpha_{sol} < \alpha_{liq}, \quad \alpha = \partial \delta H / \partial T.$$

The experimental values of the constants appearing in the expression (6.1), together with the corresponding values of the atomic constants, are given for liquid Na with different impurities in Table III.

A theoretical description of the paramagnetic relaxation of CE in liquid metals can be based, by analogy with the theory of the electrical resistance[89,94], on existing ideas about the structure and dynamics of simple liquids. At the present time, the theory of liquids give a qualitatively correct description of the temperature dependence of the electrical resistance, specific heat and viscosity. However, it is still considerably less logically rigorous and consistent than the theory of solids with a periodic structure. An analogous comment is valid with regard to the description of the state of conduction electrons in liquid conducting media[95].

To interpret the experimental data, the following expression, which is a modification of the relations (4.1)

and (5.1) for liquid metals, was used in[81] to calculate T_1theor:

$$\frac{1}{T_1} = \frac{2}{\hbar} N_0 \rho(E_F) \frac{1}{k_F^2} \int d\mathbf{q} \{ |V_a(q)|^2 (1 + g_{aa}(q))$$

$$+ c(|V_b(q)|^2 - |V_a(q)|^2) + c[\overset{\bullet}{V}_b(q) V_a(q) g_{ab}(q) - 2|V_a(q)|^2 g_{aa}(q)] \}. \qquad (6.2)$$

In the expression (6.2), $g(q)$ is the Fourier component of the pair correlation function, $q = |\mathbf{k} - \mathbf{k}'|$, and the subscript a refers to the metal-solvent and b to the impurity.

For low impurity concentrations, terms quadratic in c can be neglected.

A comparison of the terms of Eq. (6.1) depending on the impurity concentration and temperature with the corresponding terms of the expression (6.2) gives the integral values of products of $V_{a,b}(q)$ and $g(q)$ in terms of the measurable parameters A, B, D and E. The temperature dependence of T_1 in (6.2) is determined by the dependence on T of the Fourier component $g(q)$ of the pair correlation function; $g(q)$ was considered in[96], where the expression $g(q) = (b(q)/kT + 1)^{-1}$ was obtained. Here $b(q)$ is the Fourier component of the interatomic potential. For liquid sodium, $b(q) \gg kT$[97]. We can therefore assume that $g(q) \approx kT/b(q)$, which corresponds to the observed linear dependence $\delta H(T)$ in the temperature range studied. It was found that the ratios of the calculated values of the constants D in (6.1) for different impurities are in satisfactory agreement with the experimental data of[64,82]. However, a discrepancy was observed between the theoretical and experimental values of the constants B describing the temperature dependence of the impurity contribution. This is apparently connected with the difficulty of estimating the quantity B theoretically. Indeed, it can be seen from the expression (6.2) that the presence of the factor q^2 under the integral leads to an increase of the relative share of the contribution to T_1 from large-angle scattering ($q \approx 2k_F$). It is known[98] that the functional dependence $g(q)$ is strongly varying in this region of values of q, and therefore even small errors in the determination of $g(q)$ by the methods of neutron and x-ray diffraction lead to a large change in the calculated values of B.

It was observed in[64,81] that the introduction of the light impurity Li into liquid Na leads to a weakening of the temperature dependence of the linewidth (the constant B changes sign). This result agrees qualitatively with the theoretical relation (6.2), when it is taken into account that $V_{Li} \ll V_{Na}$.

In the recent papers[91,92], the CEPR linewidth for the system K + Na in the liquid phase near the melting point was investigated over the whole range of concentrations. The resulting values of T_{1exp} are in good agreement with the values of T_{1theor} calculated on the basis of the relation (6.2) using orthogonalized plane waves and with allowance for the correction coefficients arising as a result of the electron-electron interactions.

7. INFLUENCE OF SURFACE EFFECTS ON THE PARAMAGNETIC RESONANCE ABSORPTION IN METALS

The crystal structure and the fields acting on the CE in the layer adjacent to the surface differ from the corresponding entities inside the crystal. Therefore, collisions of the CE with the surface of the metal may

Table III

	z	Λ, eV	B, Oe/deg	D, Oe
Na	11	$2.12 \cdot 10^{-3}$	—	—
K	19	$7.13 \cdot 10^{-3}$	0.5 ± 0.2	$(12 \pm 1) \cdot 10^2$
Rb	37	$2.93 \cdot 10^{-2}$	43 ± 15	$(6 \pm 4) \cdot 10^3$
Tl	81	0.96	$(7 \pm 2) \cdot 10^4$	$(7 \pm 1) \cdot 10^7$
Li	3	$2.77 \cdot 10^{-5}$	$-(0.4 \pm 0.2)$	

turn out to be an effective mechanism of paramagnetic relaxation. The effect of surface relaxation on the CEPR lineshape was taken into account by Dyson[8] by means of the phenomenological introduction of a certain probability (averaged over the possible scattering angles) of a spin reorientation in a single collision of a CE with the metal surface.

a) Dyson showed that, for samples in which at least one geometric dimension $d < \delta$, the CEPR lineshape remains Lorentzian. In the full width δH there appears an additional term, due to inelastic scattering of electrons at the surface.

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_s}.$$

where T_s is the surface spin-relaxation time.

1) According to Dyson, for $d \leq \Lambda$,

$$T_s = 4\Omega/\varepsilon v_F S, \qquad (7.1)$$

where Ω is the volume of the sample and S is its surface area. Thus, for samples in the form of films with thickness d,

$$T_s = 2d/\varepsilon v_F, \qquad (7.2)$$

and the measurement of the width of the resonance signal as a function of d gives the possibility of a direct experimental determination of ϵ.

2) For samples with $d > \Lambda$, in calculating the frequency of collisions of a CE with the surface we must naturally take into account the diffusional character of its motion. In this case, $t_S \approx d^2/v_F \Lambda$ is the time between two collisions with the surface and

$$T_s = \alpha d^2/\varepsilon v_F \Lambda,$$

where α is a numerical coefficient of order two, depending on the shape of the sample. Consequently, the surface relaxation time depends explicitly on the mean free path and is related non-linearly to the small dimension d of the metal particle.

b) The relations given above are valid for sufficiently large metallic samples, such that the influence of quantum size effects on the energy spectrum of the conduction electrons is unimportant:

$$\hbar/\tau_R > \hbar^2\pi^2/2md.$$

At temperatures $T > 4°K$, for very fine metallic particles ($d \lesssim 10$ Å), the space quantization can be neglected in view of the large relaxation width of the CE energy levels. Therefore, the quantity T_S will be determined by the formula (7.1). However, in the case when the coupling of the sample to the surrounding medium is small and $T \lesssim 0.3°K$, the discrete character of the energy spectrum of the single-particle excitations substantially alters the distribution of the number of states per unit energy interval in the system and, as a consequence, changes the static and dynamic paramagnetic susceptibility of the system. The average spacing between the discrete levels is equal to

$$\Delta = 2\pi^2\hbar^2/\Omega m^2 v_F.$$

However, even if the particles have the same volume and shape, because of the fact that the CE wavelength is of the order of atomic dimensions the existence of surface irregularities on the atomic scale is sufficient for the distribution of energy levels to become random. But the average spacing between the levels remains equal to Δ.

This feature of the energy spectrum of the CE for fine particles was first pointed out in the paper by Kubo[99]. An analogous situation exists for the distribution of the higher excited levels of nuclei[100,101]. On the basis of the results of the papers[100,101], Gor'kov and Éliashberg[102] have examined the distinctive features of the electron resonance absorption, together with the thermodynamic properties, in fine metallic particles. It was found that, when the spin-orbit interaction is small and the spin remains a good quantum number, the CEPR lineshape should display quantum oscillations on variation of the magnitude of the external magnetic field; for $\mu H \gg \Delta$, these are described by the following relation:

$$\chi'' = \frac{\omega_0^2}{\omega_0^2 - \omega^2} \frac{\chi_\infty}{H} \int_0^H dH \left\{ 1 - \left(\frac{\Delta}{2\pi\mu H}\right)^2 + \frac{1 + \cos^2(2\pi\mu H/\Delta)}{2\pi\mu H/\Delta} \right\} . \quad (7.3)$$

Experimental studies of the dependence of the CEPR linewidth on the sample dimensions and on the temperature, with the purpose of elucidating the role of surface relaxation, have been undertaken in a number of papers[14,64,103-113]. For a reliable measurement of the quantity ϵ it is necessary that the contribution of the surface relaxation to δH be at least comparable with the temperature-dependent parts of the corresponding contributions from the other relaxation mechanisms. Therefore, experiments to measure ϵ are performed, as a rule, on samples containing fine metallic particles dispersed in a suitable neutral medium. We remark, however, that measurements on dispersed samples give values of ϵ averaged over an ensemble with a large number of metal particles of indeterminate shape and with a large spread in size. It is easy to show that this can lead to imprecise experimental values of ϵ. In fact, in the work[14,103-109] carried out on dispersed samples of lithium, different values of ϵ from 10^{-4} to 10^{-7} were obtained.

For a quantitative determination of ϵ, experiments on one sample, with strictly specified geometrical dimensions (e.g., on a sample in the form of a thin metal film) are necessary. In the literature there are two papers on work carried out on films[110,111]. In[110], CEPR in lithium films of thickness $0.08 \mu \leq d \leq 80 \mu$ was studied. The estimate $\epsilon \leq 9 \times 10^{-6}$ was obtained for the probability of inelastic scattering of a spin at the metal surface[64]. In[111], the measurements were performed on lithium films of thickness down to 0.01μ. A determination of ϵ from the dependence $\delta H = f(d)$ given in[111] gives a quantity $\approx 8 \times 10^{-6}$ (the authors of[111] did not themselves estimate ϵ). The temperature dependence of the contribution of the surface relaxation to the linewidth was not discovered, but the experimental points of the dependence of T_2^{-1} on d^{-1} lie on a straight line, within the error bars. This corresponds to realization of the conditions of case a), 1) (cf. formula (7.2)).

There are reports in the literature that it has been possible in the experiments of[107,112,113], to realize the conditions characteristic for especially finely dispersed systems (case a), 2)).

In conclusion, we note that the inadequate amount of reliable experimental data and the contradictory nature of the existing work means that the problem of surface relaxation remains a very real one.

8. CEPR IN SUPERCONDUCTORS

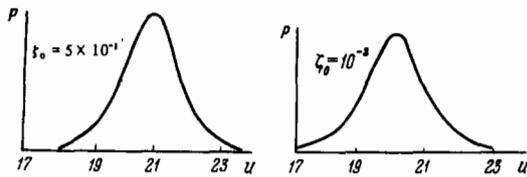An experimental realization of the possibility of observing spin resonance in superconductors could give

FIG. 6. Dependence of the resonance absorption (in arbitrary units) on $u = \omega T_1$ for a superconducting film of thickness d for $\delta = 4 \times 10^{-6}$ and different values of the parameter $\zeta_0 = d/2\lambda$ [115].

interesting information on the details of the mechanism of formation of superconducting pairs. At the present time, the only superconducting metal for which there are reports in the literature on the observation of the spin resonance phenomenon in the normal state is aluminum[25,46].

The problem of resonance absorption in the super-conducting state has been treated theoretically in the paper[114]. The small depth of penetration of the constant magnetic field into a superconducting metal ($H_0(z)$ $\approx H_0 \exp(-z/\lambda)$, $\lambda \simeq 5 \times 10^{-5}$ cm) and the condition $\Lambda > \lambda$, which is usually valid for normal electrons at low temperatures, leads, according to[114], to the result that resonance absorption in bulk superconductors is impossible (in any case, to frequencies $\omega < v_F/\Lambda$). But it is pointed out in the same paper that resonance absorption can be observed in samples of thicknesses $d < \lambda/2$.

Kaplan[115] has performed a simplified calculation of the lineshape of the CEPR signals for a superconducting film of thickness $d \ll \lambda/2$, for the case when the constant magnetic field H_0 is parallel to the surface of the metal film. In[115], from the solution of the system of Maxwell equations for spinless particles

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \mathrm{rot}\,\mathbf{A}, \quad \mathbf{A} = \alpha \mathbf{j}, \quad \alpha = \frac{4\pi}{c}\lambda^2$$

the values were found of the radio frequency field $H_1(z)$ in the sample, where $-d/2 \le z \le d/2$, and H_0 and H_1 are parallel to the x and y axes respectively.

After substitution of the resulting values of $H_1(z)$ into the modified Bloch equation (2.5), in the approximation linear in the susceptibility one can obtain for the magnetization components transverse with respect to H_0:

$$M_y(1+iu) = M_z u' \,\mathrm{ch}\,\xi + \delta \frac{\partial^2 M_x}{\partial \xi^2},$$

$$M_z(1+iu) = H_1 \chi u' \,\mathrm{ch}\,\xi - M_y u' \,\mathrm{ch}\,\xi + \delta \frac{\partial^2 M_z}{\partial \xi^2},$$

where

$$\xi = z/\lambda, \quad u = \omega T_1, \quad u' = \frac{T_1 \gamma H_0}{\mathrm{ch}\,(d/2\lambda)}, \quad \delta = T_1 D/\lambda^2.$$

The dependence on $\zeta_0 = d/2\lambda$ of the result of the numerical solution of the equations for $\delta = 4 \times 10^6$ is illustrated in Fig. 6. The interpretation of the results obtained is fairly simple. The rapid diffusion of the CE in the film leads to the result that the value of the effective constant magnetic field averaged over the interval $\Delta t \approx 1/\omega$ depends on the ratio $d/2\lambda$. By changing the values of the parameters ω, d and $\lambda(T)$, we can achieve fulfillment of the resonance conditions.

We note that the effect of surface relaxation was not taken into account in the calculation cited. In addition, quantum size effects may turn out to be important for very thin films.

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