

# Conduction electron spin echo in metals

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A theory of spin echo for conduction electrons in metals in the case of uniform alternating fields is developed by a stochastic method for an arbitrary value of the probability of spin reorientation ( $\epsilon$ ) in collisions with the surface. It is shown that the surface relaxation mechanism yields equal additive contributions to the relaxation times of the longitudinal ( $T_1$ ) and transverse ( $T_2$ ) components of the conduction electron spin magnetization. Conduction electron spin echo is studied and comparative measurements of stationary paramagnetic resonance and saturation are carried out at a number of temperatures for small spheroidal particles of pure lithium with a mean diameter  $d \approx 1.2 \mu\text{m}$ .  $T_1$  and  $T_2$  are measured independently on the basis of the decays of the primary and stimulated echoes and a direct experimental confirmation of the relation of the theory,  $T_1 = T_2$ , is obtained. From the temperature-dependent contribution to the relaxation times it is found that  $\epsilon = (5 \pm 2) \times 10^{-6}$ . The contribution of the temperature-independent relaxation within the metal is found to be  $(1.1 \pm 0.1) \times 10^{-6}$  sec.

The study of transient processes and saturation effects of electron paramagnetic resonance (EPR) yields important information concerning the kinetic properties and internal interactions of spin systems. Particular interest attaches to research of this type for the spin system of the conduction electrons in metals. Yet the theoretical and experimental studies of paramagnetic resonance on conduction electrons (PRCE) were devoted until recently mainly to stationary effects. Observation of the transients in the spin system of the conduction electrons is hindered by two factors, the short spin-lattice relaxation times and the large electron-diffusion rates. These difficulties were overcome by Taylor et al.<sup>[1]</sup>, who used a coherent detection circuit to measure the electron free-precession signals in pure bulky samples of lithium and sodium, and also in our own investigations<sup>[2]</sup>, where conduction-electron spin echo (CESE) was observed for the first time on small particles of very pure lithium.

Transient processes in metals were investigated theoretically on the basis of the equations of motion linearized with respect to the alternating magnetic field<sup>[3]</sup>. These transient processes, however, do not account for the spin-echo phenomenon, which is essentially a nonlinear effect. This is seen even from the fact that the results of the theory of<sup>[3]</sup> do not go over into the expression for the spin echo in dielectrics when electron diffusion is neglected.

In the present paper we develop, for the case of a uniform alternating field, a stochastic theory of CESE which takes the diffusion of the electrons and the spin relaxation on the surface of the metal into account. Results of the experimental investigations of CESE on particles of metallic lithium with dimensions smaller than the skin-layer depth at temperatures of 77, 300 and 410°K are presented. The same samples were used for comparative measurements of the stationary PRCE in the temperature interval 4.2–500°K and the stationary saturation of the resonance line at room temperatures.

## 1. THEORY OF CESE

In comparison with EPR in dielectrics, the description of PRCE in metals is made complicated by the need

to take into account the skin effect and the diffusion motion of the conduction electrons. The theory of the stationary PRCE in the absence of saturation effects was constructed in Dyson's classical paper<sup>[4]</sup>. The skin effect was taken into account by simultaneously solving the equations of motion for the magnetization and Maxwell's equations, while the time dependence of the conduction-electron coordinates was determined independently with the aid of the Green's function of the diffusion equation.

There exists a general approach to the description of PRCE, based on the kinetic equation for the density of the spin magnetization  $\mu(\mathbf{r})$ <sup>[5]</sup>; this approach makes it possible to take into account an arbitrary dispersion law and the Fermi-liquid properties of the conduction electrons. It turns out, however, that many results can be obtained in a simpler fashion with the aid of the modified Bloch equation<sup>[6]</sup>:

$$\frac{\partial \mu}{\partial t} = \gamma[\mu \mathbf{H}] - \frac{\mu_x - \chi H_x}{T_{2v}} \mathbf{i} - \frac{\mu_y - \chi H_y}{T_{2v}} \mathbf{j} - \frac{\mu_z - \chi H_z}{T_{1v}} \mathbf{k} + D \nabla^2 (\mu - \chi \mathbf{H}), \quad (1)^*$$

where  $\gamma$  is the gyromagnetic ratio,  $D$  is the diffusion coefficient,  $\chi$  is the Pauli susceptibility,  $\mathbf{H} = H_0 \mathbf{k} + H_x(t) \mathbf{i} + H_y(t) \mathbf{j}$ ,  $H_0$  and  $H_{x,y}(t)$  are the constant and alternating magnetic fields, and  $T_{2v}$  and  $T_{1v}$  are the relaxation times of the transverse and longitudinal components of the spin magnetization of the conduction electrons in the volume of the metal. We note that Eq. (1) can be derived from the kinetic equation<sup>[7]</sup> and that in stationary PRCE problems Eq. (1) gives results equivalent to Dyson's theory<sup>[8]</sup>.

The modified Bloch equations (1), which have given a good account of themselves in the solution of problems that are linear in the alternating field, lead to great mathematical difficulties when it comes to describing nonlinear effects, since they call for the solution of an inhomogeneous system of three second-order partial differential equations. However, so long as the diffusion motion of the electrons can be regarded as independent of the magnetic field, this difficulty can be circumvented by solving Eq. (1) without the diffusion term, but with stochastically varying electron coordinates. The time dependence of these coordinates is then determined, just in Dyson's theory, by solving the diffusion equation. An approach of this type has already been used to de-

scribe spin echo in liquid paramagnets with infinite dimensions<sup>[9]</sup>. We use this approach below for conduction electrons in metallic samples of finite dimensions. This requires, unlike the approach used by Ghosh and Sinha<sup>[9]</sup>, that account be taken of the boundary conditions, and makes it possible to consider the spin scattering of the electrons by the surface.

The starting point of the theory is the system of Bloch equations (1) without the diffusion term. We subdivide the observation time into a large number of identical intervals  $\Delta t$ . Assume that during the time  $\Delta t$  the electrons experience a sufficient number of collisions so that the stochastic character of the variation of their positions is preserved, but these changes themselves are small. At the start of the  $k$ -th interval, at  $t = t_{k-1} = (k-1)\Delta t$ , the average density of the magnetization at the point  $r_{k-1}$  is equal to  $\mu(r_{k-1}, t_{k-1})$ . Then the solution of the Bloch equations at the instant of time  $t_k$  can be expressed, by virtue of the choice of the interval  $\Delta t$ , as a solution of Eq. (1) at constant coordinates  $r_{k-1}$  and with the initial condition  $\mu(r_{k-1}, t_{k-1})$ . We denote this solution by  $\mu(r_{k-1}, t_k; \mu(r_{k-1}, t_{k-1}))$ . The stochastic variation of the coordinates in the interval  $\Delta t$  is taken into account by averaging these solutions with the probability  $P(r_k t_k | r_{k-1} t_{k-1})$  of the transition of the electron from the point  $r_{k-1}$  to the point  $r_k$  during the time  $\Delta t$  with the aid of a relation of the Kolmogorov type:

$$\mu(r_k, t_k) = \int_V d r_{k-1} \mu(r_{k-1}, t_k; \mu(r_{k-1}, t_{k-1})) P(r_k t_k | r_{k-1} t_{k-1}), \quad (2)$$

where  $V$  is the region of permissible values of the coordinate variation. Applying relation (2)  $n$  times and then letting  $\Delta t$  tend to zero, so that  $\lim n\Delta t = t$ , we can express the solution of (1) at the instant of time  $t$  in terms of the initial conditions at  $t = 0$ .

The conditional probability  $P(rt | r_0 t_0)$ , which enters in (2), is the solution of the translational-diffusion equation. To determine it completely it is necessary to specify the boundary conditions, which are determined by the physics of the problem. Following the spin reorientation on the surface, the electron drops out of the ensemble described by the Bloch equation; in terms of the diffusion motion this is equivalent to "absorption" of conduction electrons on the surface.

The number of particles absorbed by the surface element  $dS$  per unit time is by definition

$$-Dn \text{grad } P(rt | r_0 t_0) |_{s dS},$$

and the fraction of the electrons experiencing at the instant  $t$  a collision with the surface, but not absorbed, is

$$P(rt | r_0 t_0) |_{s dS}$$

( $D$  is the diffusion coefficient and  $n$  is the normal to the surface). The flux of particles reflected from  $dS$  per unit time is

$$vP(rt | r_0 t_0) |_{s dS},$$

where  $v$  is a coefficient independent of the surface point and has the dimensions of velocity. Then

$$-Dn \text{grad } P(rt | r_0 t_0) |_{s} / vP(rt | r_0 t_0) |_{s} = \frac{\epsilon}{1-\epsilon}, \quad (3)$$

where  $\epsilon$  is the probability of spin reorientation following impact against the surface.

The parameter  $v$  does not depend on  $\epsilon$ , since the falling of the electron onto the surface is not connected

with the spin relaxation. This circumstance can be used to determine  $v$ . The boundary conditions at  $\epsilon = 0$  go over into

$$\text{grad } P(rt | r_0 t_0) \Big|_{r=S}^{\epsilon=0} = 0$$

and  $P^{\epsilon=0}$  can be obtained independently of  $v$ . Then the number of electrons reflected by the entire surface per unit time is

$$v \int_S P^{\epsilon=0} dS = v(1-\epsilon) |_{\epsilon=0},$$

where  $\nu$  is the average number of collisions of the conduction electrons with the surface. Consequently the conditions (3) must be supplemented by the definition of  $v$ :

$$v = \nu \left[ \int_S P^{\epsilon=0} dS \right]^{-1}. \quad (4)$$

Dyson<sup>[4]</sup> and Walker treated  $v$  as the Fermi velocity<sup>[8]</sup> in their analysis of the boundary conditions. This is valid only in the case of collisionless motion of the electron in the volume of the sample, but then the diffusion description is literally inapplicable.

For the spherical samples that are of interest in the present paper, the conditional probability is given by

$$P^{\epsilon}(rt | r_0 t_0) = \left( \frac{4\pi}{3} R^3 \right)^{-1} \delta_{r_0} + \sum_{n, \lambda=0}^{\infty} A_{n\lambda} \exp(-\lambda_{n\lambda}^2 D(t-t_0)) \times \frac{2n+1}{4\pi} P_n(\cos \alpha) \frac{J_{n+1/2}(\lambda_{n\lambda} r)}{r^{1/2}} \frac{J_{n+1/2}(\lambda_{n\lambda} r_0)}{r_0^{1/2}},$$

$$(A_{n\lambda})^{-1} = \frac{1}{2\lambda_{n\lambda}^2} \left[ \lambda_{n\lambda}^2 R^2 + \left\{ \frac{\epsilon}{1-\epsilon} \frac{vR}{D} - \frac{1}{2} \right\}^2 - \left\{ n + \frac{1}{2} \right\}^2 \right] J_{n+1/2}^2(\lambda_{n\lambda} R), \quad \epsilon \neq 0, \quad (5)$$

where  $J_{n+1/2}(x)$  are Bessel functions,  $P_n(\cos \alpha)$  are Legendre polynomials,  $\alpha$  is the angle between  $r$  and  $r_0$ ,  $R$  is the radius of the particles, and the parameters  $\lambda_{n\lambda}$  are nonzero roots of Eq. (3) for a sphere

$$\frac{\partial}{\partial r} \left[ \frac{1}{r^{1/2}} J_{n+1/2}(\lambda r) \right]_{r=R} + \frac{\epsilon v}{(1-\epsilon)D} \frac{1}{R^{1/2}} J_{n+1/2}(\lambda R) = 0 \quad (6)$$

$$v = D/3R.$$

The expressions for the coefficients in (5) with  $\epsilon = 0$  are not given, since they will not be used henceforth.

In the case of homogeneous alternating fields, to which the experimental situation in our study corresponds, the system of Bloch equations does not contain the electron coordinate explicitly. As a result, the transition probabilities are convoluted on the intervals  $\Delta t$ , and the expression for the physical quantities contains only the probability of electron transition during the observation time  $t - t_0$  from the initial position  $r_0$  to the final position  $r$ . The spin-echo signal is excited by a sequence of two microwave pulses, whose frequencies  $\omega$  are close to the resonant frequency and whose polarization  $H_1$  is perpendicular to the constant magnetic field  $H_0$ . The pulse durations are

$$t_i \ll T_{1v}, 2v, (\Delta\omega)^{-1},$$

where  $\Delta\omega = \omega - \gamma H_0$  is the static scatter of the resonant frequencies inside the sample due to the imperfection of the magnet and to the defects. Because of this inequality, one can neglect the relaxation processes and the frequency scatter to determine the behavior of the magnetization during the time of the pulse.

The calculation of the response of the conduction electrons to two such pulses, applied with an interval  $\tau$  between them, shows that the contribution made to the echo signal at  $t = 2\tau$  by an electron situated at the point  $r_0$  at the instant  $t = t_0$  when the first pulse is applied and located at point  $r$  at the observation instant  $t > \tau + t_2$  is proportional to the quantity

$$\mu_y(r, r_0, t) = m_0 \sin \xi_i \sin^2 \frac{\xi_2}{2} \exp \left\{ -\frac{(t-t_0)}{T_{2v}} \right\} P(|r|_{r_0 t_0}) \cos \Delta \omega (t - 2\tau), \quad (7)$$

where  $m_0$  is the equilibrium value of  $\mu_z$ ,  $\xi_i = \gamma H_i^1 t_i$ , while  $H_i^1$  and  $t_i$  are the amplitude and duration of the  $i$ -th pulse.

To obtain the echo signal from all the electrons it is necessary to integrate expression (7) over the initial coordinate  $r_0$  and then average over the volume of the sample and over the scatter  $\Delta \omega$ . The distribution of  $\Delta \omega$  is described by a normal law with a second moment  $T_s^{-2}$ . Inside of metal particles having small dimensions, the deviation  $\Delta \omega$  is constant, and the parameter  $T_s$  characterizes the scatter of the resonant frequencies from particle to particle. Carrying out these averagings, we obtain

$$\begin{aligned} \mu_y(t) &= m_0 \sin \xi_i \sin^2 \frac{\xi_2}{2} \exp \left\{ -\frac{t}{T_{2v}} - \frac{(t-2\tau)^2}{2T_s^2} \right\} \langle P(t) \rangle, \\ \langle P(t) \rangle &= \delta_{n,0} + \frac{3}{4\pi R} \left( \frac{v}{1-\epsilon} R \right)^2 \sum_k A_{0k}^2 \lambda_{0k}^{-2} \\ &\times \left[ \left( 1 - \frac{v}{1-\epsilon} R \right)^2 + \lambda_{0k}^2 R^2 \right]^{-1} \exp(-\lambda_{0k}^2 D t). \end{aligned} \quad (8)$$

In formula (8) we have taken into account the fact that the boundary condition (6) goes over at  $n = 0$  into

$$\text{tg } \lambda R = \lambda R \left[ 1 - \frac{v}{1-\epsilon} R \right]^{-1}. \quad (9)$$

In the absence of surface relaxation ( $\epsilon = 0$ ), the value of  $\langle P(t) \rangle$  becomes equal to unity and, as expected, the diffusion does not affect the echo-signal damping. In the case of complete relaxation ( $\epsilon = 1$ ), the roots of Eq. (9) are

$$\lambda_{0k} = \pi k R^{-1} \quad (k = 1, 2, \dots),$$

and the expression for  $\langle P(t) \rangle$  becomes

$$\sum_{k=1}^{\infty} 12\pi^{-1} k^{-4} \exp(-\pi^2 k^2 R^2 D t).$$

Confining ourselves to the first term of this sum, we see that the damping of the echo signal at  $t = 2\tau$  is subject to the law

$$\exp \{-2\tau / T_s\}, \quad (10)$$

where

$$T_{2v}^{-1} = T_{2v}^{-1} + T_s^{-1}, \quad T_s^{-1} = \pi^2 D R^{-2}.$$

In the case  $\epsilon \ll 1$ , Eq. (9) has as a first root  $\lambda_{01} = (3\epsilon v / DR)^{1/2}$ , and the remaining roots are much larger. Confining ourselves to the first term in the sum (8), we obtain

$$\langle P(t) \rangle \approx (6/\pi) \exp \{-t / T_s\}.$$

The decrease of the echo signal is also described by expression (10), where

$$T_s^{-1} = \epsilon D R^{-2}. \quad (11)$$

Analogous calculations for the damping of the stimulated-echo signal at the instant of time  $t = \tau_1 + \tau_2$  yield

$$\mu_y(\tau_1 + \tau_2) = \text{const} \cdot \exp \left\{ -\tau_1 \left[ \frac{2}{T_{2v}} - \frac{1}{T_{1v}} + \frac{1}{T_s} \right] - \tau_2 \left[ \frac{1}{T_{1v}} + \frac{1}{T_s} \right] \right\}, \quad (12)$$

where  $\tau_1$  and  $\tau_2$  are the time intervals between the first and second and the first and third pulses, respectively, while  $T_S$  is given by formulas (10)–(11). It follows from (12) that the surface spin scattering makes an identical additive contribution  $T_S^{-1}$  not only to the transverse relaxation time but also to the longitudinal time. It also follows that measurements of the damping of the stimulated-echo amplitude with increasing interval  $\tau_2$  makes it possible to determine the longitudinal spin-relaxation time:

$$T_1^{-1} = T_{1v}^{-1} + T_s^{-1}.$$

## 2. EXPERIMENT

**A. Samples.** The observation of the CESE signals in metals, as already noted in the Introduction, is made difficult by two circumstances. First, the presence of even the most insignificant impurities greatly shortens the spin relaxation time of the conduction electrons<sup>[10]</sup>. Second, the high rate of electron diffusion (diffusion coefficient  $D \sim 50 \text{ cm}^2/\text{sec}$ ) should lead to rapid damping of the echo signal<sup>[1]</sup>. The last difficulty can be circumvented by using a sample in the form of sufficiently minute metal particles. The effective electron diffusion coefficient in the particle can then be estimated at  $D_{\text{eff}} = D(d/l)^2$ , where  $d$  is the average dimension of the metal particle and  $l$  is the distance over which the electron diffuses in the bulky metal during the time interval between the sounding pulses. By choosing a suitable particle dimension, it is possible to decrease  $D_{\text{eff}}$  by several orders of magnitude. Thus, to perform measurements of CESE it is necessary to have very pure metallic samples of small dimensions.

Among all the metals in which PRCE has been investigated, the longest spin-relaxation times have been observed for lithium, owing to the very small value of the spin-orbital interaction of the electrons for this metal. However, as a consequence of the high chemical activity of lithium, the problem of obtaining even bulky pure samples is very difficult, and the existing methods for subsequent pulverization (mechanical or ultrasonic pulverization, thermal evaporation in vacuum, etc.) are quite unsatisfactory, owing to the contaminations they introduce. The main difficulty is connected with the choice of a suitable neutral medium for liquid lithium. The most promising solution, as indicated in<sup>[11]</sup>, is to make the containers for lithium and other alkali metals out of pure halide salts of these metals. It is known that when alkali-halide crystals are irradiated and subsequently annealed by heat, colloidal particles of very pure metal are produced. Thus, in particular, very narrow EPR absorption lines have been observed in neutron-bombarded LiF single crystals due to the conduction electrons in the particles of metallic lithium<sup>[12]</sup>.

It was the foregoing considerations which dictated the choice of the method for obtaining a sample with minute particles of lithium for our measurements of CESE: a pure LiF single crystal, grown in vacuum, was bombarded in the reactor with a dose of  $\sim 10^{16} \text{ neut/cm}^2$  (in terms of thermal neutrons) at a temperature  $400\text{--}550^\circ \text{K}$ . After the bombardment, this sample revealed an intense EPR line with a peak width  $\delta H \sim 0.4 \text{ G}$ . The Lorentz shape of the line, the value of the  $g$ -factor, and the temperature dependence of the line width have made it possible to identify the observed signal uniquely with the PRCE with the radiation-induced colloids of lithium. To increase the relaxation time further, the sample was

subjected to annealing at a temperature  $\sim 1000^\circ\text{K}$  under high-vacuum conditions, with subsequent quenching in liquid nitrogen. It is known that this technique of processing radiation-induced colloids in LiF crystals increases the dimensions of the metal particles, while their shape becomes more spheroidal<sup>[12]</sup>. After heat treatment, the line width of the PRCE at room temperature decreased to  $\sim 70$  mG. This sample was used as the object for the measurements of the CESE.

An estimate of the average dimension of the particles was obtained from the asymmetry of the shape of the PRCE line at temperatures of 77 and  $300^\circ\text{K}$  (Fig. 1). For metallic samples with dimensions  $d \sim \delta$  ( $\delta$  is the depth of the skin layer at the working frequency of the measurements), the observed PRCE line shape is described by the expression  $A\chi' + B\chi''$ , where the weighting coefficients A and B are functions of  $d/\delta$ <sup>[13]</sup>. An estimate based on the data of the preceding paper<sup>[13]</sup> yielded for the metal-particle diameter in our samples  $d = 1.2 \pm 0.2 \mu$ .

**B. Measurement technique.** The spin-echo measurements were performed in a three-centimeter relaxometer<sup>[14]</sup> using the two- and three-pulse procedure with the aid of  $\sim 3$  kW sounding pulses and a minimum time shift  $\sim 0.3 \mu\text{sec}$  at fixed temperatures 77, 300, and  $410^\circ\text{K}$ .

The stationary PRCE signals were studied with a BER-418S three-centimeter radiospectrometer at temperatures 4.2, 77, and  $100\text{--}500^\circ\text{K}$  with continuous determination of the magnetic field by means of a NRM pickup, satisfying the usual requirements for correct

registration of very narrow EPR lines<sup>[15]</sup>. Experiments on continuous saturation of the stationary line were performed at room temperatures.

Registration of PRCE signals of width  $\delta H \leq 100$  mG revealed a change in the working frequency during the instant when the line was recorded, leading to an appreciable narrowing of  $\delta H$ . Thus, at room temperature the apparatus width observed in our samples was  $\approx 30$  mG. The variation of the frequency of the klystron, which was stabilized against a high-Q resonator by means of a rigid automatic frequency control system, duplicated the waveform of the dispersion  $\chi'$  of the sample. Consequently, this frequency change can be attributed to the reactive contribution made to the total impedance of the resonator by  $\chi'$ .

During recording of the resonance signal in our experiments, we continuously measured the klystron frequency and correct width measurements were made with allowance for the deviation of the working frequency<sup>2)</sup>.

### 3. RESULTS AND DISCUSSION

**A.** The total picture of the response of the spin system of the electrons to three sounding microwave pulses applied at the instants  $t = 0, \tau_1$ , and  $\tau_2$  is shown in Fig. 2. At  $t = 2\tau_1$  and  $t = \tau_1 + \tau_2$ , the signals of the fundamental and stimulated spin echo are produced, followed by three secondary echoes.

| Temperature, $^\circ\text{K}$ | Relaxation time, $10^6$ sec |                |                |               |
|-------------------------------|-----------------------------|----------------|----------------|---------------|
|                               | $T_1$                       | $T_2$          | $T_2'$         | $T_1'$        |
| 77                            | —                           | $0.7 \pm 0.2$  | $0.5 \pm 0.2$  | —             |
| 300                           | $1.06 \pm 0.15$             | $1.03 \pm 0.1$ | $0.95 \pm 0.1$ | $1.0 \pm 0.3$ |
| 410                           | $0.7 \pm 0.3$               | $0.75 \pm 0.2$ | $0.76 \pm 0.1$ | —             |

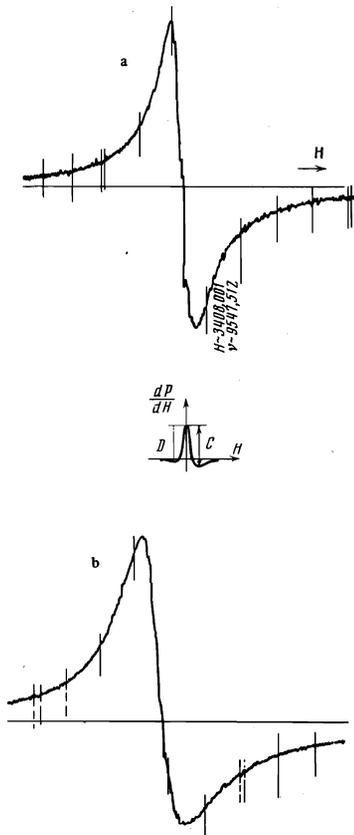


FIG. 1. Shape of stationary PRCE line: a—at  $T = 300^\circ\text{K}$  ( $C/D \approx 1.85$ ); b—at  $T = 77^\circ\text{K}$  ( $C/D \approx 1.55$ ).

The fall-off of the amplitudes of the fundamental and stimulated echoes following variation of the time intervals  $\tau_1$  and  $\tau_2$  was exponential within the limits of errors, in agreement with expressions (10)–(12). Thus, measurements of the damping of the echo amplitudes make it possible to determine independently the relaxation times  $T_1$  and  $T_2$  of the longitudinal and transverse components of the spin magnetization of the electrons.

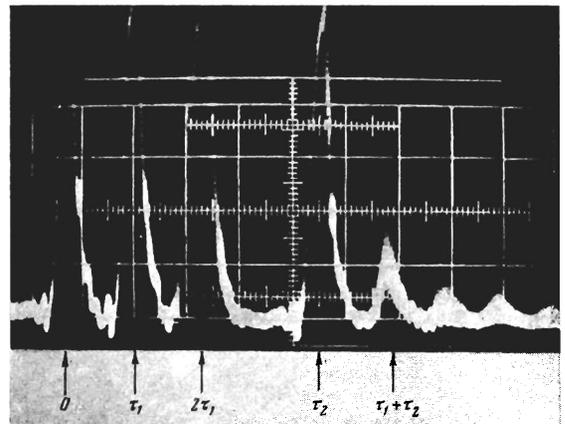


FIG. 2. Oscillogram of signals of the fundamental ( $2\tau_1$ ) and stimulated ( $\tau_1 + \tau_2$ ) spin echoes of the conduction electrons in lithium at room temperature. Time scale  $0.2 \mu\text{sec}$  per division.

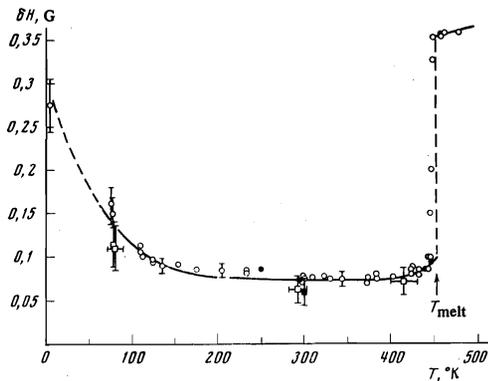


FIG. 3. Temperature dependence of the line width obtained from measurements of the stationary paramagnetic absorption and from the damping of the spin-echo signals:  $\circ$ —PRCE,  $\square$ —CESE.

The values of  $T_1$  and  $T_2$  averaged over seven measurements are listed in the table, which gives also the values of the relaxation times obtained from the measurements of the stationary-line width ( $T_2'$ ) and from experiments on saturation of the PRCE line ( $T_1'$ ).

The question of the ratio of the spin-relaxation times for the conduction electrons was considered theoretically by Andreev and Gerasimenko<sup>[16]</sup>, who found that the equality  $T_1 = T_2$  should be satisfied in isotropic metals. As follows from the table, our results are a direct confirmation of this important premise of the theory.

B. Figure 3 shows the temperature dependence of the line width, as obtained from measurements of the stationary PRCE and CESE (in the latter case, the value of  $\delta H$  was recalculated from  $T_1$  for a Lorentz line shape). The temperature dependence obtained by both methods for the line width are in good agreement, and the absolute width of the stationary line exceeds the corresponding values obtained from the CESE experiments by  $\sim 10\%$ . This broadening is connected with the random scatter in the value of the constant magnetic field, which, as is well known, makes no contribution to the damping of the echo signals. At the lithium melting temperature  $T_{\text{melt}} \approx 453^\circ\text{K}$ , the width of the stationary line experiences the discontinuity usually observed on going into the liquid phase. Owing to the strong shortening of the relaxation time, no quantitative measurements of CESE could be made above  $T_{\text{melt}}$ .

Owing to the small particle dimensions and the high purity of the metal, one should expect the effective spin relaxation rate of the conduction electrons to receive an appreciable contribution from the mechanism of inelastic scattering of the spin by the surface of the metal. At the same time, the average particle dimension is much larger than the mean free path  $\lambda$  ( $\lambda \approx 1.1 \times 10^{-6}$  cm for lithium at  $T = 273^\circ\text{K}$ ), and therefore the orbital motion of the electrons between two successive collisions with the surface has a diffusion character. Then the surface-relaxation mechanism, as shown in Sec. 1, makes an additive contribution

$$\delta H_s \approx \alpha \lambda(T) \quad (13)$$

to the total line width.

To identify the possible relaxation mechanisms it is convenient to represent the temperature dependence of the line width in accordance with formula (13) as the function  $\lambda(T)$  shown in Fig. 4. As seen from Fig. 4, the experimental points fit well the straight line  $\delta H(T)$

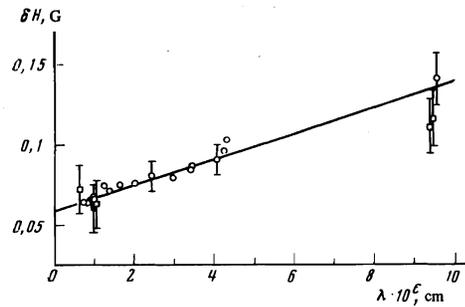


FIG. 4. Line width as a function of  $\lambda$  (the values of  $\delta H$  for the stationary PRCE have been decreased by 10 mG, which corresponds to the inhomogeneity of the constant magnetic field).

$= c_1 + c_2 \lambda(T)$ . Since we know of no other mechanism of electron spin relaxation capable of producing a temperature dependence in the form  $\delta H = \text{const} \cdot \lambda(T)$ , it is natural to attribute the entire temperature dependence of  $\delta H$  to surface relaxation. We then can determine from the experimental values of the constant  $c_2$ , with the aid of expression (11), the probability of electron spin reorientation in collisions with the surface, namely  $\epsilon = (5 \pm 2) \times 10^{-6}$ . The temperature-independent part of the line width, which equals  $c_1 \approx 60$  mG, is connected with the paramagnetic relaxation of the spins in the interiors of the metallic particles.

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$$*[\mu H] = \mu \times H.$$

<sup>1</sup>This is apparently the reason why Taylor et al.<sup>[1]</sup> were unable to perform quantitative measurements of CESE.

<sup>2</sup>We note that observations of the narrowest lines  $\approx 30$  mG in radiation-induced lithium colloids<sup>[12]</sup> is apparently connected with this effect.

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