Electron spin resonance line shape and kinetic parameters of the conduction electrons in highly anisotropic conductors: highly oriented pyrolytic graphite

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Experimental results are presented for the ESR line shape of the conduction electrons in plates of highly oriented pyrolytic graphite and the dependence of the line shape on the dimensions of the sample and on the experimental conditions. A new procedure is developed for analyzing the ESR line shape of conduction electrons in graphite plates, which takes into account the induced nonuniformity of the microwave field near the surfaces of the plates. The ESR data are used to determine the kinetic parameters of the spin and current carriers parallel and perpendicular to the carbon layers and to estimate the density of states at the Fermi level.

The method of ESR of conduction electrons has been actively used in studies of graphite[1–7] and graphite intercalation compounds.[8–15] The method is mainly used for determining the kinetic parameters of the spin carriers in these systems from an analysis of the ESR line shape[1,2,5,8–14] and for determining more accurately the electronic structure near the Fermi level.[3,4,6,7] For a long time the analysis of the ESR line shape of the conduction electrons for the graphite itself[1–7] and its intercalated compounds[8–12] have been carried out using the well-known theory of Dyson[16] and Kaplan[17] by the standard methods of Feher and Kip,[18] Kodera,[19] and of Pifer and Magno.[20] However, in a strict sense, Dyson's theory of the ESR of conduction electrons is applicable only for infinite metal plates of arbitrary thickness with isotropic conductivity and a single carrier type. Although experiments have shown the validity of using this theory for analyzing the ESR line shape of conduction electrons in metal plates with finite dimensions,[18–20] it is not obvious that it can be applied to low-dimensional conductors with strong conductivity anisotropy, in particular to graphite and its acceptor-type intercalation compounds, in which the ratio of the conductivity parallel and perpendicular to the carbon layers is $(1-3)\cdot 10^3$ (Refs. 21 and 22) and $\sim 10^5$ (Refs. 23 and 24), respectively.

In this paper we present experimental results for the dependence of the ESR line shape for conduction electrons in highly oriented pyrolytic graphite on 1) the sample dimensions, 2) the mode of the microwave field, 3) the orientation of the external static magnetic field $\mathbf{H}_0$ relative to the c axis of the graphite, and 4) the temperature. We have analyzed the nature of the interaction between the microwave field modes usually used with plates of this quasi-two-dimensional conductor. The values of the kinetic parameters of the spin and current carriers have been analyzed according to the procedure described in this paper from the ESR line shape of the conduction electrons perpendicular and parallel to the carbon layers. Data have been obtained relative to the nature of the conductivity along the c axis and the density of states at the Fermi level.

1. EXPERIMENTAL METHOD

The experiments on the ESR line shape of the conduction electrons of graphite were performed in the X-band microwave field in a rectangular (or cylindrical) cavity with the TE_{102} (H_{011}) mode. The configuration of the electromagnetic field, the orientation of the electric $\bar{\mathrm{E}}$, and the magnetic $\bar{\mathrm{H}}$ components of the microwave field, the Poynting vector $\bar{\mathrm{P}}$, and the modulated magnetic fields $\bar{\mathbf{H}}_m$ and $\mathbf{H}_0$ in the unloaded rectangular and cylindrical cavities, respectively, relative to the graphite plates are shown in Figs. 1 a and b. In both cases $\mathbf{H}$ is parallel to the vertical axis of the cavity. The effect of the frequency of $\bar{\mathbf{H}}_m$ on the ESR line shape of the conduction electrons was studied for frequencies of 2.5, 10, and 100 kHz.

All the plates needed for the experiments were cut from a single sample of pyrolytic graphite with a conductivity of $(1.2\pm 0.2)\cdot 10^4$ S/cm, and they were in the shape of rectangular parallopipeds with the dimensions width $(l)\times$height (h) $\times$thickness (d), where $h\times l$ is the area of the basal face. The basal conductivity was determined by a non-contact induction measurement of the electrical conductivity on a setup similar to the one used in the work reported in Ref. 25. The accuracy in the determination of the dimensions was $\simeq 5\cdot 10^{-4}$ cm.

The plates were fastened by the basal face on the planar surface of the goniometer rod, which was cut along its axis so that two of the side faces of the plate $(h\times d)$ were parallel to the given axis (and to $\bar{\mathrm{H}}$). With the plates fastened this way, their c axis lay in a horizontal plane. The samples were placed in the antinode of $\bar{\mathrm{H}}$.

The temperature studies of the ESR spectra of the conduction electrons of the graphite plates were carried out in the rectangular cavity in the temperature range from 100 to 600 K. The temperature was varied by regulating the rate and temperature of a nitrogen gas flow through the quartz dewar with the sample. The temperature was maintained with an accuracy of ~0.1 deg/h.

2. EXPERIMENT

At 300 K the graphite plates gave a conduction-electron ESR spectrum with an angular dependence axially symmet-

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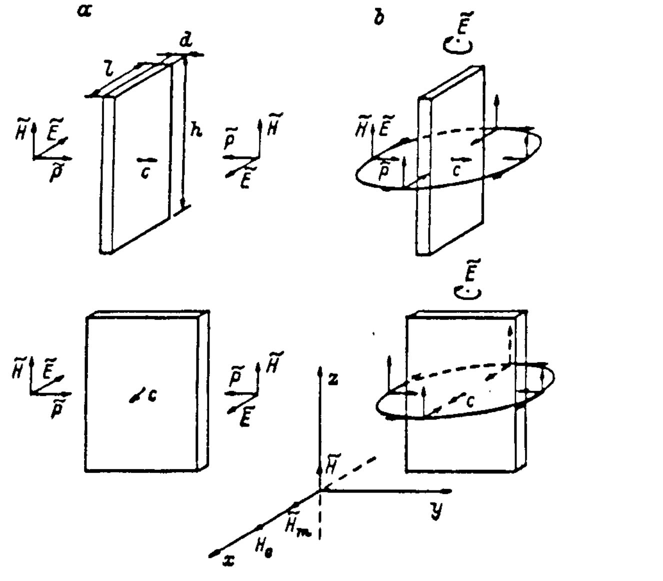

FIG. 1. Orientation of the vectors of the external static magnetic field H_0, the modulating magnetic field $\tilde{H}_m$, the electric field $\tilde{E}$ and magnetic field $\tilde{H}$ components of the microwave field, and the Poynting vector $\tilde{P}$ in an unloaded rectangular cavity (a) and in a cylindrical cavity (b) relative to a graphite plate with the geometric dimensions width (l)×height (h) ×thickness (d). The upper and lower figures refer, respectively, to H_0 perpendicular and parallel to c.

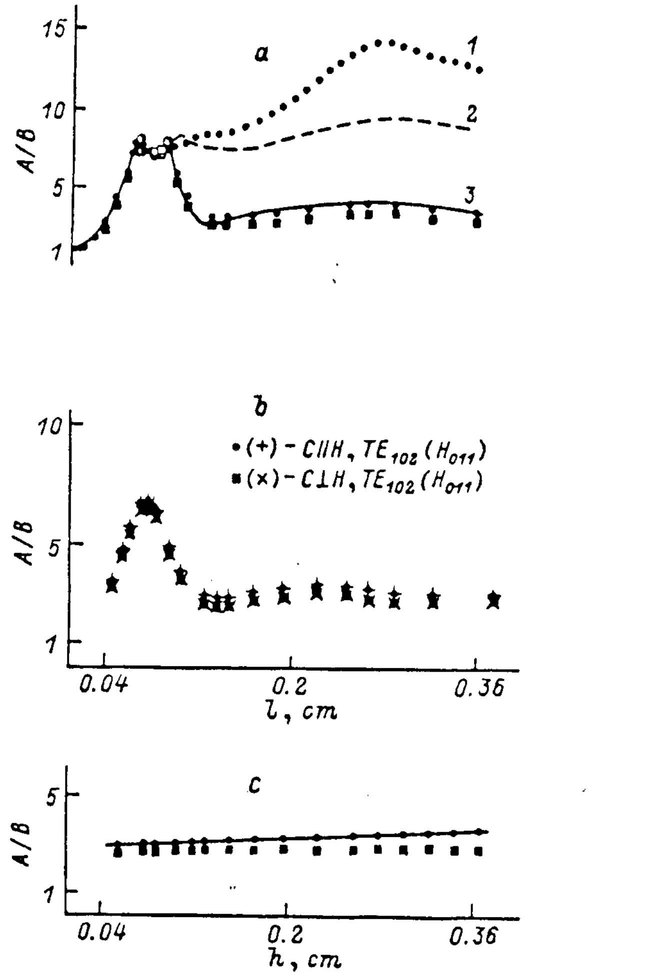

FIG. 2. Dependence of the asymmetry parameter A/B of the ESR line of graphite plates as a function of l (a,b) and h (c). Curves a and c refer to thick samples with the dimensions $l\times 0.355\times 0.072$ cm and $0.260\times h\times 0.072$ cm, respectively. Curve b refers to thin plates with dimensions $l\times 0.355\times 0.035$ cm. The shaded, open, and half-shaded points refer to the form of the line, respectively, normal, inverted, and with symmetric phase relative to the A peak. $\nu=9.52$ GHz and $T=300$ K. Curve 1 in the upper figure was calculated from the line shape equation of Dyson[16] with $R=0.2$. Curves 2 and 3 were calculated from the line shape equation (1) with $R_a=0.2$, $R_c=2$, and $T_2=1.42\cdot 10^{-8}$ s, respectively, for a uniform ($k=1$) and nonuniform (with k given by Eq. (2)) distribution of $\tilde{H}$ over the sample. The solid curve in the lower figure was calculated from the line shape equation (1) with $R_a=0.2$, $R_c=2$, $T_2=1.42\cdot 10^{-8}$ s, and k given by Eq. (2).

ric relative to the c axis. The principal values of the g tensor of the conduction-electron ESR spectrum of the plate with the largest dimensions l and d were determined by the Feher–Kip nomogram[18] or that of Kodera,[19] and were equal to $g_{\parallel}=2.0474\pm 0.0002$, and $g_{\perp}=2.0029\pm 0.0002$. For all orientations of the c axis relative to H_0 the asymmetry parameter A/B of the first-derivative ESR absorption line of the conduction electrons in this plate, equal to the ratio of the peak intensity of the more intense wing, A, to that of the less intense wing, B, was higher than 2.55, which is the value characteristic of localized spins in an isotropic metal.[18–20] The line shape is "normal" in the sense that the A peak is located in lower magnetic fields than the B peak. The integrated signal intensity calculated by the formula

$$I=(A+B)\Delta H^2,$$

where ΔH is the width at half-height of the A peak, depends only weakly on the orientation of the plate relative to H_0, and, in particular, for H_0 perpendicular and parallel to c in the two cavities the intensities are in the ratio 10:11.

In the rectangular and in the cylindrical cavity the qualitative shape of the curves of $A/B(t)$ ($t=l$, h, or d) does not depend on the orientation of the c axis relative to H_0 (Figs. 2 and 3). From the nature of the function $A/B(l)$, plates with different values of d can be provisionally divided into "thick" plates ($d>0.045$ cm) and "thin" ones ($d<0.045$ cm). A three-peak curve of $A/B(l)$, typical of the thick plates is shown in Fig. 2a. In the interval $l_{1m}<l<l_{2m}$, where $l_{1m}(l_{2m})$ is the coordinate of the first (second) peak (here and below first and second mean from the direction of smaller l) the line has an inverted line-shape phase—the A peak is located at a higher magnetic field than the B peak. At l_{1m} and l_{2m} the line is symmetrical about the A peak, and the value of A/B is a maximum. The third, weak maximum with the coordinate l_{3m} is not associated with a change of the phase of the line shape. As $l\rightarrow 0$ the line tends to a Lorentzian shape.

The two-peak shape of $A/B(l)$ typical of the thin plates is shown in Fig. 2b. These plates have no region with an inverted phase of the line shape. The coordinate of the first peak is between l_{1m} and l_{2m} of the thick plates. The coordinate of the second peak is somewhat below l_{3m} of the thick plates.

For constant d and l the dependence $A/B(h)$ for $h\rightarrow 0$ tends to a value greater than 2.55 that depends on d and l

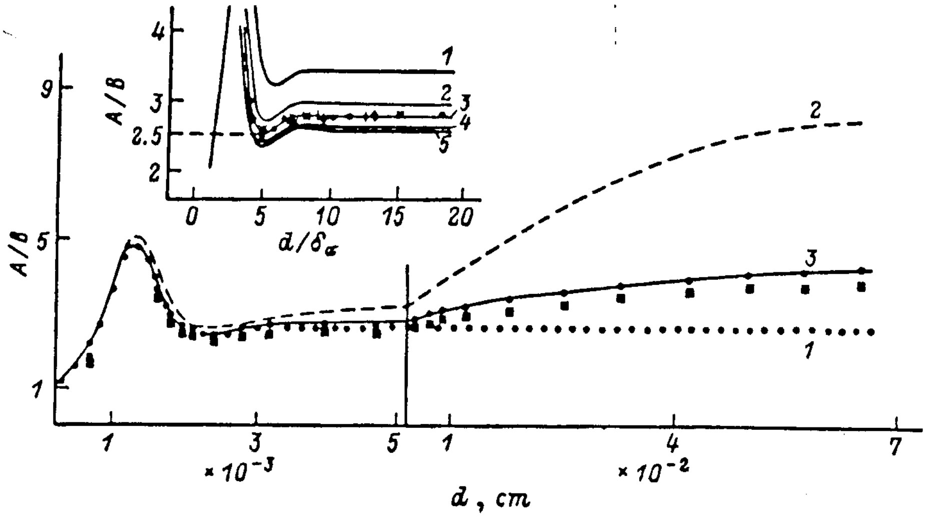

FIG. 3. Dependence on d of the asymmetry parameter A/B of the ESR line of a graphite plate of dimensions $0.262\times0.351\times d$ cm. Curve 1 in the upper figure was calculated from the line shape equation of Dyson[16] with $R=2$. Curves 2 and 3 were calculated from the line shape equation (1) with $R_a=0.2$, $R_c=2$, and $T_2=1.42\cdot10^{-8}$ s, respectively, for a uniform ($k=1$) and nonuniform [with k given by Eq. (2)] distribution of $\tilde{H}$ over the sample. The inset shows the theoretical curves of $A/B(d/\delta_a)$ calculated from the Dyson line shape equation[16] for various R in the region of the minimum of the corresponding experimental curve. The calculated geometrical figures correspond to the data of various experiments for H_0 perpendicular to c. $R=1(1)$, $1.5(2)$, $2(3)$, $3(4)$, and $4(5)$, with $\nu=9.52$ GHz and $T=300$ K.

with a normal line-shape phase. The form of the function $A/B(h)$ typical of the plates is shown in Fig. 2c.

For constant l and h, the function $A/B(d)$ for $d\to0$ at first decreases, then reaches a minimum, 2.5 ± 0.1, at $d_m^*=2.5\cdot10^{-3}$ cm (Fig. 3). The subsequent variation of A/B suggests that there is a peak in $A/B(d)$ at about $d_m=1.3\cdot10^{-3}$ cm, which is the average of the thicknesses of the first two samples (here and below, first and second mean from the direction of smaller d). The line-shape phase is normal for all the plates.

The coordinates of all the peaks of $A/B(l)$ are temperature dependent. Figure 4 shows the results of an investigation of the temperature dependence of the coordinate l_{1m} of the first peak for the thick plates with the same d and h and widths rather greater or less than l_{1m} at 300 K. The conduction-electron ESR line shape, symmetrical relative to the A peak for these plates, was determined by variation of the temperature.

When $l(d)$ decreases to $l_{2m}(d_m^*)$ the value of ΔH remains constant within experimental error regardless of the orientation of $\mathbf{H}_0$ relative to the c axis (Fig. 5). A further decrease in $l(d)$ results in some increase in ΔH, which can be explained by the transformation of the line shape to a Lorentzian.

The influence of the configuration of the microwave field on the conduction-electron ESR line shape was studied in the rectangular and cylindrical cavities with the thin samples. For the same temperature and the same placement of the plates relative to $\tilde{\mathbf{H}}$ and $\mathbf{H}_0$, the line shape parameters of the conduction-electron ESR spectra were the same for all the plates in the two cavities (Figs. 2b and 5). We note that the presence of a weak angular dependence of A/B and l on the orientation of the plates relative to $\mathbf{H}_0$ and in the cylindrical cavity means that the cause of these dependences is the interaction of the electron subsystem of the graphite with $\mathbf{H}_0$, and not with the microwave field. The frequency of $\tilde{\mathbf{H}}_m$ and the amplitude of $\tilde{\mathbf{H}}$ had no observable effect on the conduction-electron ESR line shape.

3. DISCUSSION

The current carriers in graphite are electrons and holes, which have similar concentrations and mobilities.[21-24] How-

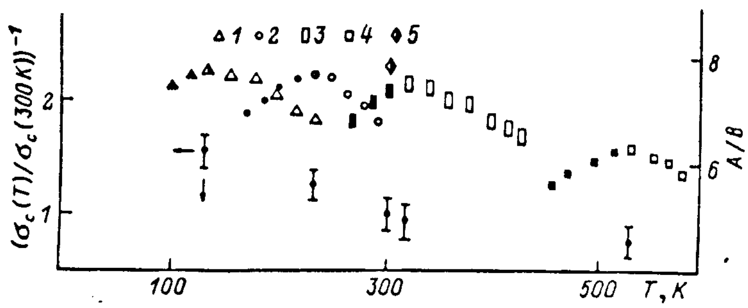

FIG. 4. Temperature dependence of the asymmetry parameter A/B of the ESR absorption line (1–5) and the ratio $(\sigma_c(T)/\sigma_c\times(300\ \text{K}))^{-1}$ of graphite plates with dimensions $(l_{1m}+\delta l)\times0.405\times0.072$ cm. $\sigma_c=7.7$ S/cm is the conductivity along the c axis at 300 K, $l_{1m}=0.061$ is the coordinate of the first peak at 300 K. The sets of points 1–5 are for plates with δl equal, respectively (in units of 10^{-2} cm), to 1.07, 0.81, −0.32, −1.12 and 0. The shaded, open, and half-shaded points refer, respectively, to the normal, inverted, and symmetric line shape phase relative to the A peak. $\mathbf{H}_0$ parallel to c, $\nu=9.52$ GHz.

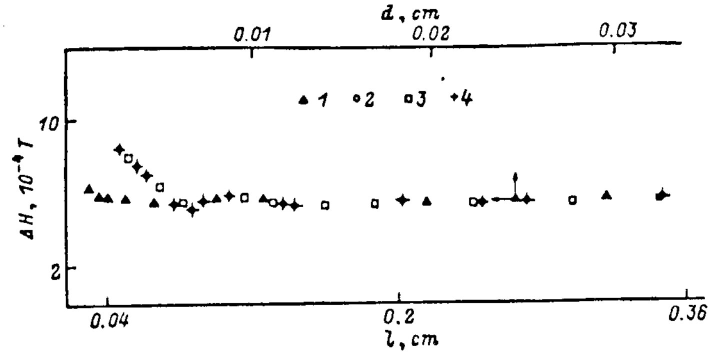

FIG. 5. Half-width at half-height ΔH of the A peak of the first-derivative ESR absorption line as a function of d (1) and of l for thick graphite plates (2) and thin graphite plates (3,4) with dimensions $0.247 \times 0.338 \times d$; $l \times 0.338 \times 0.075$, and $l \times 0.338 \times 0.035$ cm in a rectangular cavity (1–3) and cylindrical cavity (4).

ever, on the ESR time scale the electrons and holes are not resolvable because of the complete dynamic averaging of the electron and hole states.[1–7] This means that in an ESR experiment we can regard graphite as a conductor with only a single type of carrier.

If the electron mean free path in isotropic metals with a single type of current carrier is much shorter than the skin depth δ (the so-called normal skin effect), then the skin depth is related to the conductivity σ at a particular frequency by the well-known relation $\delta = c/(2\pi\sigma\omega)^{1/2}$, where c is the velocity of light. Figure 6 shows a family of curves relating the asymmetry parameter A/B of the conduction-electron ESR line to the thickness L divided by the skin depth δ of a metallic plate for various values of the ratio $R = (T_D/T_2)^{1/2}$ (where T_D is the spin diffusion time across the skin depth δ, and T_2 is the spin-lattice relaxation time) which we have calculated for this case starting from the equation for the Dyson line shape $F(\sigma, T_2, R, L)$ (Ref. 16) and have used in the interpretation of the experimental data shown in Fig. 6. These curves can be provisionally divided into two groups. The first group contains the curves with $R < 0.55$, which corresponds to spins that diffuse rapidly on the ESR time scale. These curves have the three-peak shape of the curve $A/B(L/\delta)$ with the region of inverted line shape phase for values of L/δ between the coordinates of the first two peaks and for higher values of L/δ goes to a plateau with $A/B > 5$. It should be noted that for these curves the coordinate of the first peak does not depend on R and is equal to π. The curves with $R > 0.55$ belong to the second group, which corresponds to slowly diffusing spins on the ESR time scale. These curves of $A/B(L/\delta)$ have the same shape, and for large values of L/δ also emerge to a plateau with $2.55 < A/B < 5$. For $L \to 0$ these curves pass through a minimum that precedes a peak. Beginning with $R > 2$ the value of A/B at the minimum lower than 2.55 is attained for $L/\delta = 5$ and then a maximum lower than 5.1 at $L/\delta = 2.72$.

In the cylindrical cavity with the H_{011} mode, when the sample perturbs only weakly the configuration and the density of the lines of force of the unloaded cavity, the microwave field must be absorbed through all the faces that are parallel to $\tilde{\mathbf{H}}$ (Fig. 1b). The ratio of the contributions to the resonance from regions near the different faces cannot depend on the orientation of the c axis relative to $\mathbf{H}_0$. For the rectangular cavity with the TE_{102} mode and the same assumptions as above the microwave field with $\mathbf{H}_0$ parallel (perpendicular) to c will not be absorbed through the faces perpendicular (parallel) to c (Fig. 1a). However, from the facts that 1) the coordinates of the peaks and the shape of the function $A/B(t)$ ($t = l$ and d) are the same in the rectangular cavity for $\mathbf{H}_0$ parallel and perpendicular to c (Figs. 2a and 3) and 2) the function $A/B(l)$ is the same in the rectangular cavity as it is in the cylindrical cavity, (Fig. 2b), and 3) the value of l depends only weakly on the orientation of the plate relative to $\mathbf{H}_0$, we can conclude that in the loaded cavity the structure and density of the lines of force of the microwave field near the plate do not depend on the density or configuration of the lines of force of the microwave field of the unloaded cavity at the boundary of a fictitious plate with the same dimensions located in the same place in the cavity as the irradiated plate, but are determined mainly by the

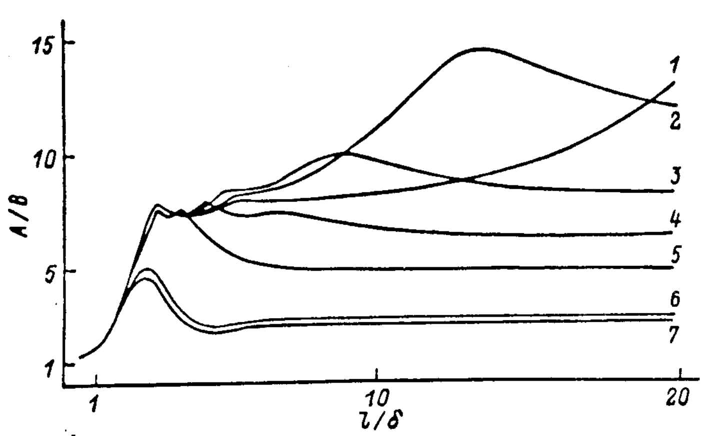

FIG. 6. Theoretical curves of the asymmetry parameter A/B of the ESR lines of mobile spin carriers as a function of the plate thickness l normalized to the skin depth δ for various values of $R = (T_D/T_2)^{1/2}$, calculated from the Dyson line shape equation.[15] R = 0.1 (1), 0.2 (2), 0.3 (3), 0.4 (4), 0.55 (5), 2.0 (6), 4.0 (7).

properties of the sample itself. From this discussion it also follows that there is no *a priori* justification to regard **H** near the vertical faces of the graphite plate as uniform.

The existence of regions with an inverted line-shape phase and the third peak of the experimental curves of $A/B(l)$ for the conduction-electron ESR lines (Fig. 2a) are characteristic features of the theoretical curves of $A/B(L/\delta)$ for rapidly diffusing spins (Fig. 6). Consequently for this series of plates we can use the ratio $l_{1m}/\delta_c=\pi$, from which we find $\delta_c=(1.94\pm0.02)\cdot10^{-2}$ cm and $\sigma_c=7.7\pm0.15$ S/cm. This value for the conductivity correlates well with that for graphite plates along the c axis ($\simeq$ 7 S/cm), as determined by four-point-probe measurements of the electrical conductivity.[26] Therefore σ_c can be identified as the conductivity of the plates along the c axis. Then, taking into account the weak effect of the height of the plates on the conduction-electron ESR line shape and also the lack of any dependence of l_{1m} on the orientation of the c axis with respect to $\mathbf{H}_0$, we can assume that for $l<l_{1m}$ the microwave field is absorbed by the plates mainly through the faces that are parallel to the c axis and to $\mathbf{H}$. In this case the conduction-electron ESR line shape of the plates with $l<l_{1m}$ in the first approximation must be described by the one-dimensional Dyson formula[16] for $F'(\mu_c, T_2, R_a, l)$ where $R_a=(T_{Da}/T_2)^{1/2}$ and T_{Da} is the spin diffusion time along the basal plane across the skin layer δ_c, which is determined by the conductivity σ_c.

The absence of an experimental dependence of A/B on d for the third peak and for $d\rightarrow0$ the existence of a minimum with $A/B=2.5$ (Fig. 3) preceding the peak are characteristics of slowly diffusing spins (Fig. 6). Therefore for this series of plates we can use the relation $d_m^*/\delta_a=5$ and $d_m/\delta_a=2.72$. From the first relation we find $\delta_a=(5\pm0.6)\cdot10^{-4}$ cm and $\sigma_a=(1.2\pm0.3)$ S/cm and from the second $\delta_a=(4.8\pm0.6)\cdot10^{-4}$ cm and $\sigma_a=(1.3\pm0.3)\cdot10^4$ S/cm. As we see, the values of σ_a are close to the conductivity along the basal plane of the initial graphite plate, while $\sigma_a/\sigma_c\simeq1.6\cdot10^3$ is of the same order of magnitude as the published data for the anisotropic conductivity of pyrolytic graphite.[21,22] These results allow us to identify σ_a as the conductivity of the samples along the basal plane. Then, on the basis of arguments similar to those used in the analysis of $A/B(l)$ we can conclude that the microwave field is absorbed by the graphite plates with $d<d_m$ primarily through the basal face regardless of their orientation relative to $\mathbf{H}_0$. This means that the conduction-electron ESR line shape for plates with $d<d_m$ in the first approximation must be described by Dyson's one-dimensional formula for $F''(\sigma_a, T_2, R_c, d)$ (Ref. 16), where $Rc=(T_{Dc}/T_2)^{1/2}$ and T_{dc} is the spin diffusion time along the c axis through the skin layer, which is determined by the conductivity σ_a.

If we allow for the well established fact that the microwave field is absorbed in the rectangular cavity through all the vertical faces of the graphite plate for $d<d_m^*$, we can explain the observed increase of A/B (Fig. 3) as well as the theoretically expected plateau (Figs. 3 and 6) for slowly diffusing spins by the increased contribution to the resonance from regions near the vertical faces parallel to the c axis with increasing d. In a similar way, the discrepancy between the values of $A/B(l)$ observed for $l>l_{2m}$ and the theoretically expected values for rapidly diffusing spins (Figs. 2 and 6) can be explained by the increasing contribution to the resonance from regions near the basal planes with increasing l. Finally, the lack of any thin plates having an inverted line shape phase for samples with $l\rightarrow0$ obviously indicates that they give a contribution to the resonance from the regions near the basal planes that is greater than the contribution from the thick plates.

Taking into account the results of the qualitative analysis of the experimental data, we carried out a quantitative analysis of the conduction-electron ESR line shape for graphite plates within the framework of a model of two independent electromagnetic plane waves incident on the different vertical faces of the graphite plates in the form of parallelopipeds with the c axis lying in the horizontal plane. The magnetic fields of the microwaves are absorbed by the plates oriented parallel to the vertical edges of the plates. The observable conduction-electron ESR signal with the line shape described by the equation for $F(\sigma_c, \sigma_a, R_a, R_c, T_2, l, d, k^2=c_1^2/c_2^2)$ was regarded as the result of the sum of the signal due to the electromagnetic wave incident only on the vertical faces parallel to the c axis and described by Dyson's one-dimensional formula $F'(\sigma_c, R_a, T_2, l)$ plus the signal due to the wave incident only on the vertical faces perpendicular to the c axis and described by Dyson's one-dimensional formula for $F''(\sigma_a, R_c, T_2, d)$

$$F(\sigma_c, \sigma_a, R_a, R_c, T_2, l, d, k^2=c_1^2/c_2^2)$$
$$=c_1^2dF'(\sigma_c, R_a, T_2, l)+c_2^2lF''(\sigma_a, R_c, T_2, d), \quad (1)$$

where the coefficients c_1 and c_2 satisfy the relation $c_1^2+c_2^2=1$ and reflect the different average values (the nonuniformity) of $\bar{\mathbf{H}}$ over the faces with different conductivity. Since the functions F' and F'' are normalized to unit area, each of them on the right-hand side of Eq. (1) is multiplied by the dimensional parameter corresponding to the side on which the wave is incident. It is clear that this solution of the two-dimensional problem as a sum of two one-dimensional Dyson solutions is valid only when the contribution to the resonance from the regions of overlap of mutually perpendicular waves is much less than the contribution from the remaining regions; i.e.,

$$\delta_a\delta_c\ll1/2\cdot[k(d-2\delta_a)\delta_c+k^{-1}(l-2\delta_c)\delta_a].$$

To approximate the line shape for the conduction-electron ESR spectra of graphite plates by means of Eq. (1) we use instead of σ_c and σ_a their values determined previously from the relations $l/\delta_c=\pi$ and $d_m^*/\delta_a=5$. The bare value of R_a in Eq. (1) was taken equal to 0.2 which is the value R of the one-dimensional theoretical curve of $A/B(l/\delta_c)$ for which the third peak coincides with l_{3m} for the thick plates (Fig. 2a). We note that this method of estimating R_a is different from that ordinarily used in calculating with the Feher–Kip nomogram[18] or that of Kodera,[19] being based on the value of A/B for the conduction-electron ESR lines for the plates with $l\gg l_{2m}$. The bare value of R_c in Eq. (1) was assumed to be equal to 2, which is the value of R_c of the one-dimensional theoretical curve of $A/B(d/\delta_a)$, which de-

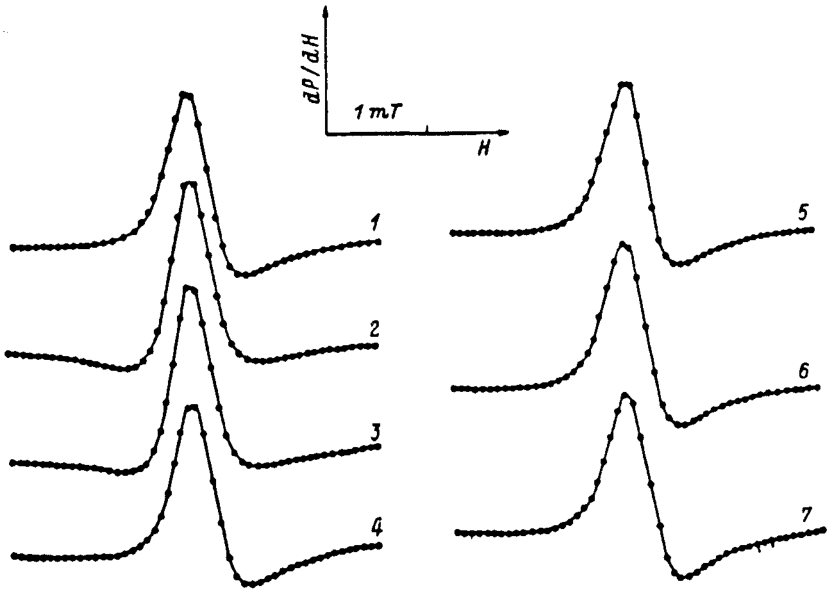

FIG. 7. A comparison of the experimental line shapes (solid lines) and the theoretical line shapes (points on the lines) for the first-derivative ESR absorption spectrum of graphite plates with dimensions $l \times 0.355 \times 0.075$ cm (1–4) and $0.355 \times 0.246 \times d$ cm (5–7). The theoretical curves were calculated from the line shape equation (1) with $R_a = 0.22$, $R_c = 4$, $T_2 = 1.3 \cdot 10^{-8}$ s and k given by equation (2). The experimental spectra 1–4 and 5–7, respectively refer to plates with $l = 0.288$, 0.083, 0.062 and 0.094 cm and $d = 0.065$, 0.031 and 0.015 cm. $H_{\parallel} \| c$, $\nu = 9.52$ GHz, $T = 300$ K.

scribes best the experimental data in the region of d_m^* (Fig. 3). The bare value of $T_2 = 1.42 \cdot 10^{-8}$ s was estimated from the relation

$$T_2^{-1} = (g_{\|}\beta/\hbar)\Delta H,$$

where β is the Bohr magneton and ΔH is the line width of the ESR spectrum of the conduction electrons for plates with $l > l_{2m}$ and $d > d_m$.

Then substituting into Eq. (1) the experimentally determined values of the parameters that enter into it, we varied k to make the ratio A/B for the theoretical line (1) coincide with the ratio for the experimental line. For constant l and h the same approximation of A/B of the plates with various values of d were possible with the same value $k = 0.45$. For constant d and h (or d and l) it was possible to approximate A/B for various values of l (or h) only by a different value of k for each $l(h)$. We note that the values of k calculated in this way for different l (h) can be approximated by functions of the form

$$K(l) = A\ \exp(-\alpha\lambda) + B\lambda^m + C\lambda + D, \tag{2}$$

$$(k(h) = A'h^n + B'), \tag{2'}$$

where

$$\lambda = l/\delta_c, \quad A = 9.79 \cdot 10^5, \quad B = 1.13, \quad C = -0.55,$$

$$D = -1.42, \quad \alpha = 3$$

and

$$m = 0.81 \quad (A' = 0.18, \quad B' = 0.38, \quad n = 0.8,$$

$$h - \text{ in cm}).$$

Substituting into (1) the value of k corresponding to the dimensions of the given plate, i.e., taking into account the contribution to the resonance from regions near all the vertical faces, we determined with greater accuracy the values of the parameters (the same for the series studied) $R_a = 0.22$, $R_c > 4$, and $T_2 = 1.3 \cdot 10^{-8}$ s, to which corresponds $T_{Da} = 6.3 \cdot 10^{-10}$ s and $T_{Dc} > 2.1 \cdot 10^{-7}$ s. The refined value of R_c is more than twice the bare value. However, for $R_c > 2$ A/B the lines depend only weakly on the value of this parameter and the values of A/B corresponding to $R_c > 4$ are less than the initial values by at most ~8% (Fig. 3). Finally, substituting into Eq. (1) the refined values of the parameters and the values of k corresponding to the dimensions, we calculated the theoretical ESR line shapes for the conduction electrons (Fig. 7). As we see, they are in good agreement with experiment. From these ideas concerning the interaction of the microwave field with the graphite plates it follows that the thick and thin samples are those for which, respectively, $d > k^{-2} l(\delta_a/\delta_c)$ and $d < k^{-2} l(\delta_a/\delta_c)$.

Because the microwave field is absorbed by the graphite plate through all the vertical faces that are parallel to $\bar{H}$, the use of the generally accepted procedure of Feher and Kip[18] or of Kodera[19] to analyze the ESR line shape of the conduction electrons for isotropic metals is incorrect and generates large errors. Moreover, the nonuniformity in $\bar{H}$ that appears about the vertical faces of the plates means that the analysis of the line shape cannot be done by the procedure suggested by Saint-Jean and Blinowski[13,14,27] either, since the latter is based on the assumption that the distribution of $\bar{H}$ is uniform near the sample and that the orientation of $\bar{P}$ is constant relative to the vertical faces of an intercalated graphite anisotropic conductor. Indeed, the values of the parameters R_a and T_{Da}, respectively, calculated using the Feher–Kip procedure[18] starting from the parameters of the conduction-electron ESR spectrum for the graphite plate with the largest values of l and d were equal, respectively, to 1 and $1.3 \cdot 10^{-8}$ s. With the assumption of a uniform distribution of H near the vertical faces of this plate the values of these parameters turned out to be 0.88 and $1 \cdot 10^{-8}$ s as obtained by a variation of R_a to fit the theoretical line shape given by expression (1) with $k = 1$ and $R_c > 4$ to the experimental line shape. As we see, the values of T_{Da} calculated by these two methods are more than an order of magnitude larger than those calculated by the procedure used in the present work (Figs. 2 and 3). It should also be noted that in the calculation of R_a without taking into account the nonuniformity of $\mathbf{H}$ near the vertical faces of the sample, its value depends on the dimensions of the plate. On the other hand, the calculations show that the values of the **g**-tensor calculated according to different published procedures[13,18] differ by less than 10^{-4} among themselves and from the values calculated with allowance for the nonuniformity of $\mathbf{H}$ near the vertical faces of the graphite plates.

From the results of the temperature dependence $l_{1m}(T)(=\pi\delta_c(T))$ (Fig. 4) it can be seen that as the temperature increases the conductivity along the c axis also increases; i.e., in this direction the graphite plates have a nonmetallic conductivity. Assuming that the transport is purely diffusional along the c axis, we can use the Dyson relation[16] for the diffusion constant $D=\delta^2/2T_D$ to estimate the spin diffusion constant in graphite along the c axis, $D_c=\delta_c^2/2T_{Dc}<0.4$ cm^2/s. We note that in the approximation of independent electrons we can, by analogy with D_c, also introduce the two-dimensional spin diffusion constant along the carbon layers, $D_a=\delta_a^2/2T_{Da}=5\cdot 10^5$ cm^2/s.

The diffusion constant is related to the mobility by the well-known Einstein relation $\mu=eD/kT$. In turn, the mobility is related to the conductivity by the relation $\sigma=Ne\mu$, that is, $\sigma=Ne^2D/kT$, where N is the number of current carriers per unit volume. In degenerate metals only the charge carriers in an interval $\sim kT$ at the Fermi level can hop from layer to layer. Consequently $N=N(E_F)kT$, where $N(E_F)$ is the density of states at the Fermi level, and $\sigma=N(E_F)e^2D$. From this last relation, when we substitute into it for σ and D the values of σ_c and D_c obtained in the ESR experiment, we find that in pyrolytic graphite the density of states at the Fermi level is $N(E_F)>1.1\cdot 10^{20}$ eV^{-1} cm^{-3}. This estimate of $N(E_F)$ correlates with the results of calculations of the density of electron states using measurements of the differential capacitance: $N(E_F)=2.5\cdot 10^{20}$ eV^{-1} cm^{-3} (Ref. 28).

In summary, the main result of this work is the experimental justification and application of a new procedure of analyzing the conduction-electron ESR line shape and calculating the kinetic parameters of the spin carriers in graphite plates. It may be supposed that the difficulties that arise in attempts to predict theoretically the configuration and density of the lines of force of the microwave field near the surface of a plate of an anisotropic conductor will in the future lead to an appreciation of the advantages of analyzing the ESR line shape of the conduction electrons by the method outlined in this paper.

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