TEMPERATURE DEPENDENCE OF CURRENT CARRIER'S SPIN RELAXATION IN GRAPHITE

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Introduction

The first systematic study of temperature dependences of graphite Conduction ESR (CESR) signal parameters was carried out as early as 1960 by Wagoner [1] using a natural single crystal specimen in the temperature range from 77 K up to 600 K. After Wagoner a number of authors [2-6] conducted similar studies on a variety of well-defined specimens of graphite, and have obtained nearly the same results. In particular, in all samples investigated and for all orientations of $\boldsymbol{H}_0$ relative to the $\boldsymbol{c}$-axis the graphite CESR signal linewidth increases first with decreasing temperature. According to the data of Matsubara *et al*. [5], the ?H(T)-dependence forms a distinct peak near 20 K and then falls off.

At present there is no consensus between researchers on both the graphite CESR linewidth and its temperature dependence origin. Kawamura *et al*. [4] showed that at $\boldsymbol{H}_0 \| \boldsymbol{c}$ the Elliot's [7] expression for the CESR linewidth due to carriers interacting with phonons and/or impurities, which for T>>?$_D$ (?$_D$ is Debye temperature) can be written as:

$$?H_i = const?(?g_i)^2/?m^*?(T) \quad \text{(i=a, c)} \qquad (1)$$

(?g_i=g_i-g_0 (i=a, c), where g_0 is the g-factor value for free electron, ? is the electronic gyromagnetic ratio, m* is the carriers effective mass, and *?(T)* is the carriers mobility), describes the graphite CESR linewidth in the interval 77?300 K qualitatively at least. Matsubara *et al*. [5] considered the temperature variation of graphite CESR linewidth at $\boldsymbol{H}_0 \|$***?*** as a direct consequence of motional narrowing effect through an averaging process of g-values of scattered carriers over the Fermi surface in the limit of incomplete line averaging. In this limit the g-shift is averaged over all energy states of current carriers in $\boldsymbol{k}$-space, but the linewidth contains the components which are proportional to the square of the microwave frequency. Kotosonov [3] pointed out that the small ?H values of the spectral lines suggest complete averaging of the g-factor over all the energy states of current carriers during the spin-lattice relaxation. Thus, for example, in synthetic graphite samples the temperature change from 40 K to 100 K leads to the g_c changing by ~0.2, which agrees with the resonance field shift by ~3?10^{-2} T, whereas the CESR linewidth remains within the limits of several oersteds.

According to the literature data [8, 9] the Debye temperature of graphite is nearly 400 K. Therefore the description of the graphite CESR linewidth temperature dependence by Exp. (1), proposed by Elliot for T>>?$_D$, is not obvious. Furthermore, this expression does not explain the presence of linewidth temperature dependence at $\boldsymbol{H}_0$? ***?*** even at a qualitative level since in this orientation of $\boldsymbol{H}_0$ the value of g_a does not depend on temperature. The independence of the CESR linewidth on the microwave frequency shows that Matsubara's *et al.* [5] interpretation of the linewidth temperature dependence as a result of the motional narrowing of the incomplete averaging line is not correct also. Besides, the presence of low-temperature peak in ?H(T) curve also at $\boldsymbol{H}_0$? ***?***, where g–factor is temperature independent, shows that the origins of low-temperature peaks in g_c(T) and ?H(T) dependences are different. The Kotosonov`s [3] point of view does not contradict to the experimental data, but he did not consider the nature of linewidth temperature dependence.

We have studied the dependences of CESR signal linewidth in highly oriented pyrolitic graphite (HOPG) on temperature and sample dimensions and have shown that all experimental data on CESR linewidth in graphite may be explained well, if the surface spin relaxation of current carriers is taken into consideration.

Experimental

CESR measurements were carried out using an X-band E-line spectrometer in a rectangular cavity with TE_{102} mode. The constant magnetic field ($\boldsymbol{H}_0$) modulation frequency and amplitude were 2.5 kHz and 0.1 mT, respectively.

All experiments were carried out on samples in the shape of rectangular parallelepipeds with the dimensions: width (l)?height (h)?thickness (d), where h?l is the area of the basal plane. At the experiments, the basal l×h and lateral d×h sides were parallel and the $\boldsymbol{c}$-axis was perpendicular to the magnetic component ($\boldsymbol{H}_{rf}$), of the microwave field (Fig. 1). Note, that in the rectangular resonator, the structure of electromagnetic field of TE_{102} mode has such a form that, at a conventional setting of the resonator, $\boldsymbol{H}_0$ is parallel to the electrical component ($\boldsymbol{E}_{rf}$) of microwave field (Fig. 1).

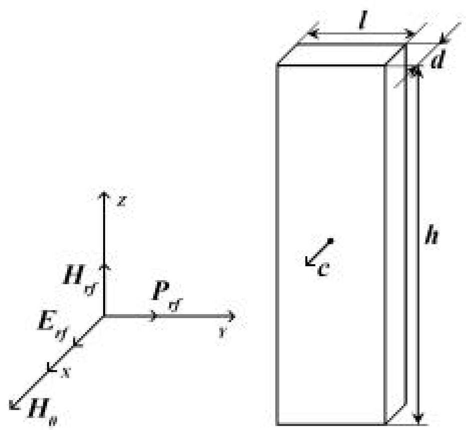

Figure 1. The orientation of the HOPG slab with respect to the external magnetic field $\boldsymbol{H}_0$ and the cavity axis (*X*, *Y* and *Z*). $\boldsymbol{H}_{rf}$, $\boldsymbol{E}_{rf}$ and $\boldsymbol{P}_{rf}$ are the magnetic and electric components of the radio-frequency field, and the Pointing vector in an unloaded rectangular cavity, respectively.

The study of dependences of graphite CESR lineshape parameters on sample dimensions were carried out on HOPG plates with dimensions: l? 0.355? 0.072 cm^3. The accuracy in the determination of the sample dimensions was ~ 5? 10^{-4} cm.

The temperature studies of CESR spectra samples investigated were carried out in the temperature range from 100 K to 350 K. The temperature was varied by regulating the rate and temperature of nitrogen or helium gas flow through the quartz dewar with the sample. The temperature was maintained and measured with an accuracy of ~0.1 K/h and ~0.5 K, respectively.

Results

Graphite. For HOPG plates studied the CESR spectrum consists of a single asymmetric line determined by Dyson mechanism [10] and with the principal values of g – factor being equal to: g_c=2.0474? 0.0002 ($\boldsymbol{H}_0$||**?**) and g_a=2.0029? 0.0002 ($\boldsymbol{H}_0$? **?**).

For the "thick" plates (d>0.045 cm) the dependence of asymmetry parameter, A/B, of the first derivative of CESR absorption line, which is equal to the ratio of the peak intensity of the more intense wing, A, to that of the less intense wing, B, vs. l has three-peak form (Fig. 2). In the interval l_{1m}< l < l_{2m}, where l_{1m} (l_{2m}) is the coordinate of the first (second) peak - in the direction of l increase, 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, diffuse maximum is not associated with the change of phase of the line shape.

At l? 0 the experimental values of CESR linewidth tend to the infinity (Fig. 3).

For all orientations of $\boldsymbol{H}_0$ relative to the $\boldsymbol{c}$-axis the ? H increases first with decreasing temperature, forms a distinct peak at about 20 K and then falls off leftward (Fig. 4). The g–factor for $\boldsymbol{H}_0$? $\boldsymbol{c}$ almost independent of temperature (Fig. 5). With the $\boldsymbol{H}_0$||$\boldsymbol{c}$, the g-value increases first with decreasing temperature, but it forms a distinct peak at about 20 K in a manner similar to that of the ? $H(T)$ (Fig. 5).

Discussion

CESR lineshape and linewidth dependences on sample size. The dependences of CESR lineshape asymmetry parameter *A/B* and linewidth ? H on graphite plate width (Figs. 2 and 3) essentially differ from the known theoretical curves, calculated from the Dyson [10] CESR lineshape expression without taking into account the effects of surface spin relaxation. First, the presence of l values, for which the CESR lineshape has an 'inverted' phase is a characteristic property of the theoretical curves $A/B(l)$ for the ratio R_a=$(T_{Da}/T_2)^{1/2}$ (where T_{Da} is the time of spin diffusion across the skin-depth ?$_c$ governed by the ?$_?$ – conductivity, and T_2 is the intrinsic spin-relaxation time) being less than 0,6 (Fig. 6), whereas the experimental values of *A/B* for l >> ?$_c$ are consistent with the theoretical values of this parameter for R_a>0.8. Second, the values of *A/B* in the extrema of the experimental $A/B(l)$ dependence differ considerably from those for the theoretical curves (Fig. 6). Third, at l? 0 the experimental values of CESR linewidth tends to the infinity (Fig. 3), whereas the corresponding theoretical curve calculated from the Dyson [10] CESR lineshape expression without taking into account the effects of surface spin relaxation tends to the finite value, which differs from that for plates with l >>?$_c$ by 10% only (Fig. 3).

The character of temperature dependence of CESR linewidth on l (Fig. 3) uniquely specifies the presence of the contribution of surface spin relaxation into total spin relaxation of current carriers in HOPG plates investigated. Basing on this conclusion the above peculiarities of experimental results were analyzed in the frameworks of the

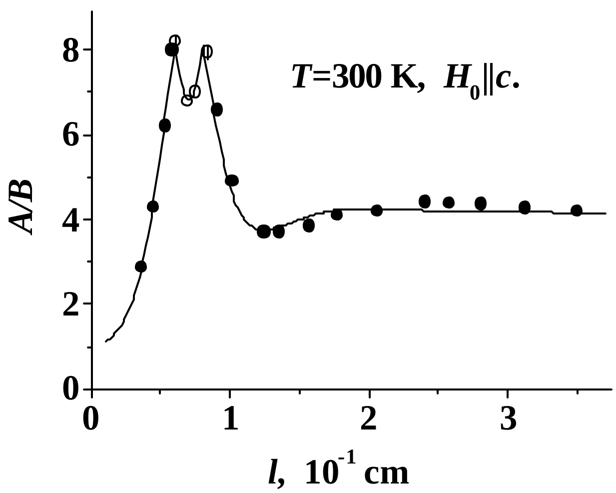

Figure. 2. The experimental (dots) and the theoretical (solid line) values of CESR line shape asymmetry parameter, *A/B*, in graphite vs. sample width *l*. The shaded and open dots are referred to the normal and 'reversed' lineshape, respectively; half-shaded dot corresponds to the lineshape with symmetric phase with respect to the *A* peak. G_a=200 cm^{-1}, R_a=2.35, R_c=6, T_2=1.16? 10^{-8} s. $R_i=(T_{Di}/T_2)^{1/2}$ (T_{Di} (i=a, c) is the time of spin diffusion across the skin-depth ?$_i$ (i=c, a) governed by the ?$_i$ – conductivity (i=c, a), and T_2 is the intrinsic spin-relaxation time). The X-band.

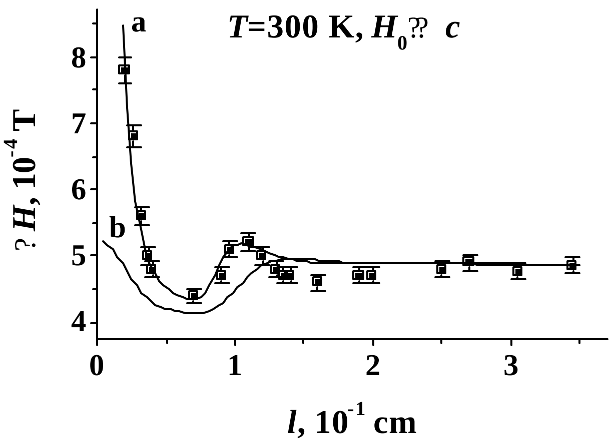

Figure. 3. The experimental (dots) and the theoretical (solid lines) values of linewidth, ? *H*, in graphite vs. sample width *l*. The curve a (b) corresponds to the value of Dyson [10] surface spin relaxation parameter G_a=200 (0) cm^{-1}. R_a=2.5, R_c=6, T_2=1.38? 10^{-8} s. $R_i=(T_{Di}/T_2)^{1/2}$ (T_{Di} (i=a, c) is the time of spin diffusion across the skin-depth ?$_i$ (i=c, a) governed by the ?$_i$ – conductivity (i=c, a), and T_2 is the intrinsic spin-relaxation time). The X-band.

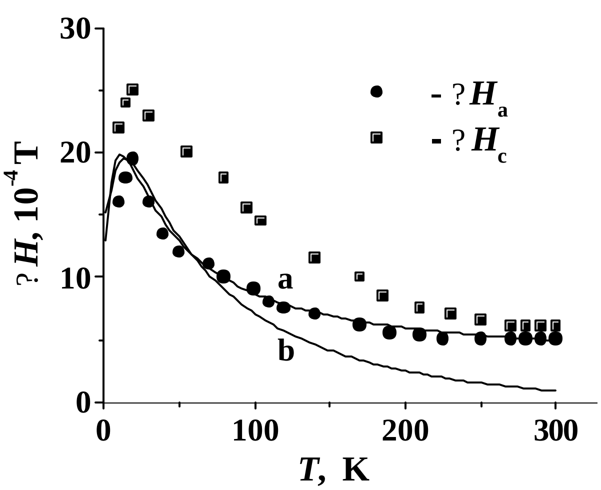

Figure 4. The experimental (dots) and theoretical (lines) values of CESR linewidth, ? *H*, in HOPG plates vs. temperature *T*. The theoretical curves (a) and (b) were calculated using the Exp. (2) with constant (= 4.4? 10^{-4} T) and determined by the Exp. 4 values of linewidths (intrinsic conduction electron spin relaxation time), respectively, and Dyson [10] surface spin relaxation parameter G_a=180 cm^{-1}. The X-band.

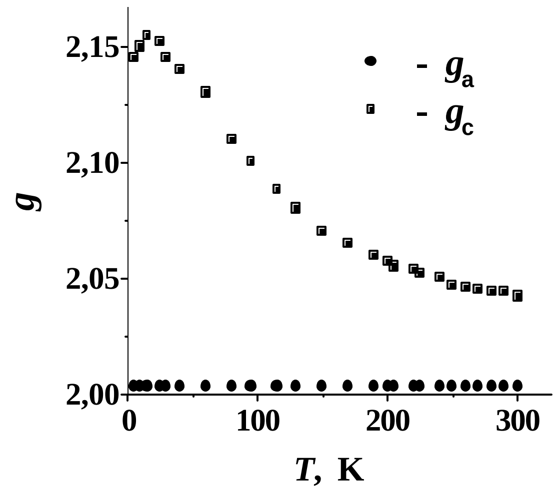

Figure 5. Temperature dependence of *g*-factor of graphite. The X-band.

extended Dyson theory [10] including the effects of surface spin relaxation of current carriers. In Figs. 2 and 3, the results of theoretical calculations, respectively, of $A/B(l)$ and $?H(l)$ dependences in the frameworks of the extended Dyson [10] theory are presented. (At calculation of the theoretical curve $A/B(l)$, the absorption of microwave field through all lateral surfaces both parallel and perpendicular to the **?**- axis was taking into account and the uniform distribution of microwave field near the vertical surfaces of the plates was supposed). From Fig. 2 and 3 it can be seen that the theoretical curves with the value of Dyson [10] surface spin relaxation parameter $G_a=(3e/4?_a)=200$ cm^{-1} (e is a probability of spin reorientation during the collision of current carriers with the surface and $?_a$ is a mean free path of current carriers in a basal plane) describes the experimental $A/B(l)$ and $?H(l)$ data well.

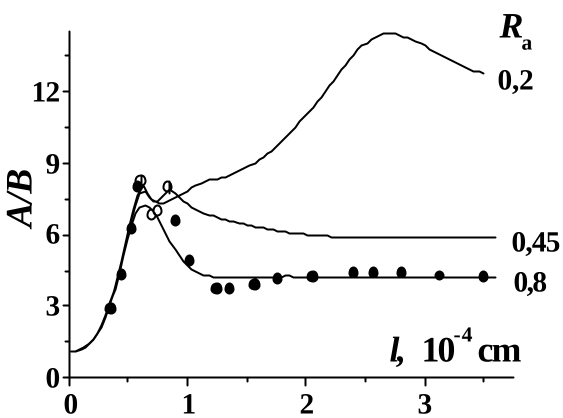

Figure 6. Experimental (dots) and theoretical (lines) values of CESR lineshape asymmetry parameter, A/B, on sample thickness l. The theoretical curves were calculated using the Dyson [10] expressions for CESR lineshape without taking into account the effects of surface spin relaxation of current carriers. The shaded and open dots are referred to the 'normal' and 'reversed' lineshape, respectively; half-shaded dot corresponds to the lineshape with symmetric phase with respect to the A peak. $R_a=(T_{Da}/T_2)^{1/2}$ (T_{Da} is the time of spin diffusion across the skin-depth $?_c$ governed by the $?_?$ – conductivity, and T_2 is the intrinsic spin-relaxation time).

The temperature dependence of CESR linewidth.

Above, it was pointed out that the characters of the $?H(l)$ (Fig. 3) and $A/B(l)$ (Fig. 2) dependences of CESR line in graphite uniquely specifies the presence of the contribution of surface spin relaxation into total spin relaxation of current carriers in samples investigated. Basing on this fact, we considered the temperature dependence of CESR linewidth in HOPG also in the frameworks of model including surface spin relaxation effects of graphite ?-electrons. Additionally, we suppose the presence of a small amount of the localized spins (~1% of the current carrier concentration or near one localized spin per 10^6 carbon atoms) and complete averaging of g-factors of the conduction electrons and localized spins. In such case, the CESR linewidth $?H_i$ (i=a, c) can be presented in the following form:

$$?H_i = ?H_{ie}(?_e/?_e+?_s)+?H_{is}(?_s/?_e+?_s) \quad (i = a, c), \qquad (2)$$

where $?H_{ie}$? $?H_{is}$ are the linewidths of CESR signal due to conduction electrons and localized spins, respectively; $?H_{ie}=?H_{ie}^{surf}+?H_{ie}^{intr}$, where $?H_{ie}^{surf}$ and $?H_{ie}^{intr}$ are contributions to the total conduction electron linewidth due to their interactions with sample surface and inner imperfections, respectively; $?_e$ and $?_s$ are the Curie and Pauli paramagnetic susceptibilities, respectively. At the calculations we assumed, that

$$?H_{ie}^{surf}=a_{?i}\,?_{ai}(T) \qquad (i=a, c), \qquad (3)$$

where $a_{?i}$ is a constant depending on physical properties of a sample surface and orientation of $\boldsymbol{H}_o$ relative to the ***c***-axis. Because the Elliot's expressions [7] for the intrinsic spin relaxation of current carriers were calculated for the simple isotropic metals, their applications to the graphite is not obvious. Therefore, the calculations of $?H_i$ were carried out by us with values of $?H_{ie}^{intr}$ both independent, and dependent on temperature according to the Elliot [7] law for $T<<?_D$:

$$?H_i = const?(?g_i)^2?_D/?m^*?_{ai}(T)\,T^2 \quad (i = a, c). \qquad (4)$$

Basing on the analysis of literature data on the temperature dependence of current carriers mobility in graphite basal plane [11] $?_{ai}(T)$ (i= a, c; this subindex was introduced for the account of dependence of carriers mobility on $\boldsymbol{H}_0$-orientation) was approximated by the following expression

$$?_{ai}(T) = a_i + b_i/(c_i+T)^{1.6} \quad (i = a, c),$$

where a_i, b_i and c_i are the varied parameters; at calculations of $?H_i$ for $\boldsymbol{H}_0$? **?**, their initial values were taken equal to –4 m^2/Vs, 63?10^3 m^2·K$^{1.6}$/Vs and 55 K, respectively, for intrinsic linewidth temperature dependence determined by the Exp. 4 and were taken equal to –0.4 m^2/Vs, 13.25?10^3 m^2·K$^{1.6}$/Vs and 24.5 K, respectively, for constant intrinsic linewidth (in both cases, for the chosen values of parameters the $?_{ac}(T)$-dependences approximately correspond to the in-plane mobility of carriers in the average on quality HOPG). Taking into consideration the data of irradiated graphite CESR-measurements [12] the values of g_s and ?H_{is} were taken equal to 2,0023 ? 0,25 mT, respectively. The values of $a_{?i}$ in Exp. (3) and constants in Exp. (4) were calculated using the literature data on the value of ?$_{ai}(T)$ in HOPG [11] and surface and intrinsic spin relaxations times at room temperature extracted from the analysis of experimental ?$H(l)$ data (Fig. 4), respectively.

The results of approximation of experimental temperature dependence of CESR linewidth at $\boldsymbol{H_0}$? ***?*** by Exp. (2) are presented in Fig. 3. As it is seen from this figure, for both forms of temperature dependence of intrinsic spin relaxation rate the theoretical curve ?$H_i(T)$ contains the distinct peak near 20 K. At the same time, the theoretical analysis of Exp. (2) has shown, that this peak is absent if

?H_{ie}^{surf}=0.

In the frameworks of the model considered in all temperature interval of investigations the best description of the experimental temperature dependence of CESR linewidth by Exp. (2) was achieved with temperature independent value of intrinsic spin relaxation rate (see Fig. 4). We believe that this fact has a physical sense and it is a consequence that in a real graphite the collisions of current carriers with the graphite crystallite boundaries introduce main contribution into intrinsic spin relaxation rate.

Conclusions

For all orientations of the external constant magnetic field relative to the graphite plate **c**-axis the linewidth of graphite conduction ESR (CESR) signal increases first with decreasing temperature, forms a distinct peak at ~20 K and then falls off. Up to the present, the nature of this peculiarity of graphite CESR linewidth temperature dependence was not clear. In this work we show that a low temperature peak in the curve of CESR linewidth temperature dependence appears if the surface spin relaxation effects of graphite current carriers are taken into consideration.

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