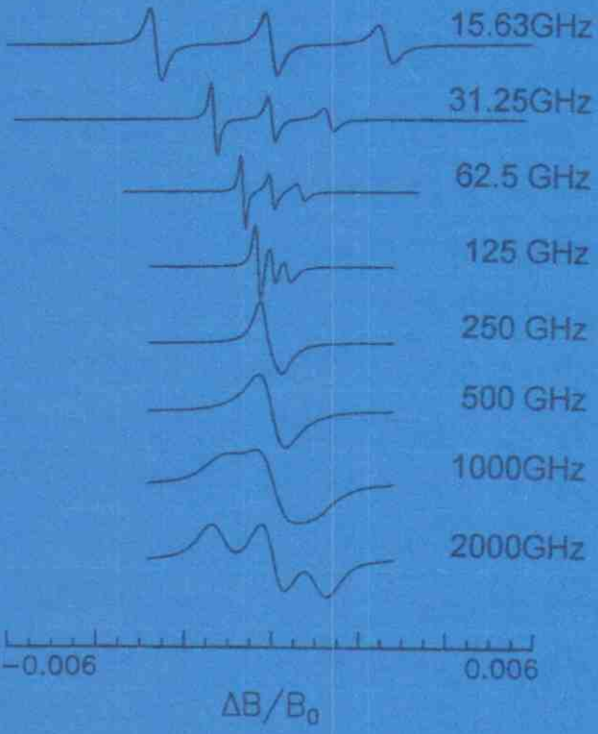
EPR IN THE 21^{ST} CENTURY:

BASICS AND APPLICATIONS TO MATERIAL, LIFE AND EARTH SCIENCES



Editors

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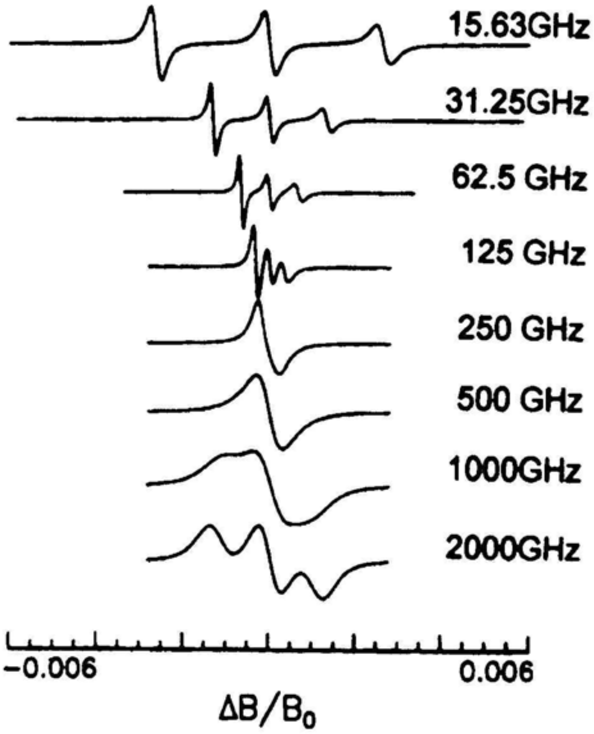

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EPR in the 21st Century
A Kawamori, J Yamauchi and H Ohta (Editors)

The nature of conduction ESR linewidth temperature dependence in graphite

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For all orientations of the external constant magnetic field, $\boldsymbol{H}_0$, relative to the graphite plate $\boldsymbol{c}$-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. The value of g-factor for $\boldsymbol{H}_0$ along the $\boldsymbol{c}$-axis increases with lowering temperature by a manner similar to that of the CESR linewidth, but for $\boldsymbol{H}_0$ along the basal plane its value does not depent on temperature. Up to the present, the nature of graphite conduction ESR linewidth temperature dependence and origin of its low temperature peak were not clear. In this work we show that a low temperature peak in the CESR linewidth temperature dependence is predictable, if the surface spin relaxation effects for graphite current carriers were taken into consideration.

1. 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 [2-7] 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 the external constant magnetic field, $\boldsymbol{H}_0$, relative to the c-axis the graphite CESR signal linewidth increases first with decreasing temperature. According to the data of Matsubara *et al.* [7], the $\Delta H(T)$-dependence forms a distinct peak near 20 K and then falls off.

At present there is no consensus between researchers on both the origin of graphite CESR linewidth and of its temperature dependence. Kawamura *et al.* [4] showed that at $H_0 \| c$ the Elliot [8] expression for the CESR linewidth, ΔH_c, due to carriers interacting with phonons and/or impurities, which for $T \gg \Theta_D$ (Θ_D is Debye temperature) can be written as:

$$\Delta H_c = const \times (\Delta g_c)^2 / \gamma m^* \mu(T) \quad (1)$$

($\Delta g_c = g_c - g_0$, where g_c and g_0 are the g-factor values respectively for graphite current carriers and for free electron, γ is the electronic gyromagnetic ratio, $\boldsymbol{m^*}$ is the carriers effective mass, and $\mu(T)$ is the carriers mobility), describes the graphite CESR linewidth dependence in the interval 77÷300 K qualitatively at least. Matsubara *et al.* [7] considered the temperature variation of graphite CESR linewidth at $\boldsymbol{H}_0 \| \boldsymbol{c}$ 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 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 spectral linewidth in graphite may result from complete averaging of the g-factors over all 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 $\sim 3\times10^{-2}$ 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 about 400 K. Therefore, the description of the graphite CESR linewidth temperature dependence by Eq. (1), proposed by Elliot for $T >> \Theta_D$, is not obvious. Furthermore, this expression does not explain the presence of linewidth temperature dependence at $\boldsymbol{H}_0 \perp \boldsymbol{c}$ even at a qualitative level since in this orientation of $\boldsymbol{H}_0$ the value of g-factor, g_a, does not depend on temperature. The independence of the CESR linewidth on the microwave frequency shows that Matsubara *et al.* [7] interpretation of the linewidth temperature dependence as a result of the motional narrowing of incomplete averaging line is not correct also. Besides, the presence of low-temperature peak in $\Delta H(T)$ curve also at $\boldsymbol{H}_0 \perp \boldsymbol{c}$, where g–factor is temperature independent, shows that the origins of low-temperature peaks in $g_c(T)$ and $\Delta H_c(T)$ 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 sample dimensions and on temperature for different orientations of $\boldsymbol{H}_0$ and have shown that all obtained experimental data on CESR linewidth in graphite may be explained well, if the surface spin relaxation of current carriers was taken into consideration.

2. EXPERIMENTAL

The CESR measurements were carried out using an X-band E-line spectrometer in a rectangular cavity with TE_{102} mode. The frequency and amplitude of $\boldsymbol{H}_0$ modulation 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 $h\times l$ is the area of basal plane. At the experiments, the basal $l\times h$ and lateral $d\times h$ sides were parallel to the magnetic component, $\boldsymbol{H}_{rf}$, of the microwave field and the $\boldsymbol{c}$-axis was perpendicular to it. 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, $H_0 \parallel E_{rf}$ (the electrical component of the microwave field).

The study of dependences of graphite CESR lineshape parameters on sample dimensions were carried out on HOPG plates with dimensions: $l\times0.355\times0.072$ cm^3. The accuracy in the determination of the sample dimensions was $\sim 5\times10^{-4}$ cm.

The temperature studies of CESR spectra of the 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 tube with the sample. The temperature was maintained and measured with an accuracy of ~0.1 K/h and ~0.5 K, respectively.

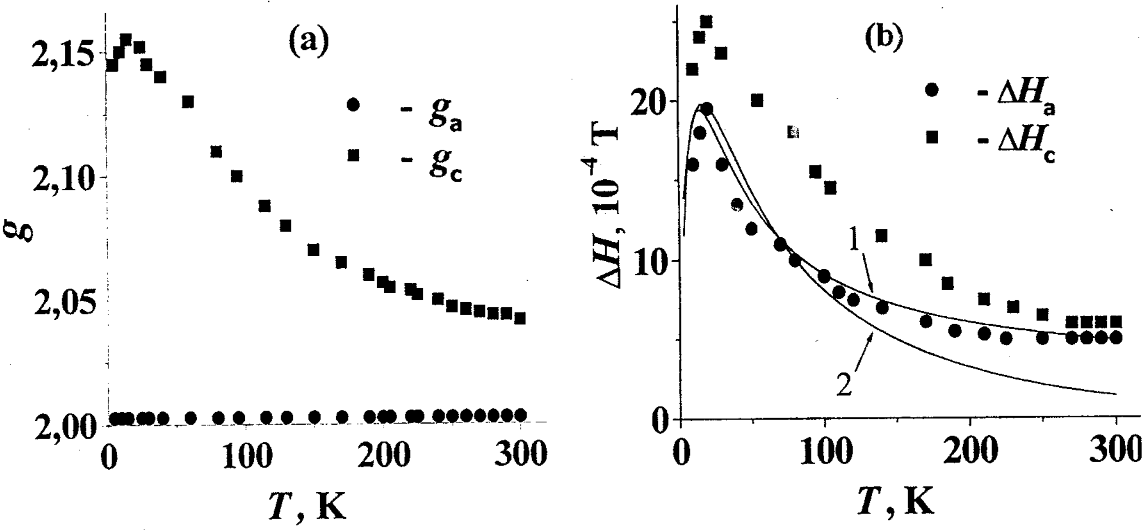

Figure 1. Temperature dependence of g-factor (a) and linewidth (b) for graphite. In (b), the theoretical curve 1 (2) was calculated with constant (determined by the Exp. (4)) value of intrinsic conduction ESR linewidth.

3. RESULTS

For HOPG plate investigated the CESR line is of typical Dyson [11] form and indicates a large g-factor anisotropy. The g_c-value is about 2.047 at room temperature and first increases monotonously with lowering temperature so as to exceed 2.16, forms a peak at ~20 K, and then steeply falls off (Figure 1a). The g_a-value shows almost no shift from the free-electron value (g_o=2.0023) irrespective of temperature ($\Delta g_a = g_a - g_o \sim$ ~3×10^{-4}) (Figure 1a).

When H_0 is in the c-direction, the linewidth as narrow as ~6×10^{-4} T near room temperature and first increases remarkably with lowering temperature, and then the rise of the ΔH_c is followed also by a distinct peak at ~20 K similar to that of the g_c-shift (Figure 1b). When $H_0 \perp c$ the linewidth also increases with lowering temperature (Figure 1b), by a manner similar to that of the ΔH_c, despite the fact that Δg_a does not depend on temperature (Figure 1a). The value of CESR linewidth monotonously changes with on the constant magnetic field

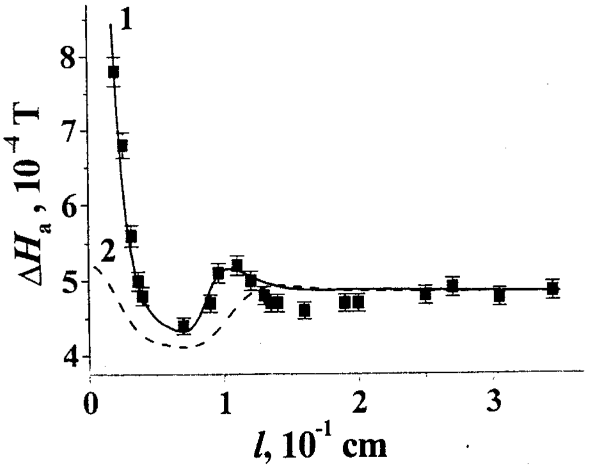

Figure 3. The experimental (dots) and theoretical (lines) values of CESR linewidth, ΔH, in graphite vs. sample width l. The line 1 (2) was calculated using the value of G=180 (0) cm^{-1}. T=300 K; $H_0 \perp c$.

orientation. At all temperatures the ΔH_c is larger than the ΔH_a.

The value of CESR linewidth tends to the infinity, while l (HOPG plate size in a basal plane) tends to zero (Figure 2).

At all temperatures the microwave field power and frequency, and the frequency of H_0 modulation had no observable effect on the CESR linewidth.

3. DISCUSSION

The character of temperature dependence of CESR linewidth on l (Figure 2) unequivocally specifies the presence of the contribution of surface spin relaxation into total spin relaxation of current carriers in HOPG plates investigated. Indeed, while the experimental linewidth tends to the infinity, the corresponding theoretical values calculated using the well-known Dyson [11] expression for CESR line shape, which is not containing the surface spin relaxation parameter $G_a=3\varepsilon_a/4\Lambda_a$ (ε_a is the mean probability of spin reorientation during the collisions of current carriers with the lateral graphite surfaces and Λ_a is a mean free path of current carriers in a basal plane) tends to the finite value, which differs from that for wide plates by ~10% only. At the same time, the theoretical curves $\Delta H(l)$ with the value of Dyson [11] surface spin relaxation parameter $G_a=180$ cm^{-1} describes the experimental $\Delta H(l)$ data well (Figure 2). Basing on this fact, we also considered the temperature dependence of CESR linewidth in HOPG studied in the frameworks of the model including surface spin relaxation effects of current carriers. Moreover, 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 HOPG studied. In such case, the CESR linewidth ΔH_i (i=a, c) can be presented in the following form:

$$\Delta H_i = \Delta H_{ie}(\chi_e/\chi_e+\chi_s) + \Delta H_{is}(\chi_s/\chi_e+\chi_s) \qquad (i = a, c), \tag{2}$$

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

$$\Delta H_{ie}^{surf}=a_{\mu i}\,\mu_{ai}(T) \qquad (i = a, c), \tag{3}$$

where $a_{\mu i}$ is a constant depending on physical properties of the sample surface. Because the Elliot`s expressions [8] for the intrinsic spin relaxation of current carriers were calculated for the simple isotropic metals, their applications to graphite is not obvious. Therefore, the calculations of ΔH_i were carried out by us with values of ΔH_{ie}^{intr} both independent, and dependent on temperature according to the Elliot [8] law for $T << \Theta_D$:

$$\Delta H_{ie}^{intr} = const\times(\Delta g)^2\,\Theta_D\,/\gamma m^*\mu(T)\,T^2. \tag{4}$$

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$$\Delta H_{ie}^{intr} = const\times(\Delta g)^2\,\Theta_D\,/\gamma m^*\mu(T)\,T^2. \tag{4}$$

Basing on the analysis of literature data on the temperature dependence of current carriers mobility in graphite basal plane [12] $\mu_{ai}(T)$ was approximated by the following expression

$$\mu_{ai}(T) = a + b/(c + T)^{1.2} ,$$

where a, b and c are the variable parameters; at calculations for $\boldsymbol{H}_0 \perp c$, their initial values were taken equal to -1.8 m^2/V·s, 2.6×10^3 m^2·K$^{1.2}$/V·s and 17 K, respectively (at these values of parameters $\mu_{ai}(T)$ approximately describes the in-plane mobility of carriers in HOPG sample of average quality). Taking into consideration the data of irradiated graphite CESR-measurements [13] the values of g-factor for localized spins and ΔH_{is} were taken to be equal to 2,0023 and 0,25 mT, respectively. The values of $a_{\mu i}$ in Eq. (3) and constants in Eq. (4) were calculated using the literature data on the value of μ_{ai}(T) in HOPG [12] and surface and intrinsic spin relaxation times at room temperature obtained from the analysis of experimental $\Delta H(l)$ data (Figure 3), respectively.

The results of approximation of experimental CESR linewidth at $\boldsymbol{H}_0 \perp c$ by Eq. (2) are presented in Figure 1b. As is clear from this figure, for both forms of temperature dependence of intrinsic spin relaxation the theoretical curve $\Delta H_i(T)$ contains the distinct peak near 20 K. At the same time, the theoretical analysis of Eq. (2) has shown, that this peak is absent if $\Delta H_{ie}^{surf} = 0$.

Thus, in this work we have shown that a low temperature peak in the curve of CESR linewidth temperature dependence appears, when the surface spin relaxation effects of graphite current carriers are taken into consideration.

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