AMPERE 2000

AMPERE 2000

30th CONGRESS AMPERE on Magnetic Resonance and Related Phenomena

Lisbon, Portugal, 23-28 July 2000

Under the auspices of
The GROUPEMENT AMPERE

Proceedings

Edited by:

A.F. MARTINS, A.G. FEIO and J.G. MOURA

Sponsoring organizations:

Universidade Nova de Lisboa
Faculdade de Ciências e Tecnologia

FUNDAÇÃO
CALOUSTE
GULBENKIAN

FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA E DA TECNOLOGIA

BRUKER

ISBN: 972-98802-0-4 Legal Deposit: 175197-02

SURFACE SPIN RELAXATION OF CURRENT CARRIERS IN GRAPHITE AS A REASON FOR LOW TEMPERATURE PEAK FORMATION IN TEMPERATURE DEPENDENCE OF CONDUCTION ESR LINEWIDTH

A.M. Ziatdinov and V.V. Kainara

Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences.
159, Prosp. 100-letiya, 690022 Vladivostok, RUSSIA. E-mail: chemi@online.ru.

Abstract: For all orientations of the external constant magnetic field relative to the graphite plate **c**-axis the line width 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 line width temperature dependence was not clear. In this work we show that a low temperature peak in the curve of CESR line width temperature dependence appears if the surface spin relaxation effects of graphite current carriers are taken into consideration.

Introduction

The first systematic study of the conduction ESR (CESR) in graphite in the temperature range from 77 K up to 600 K was carried out as early as 1960 by Wagoner [1] using a natural single crystal specimen. Wagoner's work is noted to be also the first observation of ESR due to charge carriers in a material having degeneracy at the band edge. 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 for all orientations of the external constant magnetic field, $\mathbf{H}_0$, relative to the graphite plate **c**-axis the line width, ΔH, of graphite CESR signal increases first with decreasing temperature. According to the data of Matsubara *et al.* [7], the ΔH(T)-dependence forms a distinct peak near 20 K and then falls off.

At present there is no consensus between researchers on both the CESR line width and its temperature dependence origin. Kawamura *et al.* [4] showed that at $\mathbf{H}_0 \parallel \mathbf{c}$ the Elliot's [8] expression for the CESR line width due to carriers interacting with phonons and/or impurities, which for T>> Θ_D (Θ_D is Debye temperature) can be written as :

$$\Delta H = const\times(\Delta g)^2/\gamma m^*\mu(T) \tag{1}$$

(Δg is the g-shift, γ is the electronic gyromagnetic ratio, m^* is the carriers effective mass, and $\mu(T)$ is the carriers mobility), describes the graphite CESR line width in the interval 77÷300 K qualitatively at least. Matsubara *et al.* [7] considered the temperature variation of graphite CESR line width at $\mathbf{H}_0 \parallel \mathbf{c}$ 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 line width contains the components which are proportional to the square of the microwave frequency. Kotosonov [3] pointed out that the small ΔH 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 (g-factor at $\mathbf{H}_0 \parallel \mathbf{c}$) changing by ~0.2, which agrees with the resonance field shift by $\sim3\times10^{-2}$ T, whereas the CESR line width remains within the limits of several oersteds.

According to the literature data [9,10] the Debye temperature of graphite is nearly 400 K. Therefore the description of the graphite CESR line width temperature dependence by Exp. (1), proposed by Elliot for $T \gg \Theta_D$, is not obvious. Furthermore, this expression does not explain the presence of line width temperature dependence at $\mathbf{H}_0 \perp \mathbf{c}$ even at a qualitative level since in this orientation of $\mathbf{H}_0$ the value of *g*-factor, g_a, does not depend on temperature (Fig.1A). The independence of the CESR line width on the microwave frequency shows that Matsubara's *et al.* [7] interpretation of the line width 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 ΔH(T) curve also at $\mathbf{H}_0 \perp \mathbf{c}$, where g – factor is temperature independent, shows that the origins of low-temperature peaks in g_c(T) and ΔH(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 line width temperature dependence.

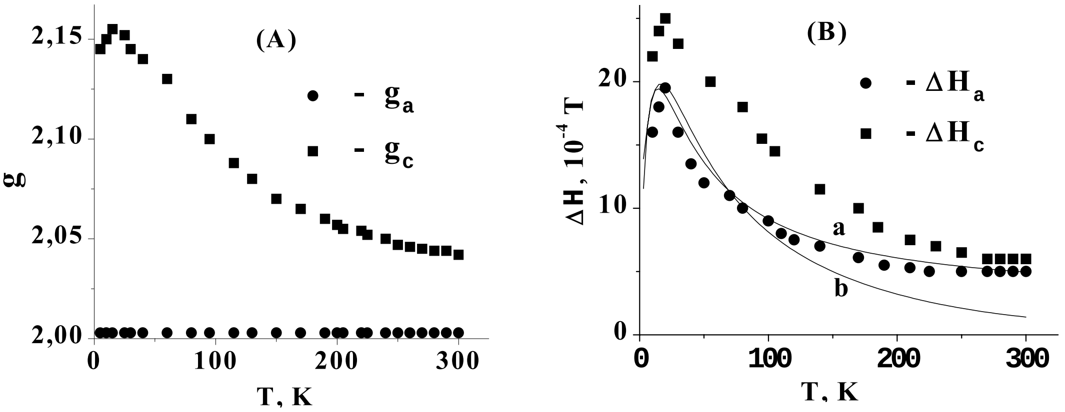

Fig. 1. Temperature dependence of g-factor (A) and linewidth (B) of graphite. In the right figure, the theoretical curve a (b) was calculated with constant value of intrinsic conduction electron spin relaxation time (using the Elliot [8] law for temperatures much less than the Debye temperature).

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

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 (Fig. 1A). The g_a-value shows almost no shift from the free-electron value (g_o = 2.0023) irrespective of temperature ($\Delta g_a = g_a - g_o \sim 3\times10^{-4}$) (Fig. 1A).

The line width, when $\mathbf{H}_0$ is in the **c**-direction, ΔH_c, is as narrow as ~6×10^{-4} T near room temperature and first increases remarkably with lowering temperature, and then the rise of ΔH_c with decreasing temperature is followed also by a distinct peak at ~20 K in a manner similar to that of the g_c-shift (Fig. 1B). When $\mathbf{H}_0 \perp \mathbf{c}$ the line width, ΔH_a, also increases with

lowering temperature (Fig. 1B), by a manner similar to that of the ΔH_c, despite the fact that Δg_a does not depend on temperature (see Fig. 1A). At all temperatures the line width for $\mathbf{H}_0 \parallel \mathbf{c}$ is larger than for $\mathbf{H}_0 \perp \mathbf{c}$ and monotonously depends on the field orientation.
The value of CESR linewidth tends to the infinity, while *l* (HOPG plate size in a basal plane) tends to zero (Fig. 2). At all temperatures the microwave field power and frequency, and the frequency of $\mathbf{H}_0$ modulation had no observable effect on the CESR line width.

Discussion

The character of temperature dependence of CESR linewidth on *l* (Fig. 2) unequivocally specifies the presence of the contribution of surface spin relaxation into total spin relaxation of current carriers in HOPG plates investigated. Really, while the experimental line width 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 $g=(3\varepsilon/4\Lambda_a)$ (ε is a probability of spin reorientation during the collision of current carriers with the surface 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=200 cm^{-1} describes the experimental $\Delta H(l)$ data well (Fig. 2). Basing on this fact, we also considered the temperature dependence of CESR line width in HOPG studied in the framework of model including surface spin relaxation effects of current carriers. 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 HOPG studied. In such case, the CESR line width ΔH_i ($i=a, c$) can be presented in the following form

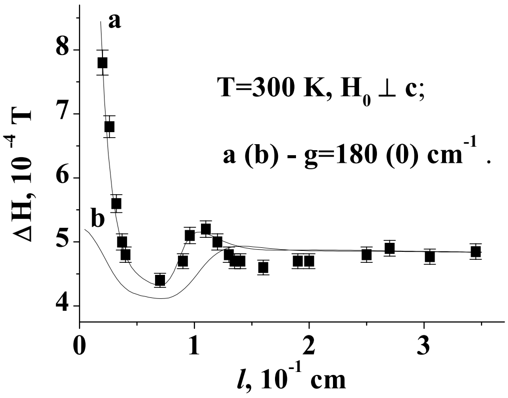

Fig. 2. The experimental (dots) and the theoretical (solid lines) values of graphite CESR signal linewidth, ΔH, vs. sample width, *l*.

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

where ΔH_{ie} и ΔH_{is} are the line widths 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 line width 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

$$\Delta H_{ie}^{sur1}=a_{\mu i}\,\mu_{ai}(T) \qquad (i = a, c), \tag{3}$$

where $a_{\mu i}$ is a constant depending on physical properties of a sample surface. Because the Elliot`s expressions 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 ΔH_i were carried out by us with values of ΔH_{is}^{intr} both independent, and dependent on temperature according to the Elliot [8] law for T << Θ_D:

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

Basing on the analysis of literature data on the temperature dependence of current carriers mobility in graphite basal plane [13] μ_{ai}(T) was approximated by the following expression

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

where a, b and c are the varied parameters; at calculations for $\mathbf{H}_0 \perp \mathbf{c}$, their initial values were taken equal to -2 m^2/Vs, 3×10^3 $m^2\cdot K^{1.2}/Vs$ and 20 K, respectively (at these values of parameters $\mu_{ai}(T)$ approximately describe the in-plane mobility of carriers on the average on quality HOPG). Taking into consideration the data of irradiated graphite CESR-measurements [12] the values of g_s and ΔH_{is} were taken equal to 2,0023 и 0,25 mT, respectively. The values of $a_{\mu i}$ in (3) and constants in Exp. (4) were calculated using the literature data on the value of μ_{ai}(T) in HOPG [13] and surface and intrinsic spin relaxations times at room temperature extracted from the analysis of experimental $\Delta H(l)$ data (Fig. 2), respectively.

The results of approximation of experimental CESR linewidth at $\mathbf{H}_0 \perp \mathbf{c}$ by exp. (2) are presented in Fig. 1B. As it is seen from this figure, for both forms of temperature dependence of intrinsic spin relaxation the theoretical curve ΔH_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 $\Delta H_{ie}^{surf} = 0$. Note, that the experimental data can be described also well, but with order less concentration of localized spins, if the relaxation of spins on surface of small graphite crystallites additionally is taken into consideration.

Acknowledgments

The authors are grateful to L.B. Nepomnyashchii (Scientific Research Centre for Graphite, Moscow) for providing the HOPG. This work was partially supported by the Russian Foundation for Basic Research (grant No. 00-03-32610a).

References

[1] G. Wagoner, *Phys. Rev.*, **118**, 647(1960).
[2] L.J. Singer and G. Wagoner, *J. Chem. Phys.*, **37**, 1812(1962).
[3] A.S. Kotosonov, *JETP Lett.,* **29**, 307(1979).
[4] K. Kawamura, S. Kaneko, and T. Tsuzuku, *J. Phys. Soc. Jpn.,* **52**, 3936(1983).
[5] A.M. Ziatdinov, and N.M. Mishchenko, *Phys. Solid State (St. Petersburg, Russia),* **36**, 1283(1994).
[6] A.S. Kotosonov, *Carbon*, **26**, 189(1988).
[7] K. Matsubara, T. Tsuzuku, and K. Sugihara, *Phys. Rev.*, **B44**, 11845(1991).
[8] R.J. Elliot, *Phys. Rev.,* **96**, 266(1954).
[9] K.A. Jr. Gschneider, Solid State Phys., **16**, 275(1964).
[10] V. Mizutani, T. Kondow, and T. B. Massalski, *Phys. Rev.*, **B17**, 3165(1978).
[11] F.J. Dyson, *Phys. Rev.,* **98**, 349(1955).
[12] M. Miyake, W. Saiki, T. Daimon, P. Son, C. Miyake, and H. Ohya-Nishiguchi, *J. Nucl. Mat.,* **187,** 138(1992).
[13] M.S. Dresselhaus and G. Dresselhaus, *Adv. in Phys.,* **30**, 139(1981).