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Dieter Ziessow

Wolfgang Lubitz

Friedhelm Lendzian

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Conduction ESR and Surface Relaxation Effects in Graphite and Acceptor Graphite Intercalation Compounds

A.M. Ziatdinov and V.V. Kainara
Institute of Chemistry, Far-East Branch of RAS, Vladivostok 690022, Russia

Introduction

Conduction Electron Spin Resonance (CESR) is one of the most powerful methods of studying the dynamic properties of carriers in conductors. It is just natural, therefore, that this technique should have been extensively applied to graphite and graphite intercalation compounds (GICs) to study electronic and other properties of these anisotropic conductors. In this work we present the results of investigation of previously unknown aspects of the CESR phenomenon in graphite and acceptor GICs, namely, the contribution of surface relaxation effects to the conduction electron spin relaxation rate and its dependence on temperature and aggregate state of the intercalate.

Experimental results and theoretical analysis

In graphite the dependence of CESR line shape asymmetry parameter A/B on the sample width l in the basal plane has some peculiarities. First, this dependence has a two-peak form with the region of inverted line shape phase for values of l between the coordinates of these peaks. This is a characteristic property of the theoretical curves $A/B(l)$ for 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-relaxation time) less than 0.6 [1]. Whereas the experimental values of A/B for large values of l ($l \gg \delta$) are noticeably less than the corresponding theoretical values of A/B for $R < 0.6$ and are consistent with the theoretical values of A/B for $R \geq 1$. Second, the experimental values of A/B in extrema of the $A/B(l)$ dependence differ essentially from that for theoretical curves. Similar differences between the experimental and theoretical curves of $A/B(l)$ dependence plus the new weak extremum at $l \approx 0.06$ cm were found in GICs $C_{10}HNO_3$. Third, the A/B value of the first maximum (from the direction of smaller l) of the experimental dependence $A/B(l)$ decreases at the temperature increase. All above problems of the theoretical interpretation of the experimental dependence $A/B(l,T)$ may be resolved, if the surface relaxation effects will be included into consideration (Fig.1). In particular, it follows from such calculations that in graphite the contribution of the surface relaxation effects increases at lowering the temperature. Note that this result is consistent with the general principles of the surface relaxation theory [2]. The suggestion has been made that in graphite and some acceptor GICs the unusually large contribution of surface relaxation effects to the spin relaxation rate is due to their domain or/and block structure. We believe that origin of the similar temperature dependence of the basal plane electroconductivity and CESR line width is also connected with the domain or

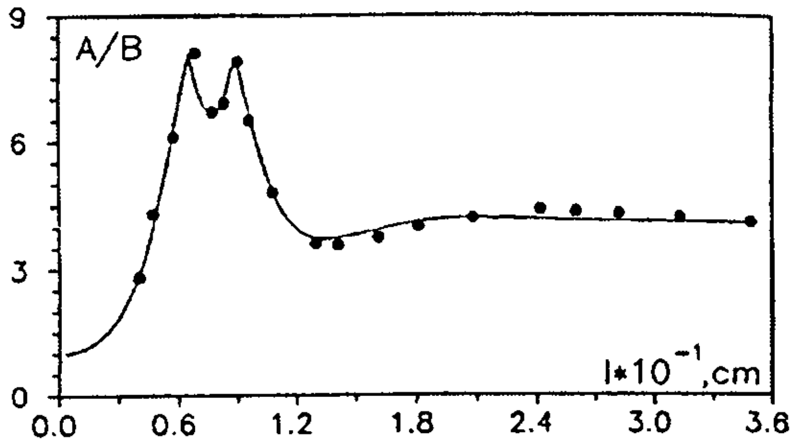

Figure 1. $A/B(l)$ dependence in graphite. Solid line is the theoretical curve in the framework of the two-dimensional microwave penetration model. The surface relaxation parameter $Q'=Qxl^{1}=50$, the skin-depth $\delta=2.5x10^{-2}$ cm, $R=2.4$, $T_2=2.8x10^{-7}$ s, $T=300$ K.

block structure of compounds under consideration, or, more precisely, with the spin-orbit interactions in the vicinity of the intercalate domain walls and graphite crystallites. In GICs $C_{10}HNO_3$, for the interpretation of the CESR data, it is necessary to take into consideration the presence of small concentration of the localized spins, in addition to the surface relaxation,effects. In the latter case the contribution of the surface relaxation effects and concentration of the localized spins undergo the step-wise changes at the aggregate phase transition in the intercalate subsystem of GICs.

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