Electron Spin Resonance Signal of Luttinger Liquids and Single-Wall Carbon Nanotubes

B. Dóra,[1,*] M. Gulácsi,[1] J. Koltai,[2] V. Zólyomi,[3] J. Kürti,[2] and F. Simon[4]

[1]Max-Planck-Institut für Physik Komplexer Systeme, Nöthnitzer Str. 38, 01187 Dresden, Germany
[2]Department of Biological Physics, Eötvös University, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary
[3]Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, H-1525 Budapest, Hungary
[4]Budapest University of Technology and Economics, Institute of Physics
and Condensed Matter Research Group of the Hungarian Academy of Sciences, H-1521 Budapest, Hungary

(Received 2 May 2008; published 5 September 2008)

A comprehensive theory of electron spin resonance (ESR) for a Luttinger liquid state of correlated metals is presented. The ESR measurables such as the signal intensity and the linewidth are calculated in the framework of Luttinger liquid theory with broken spin rotational symmetry as a function of magnetic field and temperature. We obtain a significant temperature dependent homogeneous line broadening which is related to the spin-symmetry breaking and the electron-electron interaction. The result crosses over smoothly to the ESR of itinerant electrons in the noninteracting limit. These findings explain the absence of the long-sought ESR signal of itinerant electrons in single-wall carbon nanotubes when considering realistic experimental conditions.

DOI: 10.1103/PhysRevLett.101.106408 PACS numbers: 71.10.−w, 73.63.Fg, 76.30.−v

The experimental and theoretical studies of strong correlation effects are in the forefront of condensed matter research. Low-dimensional carbonaceous systems, fullerenes, carbon nanotubes (CNTs), and graphene exhibit a rich variety of such phenomena including superconductivity in alkali doped fullerenes [1], quantized transport in SWCNTs, and massless Dirac quasiparticles showing a half integer quantum Hall effect in graphene even at room temperature [2]. A compelling correlated state of one-dimensional systems is the Luttinger liquid (LL) state. There is now abundant evidence from both theoretical [3–8] and experimental [9–12] side that the low-energy properties of CNTs with a single shell, the single-wall carbon nanotubes (SWCNTs) can be described with the LL state.

Electron spin resonance (ESR) is a well-established and powerful method to characterize correlated states of itinerant electrons. It helped to resolve, e.g., the singlet nature of superconductivity in elemental metals [13], the magnetically ordered spin-density state in low-dimensional organic metals [14] and in alkali doped fullerides [15]. In three-dimensional metals, the ESR signal intensity is proportional to the Pauli spin-susceptibility, the ESR linewidth and g factor are determined by the mixing of spin up and down states due to spin-orbit (SO) coupling in the conduction band. These ESR measurables are affected when correlations are present and thus their study holds information about the nature of the correlated state.

This motivated a decade long quest to find the ESR signal of itinerant electrons in SWCNTs and to characterize its properties in the framework of the expected correlations [16–19]. Detection of ESR in SWCNTs is also vital for applications as it enables to determine the spin-lattice relaxation time, T_1, which determines the usability for spintronics [20]. However, to our knowledge no conclusive evidence for this observation has been reported. An often cited argument for this anomalous absence of the ESR signal is the large heterogeneity of the system, the lack of crystallinity, and the presence of magnetic catalyst particles [16–19]. However, ESR signal of conduction electrons has been observed for electron doped SWCNTs [17], which are known to be Fermi liquids rather than the pristine SWCNTs [12]. Thus the above properties of SWCNTs should hinder the observation of the ESR signal also for the Fermi liquid state, which is clearly not the case. We suggest that the LL state inherently prohibits the observation of ESR of the itinerant electrons, calling for a realistic description of such experiments. A recent experiment by Kuemmeth *et al.* [21] shed new light on the spin degree of freedom of SWCNTs. It was shown that SO coupling and, correspondingly, the lifting of the spin rotational invariance, is unexpectedly large. As we show below, this results in a uniquely large homogeneous broadening of the ESR line which explains the absence of an intrinsic ESR signal of SWCNTs. Previous theories of ESR in the SWCNTs concentrated on noninteracting spin sector with spin-orbit coupled quasiparticles [22,23].

One-dimensional interacting fermions usually form a LL, replacing the canonical Fermi liquid picture in higher dimensions. The quasiparticle description breaks down and low-energy properties are described by collective modes of separate spin and charge excitations [24,25]. This results in anomalous power-law dependence of correlation functions at low energies, with critical exponents depending on the interaction strength.

Here, we study the ESR signal in a LL with broken spin rotational symmetry. While at low temperatures the characteristic noninteger power laws characterize the response, the high temperature behavior crosses over to the standard Lorentzians, whose width, in contrast to the Fermi-liquid picture [26], is determined by the LL parameters. We show that this explains the absence of itinerant electron spin resonance in this system by combining DFT calculations of the spin-susceptibility on metallic SWCNTs with a critical evaluation of the experimental conditions.

To describe a metallic SWCNT, we apply an effective low-energy theory. We neglect the "flavor" index coming from the two K points [23] since we are interested in the spin properties only. The standard LL Hamiltonian is expressed as a sum of independent spin and charge excitations as

$$H = \sum_{\nu=c,s} \frac{\hbar v_\nu}{2} \int dx \left(K_\nu \Pi_\nu^2 + \frac{1}{K_\nu} (\partial_x \phi_\nu)^2 \right), \quad (1)$$

where K_ν's are the LL parameters, $\nu = c, s$ denotes the charge and spin sector, respectively, Π_ν and ϕ_ν are canonically conjugate fields with velocity v_ν. The LL parameter in the spin sector, $K_s = 1$ for SU(2) symmetric models as these preserve the spin rotational symmetry. However, the presence of spin-orbit and magnetic dipole-dipole interaction between the conduction electrons [24,27] produces spin dependent interactions and breaks the spin rotational symmetry, leading to $K_s \neq 1$. In addition, these processes are also responsible for the g-factor anisotropy. The motion of the electrons is restricted in the x direction.

The original fermionic field operators are expressed in terms of the bosons as $\Psi_{r\sigma}(x) = \eta_{r\sigma} \exp\{i\sqrt{\frac{\pi}{2}}[r\phi_c(x) + r\sigma\phi_s(x) + \Theta_c(x) + \sigma\Theta_s(x)]\}/\sqrt{2\pi\alpha}$, which are needed to express the spin operators in the bosonic language, $\eta_{r\sigma}$ is the Klein factor, $\Theta_\nu(x) = -\int_{-\infty}^{x} dx' \Pi_\nu(x')$, $r = R/L = \pm$ denotes the chirality of the electrons, and $\sigma = \pm$ is the electron spin.

The ESR experiments are performed in a longitudinal static magnetic field, B, applying a transversal perturbing microwave radiation with a magnetic component, $B_\perp$. For the ESR description, the above Hamiltonian is completed with the Zeeman term:

$$HZ = -g\mu_B B \int dx \partial_x \phi_s(x). \quad (2)$$

The ESR signal intensity is given by the absorbed microwave power that is [26]

$$I(\omega) = \frac{B_\perp^2 \omega}{2\mu_0} \chi_\perp''(q = 0, \omega) V, \quad (3)$$

where μ_0 is the permeability of the vacuum, $\chi_\perp''$ is the imaginary part of the retarded spin-susceptibility for the transversal direction, and V is the sample volume. The spin operators required to calculate $\chi_\perp''$ are $S^\pm(x) = \sum_{r,r'} \exp(i(r' - r)k_F)\Psi_{r\pm}^+(x)\Psi_{r'\mp}(x)$. Since ESR measures the $q = 0$ response, only the $r = r'$ terms contribute, the others contain fast oscillating terms $\sim\exp(\pm 2ik_F)$ and average to zero.

The Zeeman term in Abelian bosonization is the simplest when the longitudinal magnetic field points in the spin quantization axis (the z axis). For a different field orientation, the Zeeman term becomes more complicated but it can be rotated along the z direction, at the expense of changing the LL parameters K_ν [27]. The external magnetic field further lowers the SU(2) symmetry in addition to the spin-orbit and dipole-dipole interactions, resulting in a further renormalization of K_s.

From now on, we set $\hbar = k_B = g\mu_B = 1$ and they will be reinserted whenever necessary. The retarded spin-susceptibility is built up from correlators of the type [28]

$$\langle S^+(x, t) S^-(0, 0) \rangle = c_\perp^2 \left(\frac{\pi T \alpha / v_s}{\sinh[\pi T (x/v_s - t + i\alpha)]} \right)^{2+\gamma} \times \left(\frac{\pi T \alpha / v_s}{\sinh[\pi T (x/v_s + t - i\alpha)]} \right)^{\gamma} \times \exp\left(\frac{ibx}{v_s} \right), \quad (4)$$

where $b = K_s B$, $c_\perp$ is determined by the short distance behavior and cannot be obtained by the methods used here. Here we introduced the $\gamma = (K_s + 1/K_s - 2)/2$ parameter, which encodes information about spin-symmetry breaking processes. Upon Fourier transformation, we obtain the retarded spin susceptibility.

Putting all this together, we find for the ESR intensity (following Ref. [25], Appendix C):

$$I(\omega) = -A \sin(\pi\gamma) \omega \left(\frac{2\pi\alpha T}{v_s} \right)^{2\gamma} \mathrm{Im}[F(2 + \gamma, k_1) F(\gamma, k_2) + F(2 + \gamma, k_2) F(\gamma, k_1)], \quad (5)$$

where $k_{1,2} = (\omega \mp b)/2\pi T$ and $F(x, y) = B((x - iy)/2, 1 - x)$, where $B(x, y) = \Gamma(x)\Gamma(y)/\Gamma(x + y)$ is Euler's beta function, $\Gamma(x)$ is Euler's gamma function, A is a constant, whose value is determined further below. In the $\gamma = 0$ limit, SU(2) spin symmetry is conserved by the Hamiltonian and the ESR resonance becomes completely sharp, located at $\pm B$ as $\sim B^2 \delta(\omega \pm B)$.

The influence of interactions is most clearly seen at $T = 0$, when the ESR signal is completely asymmetric around $\omega = \pm b$, and cannot be approximated by Lorentzians:

$$I(\omega) = A \left(\frac{\alpha}{2v_s} \right)^{2\gamma} \sin^2(\pi\gamma) \frac{\Gamma^2(1 - \gamma)}{\gamma(1 + \gamma)} \frac{2|\omega|(\omega^2 + b^2)}{(\omega^2 - b^2)^{1-\gamma}} \quad (6)$$

for $|\omega| > b$, and zero otherwise. The ESR intensity vanishes below a threshold set by the magnetic field, and falls off in a power-law fashion, depending on the explicit value of K_s.

However, the sharp threshold disappears with increasing temperature and the spectrum broadens. In the limit of $T \gg \omega$, B and $\gamma \ll 1$, which is relevant for realistic experiments, the intensity can be approximated by (upon reinserting original units)

$$I(\omega) = A 2\pi (\hbar\omega)^2 \left[\frac{\eta}{(\hbar\omega - K_s g\mu_B B)^2 + \eta^2} + \frac{\eta}{(\hbar\omega + K_s g\mu_B B)^2 + \eta^2} \right], \quad (7)$$

where $\eta = 2\gamma\pi k_B T$. This expression works well outside of its range of validity and it consists of two Lorentzians, centered around $\pm K_s g\mu_B B$, characterized by a width of η. Hence, the interaction (γ) together with the temperature determines the width of the resonance and shifts the resonance center as well, as is seen in Fig. 1.

This expression allows us to make contact with the conventional Fermi liquid case. In that case, $K_s = 1$ (together with $\gamma \to 0$), which signals a noninteracting spin sector. The ESR intensity reduces to

$$I(\omega) = A2\pi^2(g\mu_B B)^2[\delta(\hbar\omega - g\mu_B B) + \delta(\hbar\omega + g\mu_B B)]. \quad (8)$$

Thus the integrated ESR intensity reads as $\int d\omega I(\omega)/\omega = A4\pi^2 g\mu_B B$. In a Fermi liquid, this is expressed in terms of the static spin-susceptibility [26], χ_0, as $\int d\omega I(\omega)/\omega = \chi_0 B_\perp^2 V\pi g\mu_B B/2\mu_0\hbar$. This fixes the so far unknown numerical prefactor as $A = \chi_0 B_\perp^2 V/2\mu_0\hbar\pi$. In summary, the ESR signal of a LL with broken spin rotational symmetry (i) is significantly broadened due to the interaction and spin-symmetry breaking and (ii) has a signal intensity which matches that of the noninteracting state.

These results are similar to those found for the 1D antiferromagnetic Heisenberg model [29], whose low-energy theory is identical to the spin sector of a LL, Eq. (1). The ESR linewidth also scales with T at low temperatures. The exchange anisotropy, causing the broadening of the ESR signal, shares common origin with the

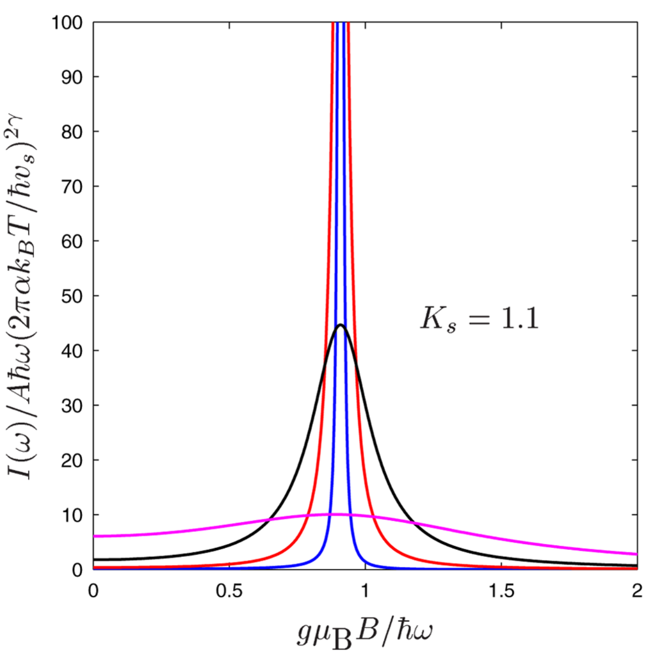

FIG. 1 (color online). The ESR *signal* intensity, Eq. (5) is shown as a function of the magnetic field for $K_s = 1.1$ (corresponding to $\gamma = 0.0045$), $k_B T/\hbar\omega = 0.1$ (blue), 1 (red), 5 (black), and 25 (magenta). The resonance occurs at $g\mu_B B/\hbar\omega = 1/K_s \approx 0.91$ for small temperatures.

g-factor anisotropy in terms of spin-orbit coupling, scaling with $(\Delta g/g)^2$.

In Refs. [22,23], a noninteracting spin sector was considered (with $K_s = 1$) together with explicitly spin-orbit coupled quasiparticles, leading to a narrow two peak spectrum. Our approach takes general spin anisotropies due to spin-orbit coupling, spin backscattering, dipole-dipole interactions and magnetic field into account in our starting Hamiltonian [Eq. (1)]. These processes introduce interactions in the spin sector [27], resulting in $K_s \neq 1$.

The spin-orbit coupling in SWCNTs was found to be unexpectedly large, around 1 meV for a nanotube with diameter of 1 nm, resulting in a g-factor enhancement $g = 2.14$ in a few electron carbon nanotube quantum dot [21]. In the presence of many electrons, the interplay of interactions, low dimensionality and spin-orbit coupling determines the strongly correlated ground state and it can further enhance spin-symmetry breaking. $K_s \sim 1.3$ for quantum wires [30] like InAs, which is another possible realization of LL. These materials possess a spin-orbit coupling of the same order of magnitude than SWCNTs but they have a 3 times smaller Fermi velocity. Following a similar line of reasoning for SWCNTs, we use [25] $K_s \approx 1 + g_s/(2\pi v_F)$ with g_s the effective interaction in the spin sector using the g-ology notations [23,25], influenced by the spin-orbit coupling (the same as for quantum wires [30], but with $v_F \approx 3v_{F,\mathrm{wire}}$) and take a conservative estimate of K_s to be around 1.1.

In the following, we discuss the relevance of the results on the absence of an ESR signal in SWCNTs. As we showed above, the ESR signal intensity of a LL crosses over smoothly for the noncorrelated case to the static susceptibility that is the Pauli susceptibility of metallic SWCNTs [31]: $\chi_0 = \mu_0 g^2/\mu_B^2 D(E_F)/4$, where $D(\epsilon_F)$ is the density of states (DOS) at the Fermi energy. To have an accurate value for the DOS in a realistic sample, we performed density functional theory calculations with the Vienna *ab initio* simulation package [32] within the local density approximation for metallic nanotubes. The projector augmented-wave method was used with a plane-wave cutoff energy of 400 eV. The DOS was obtained with a Green's function approach from the band structure. We considered SWCNTs with chiral indices [33] of (9,9), (15,6), (10,10), (18,0), and (11,11). These tubes are within the Gaussian diameter distribution of a usual SWCNT sample with a mean diameter of 1.4 nm and a variance of 0.1 nm. We confirmed by nearest-neighbor tight binding calculations on *all* the metallic SWCNTs in the above diameter distribution that the DOS depends very weakly on the chirality; thus, the above SWCNTs chiralities are indeed representative for the ensemble of the metallic tubes.

We obtain that such a tube ensemble has a DOS of $D(E_F) = 4.6 \times 10^{-3}$ states/eV/atom by averaging the DOS for the above SWCNTs and taking into account that only one third of the tubes are metallic for this diameter range [33]. This is a very low DOS which results from the one-dimensionality of the tubes and from the fact that the majority of the tubes are nonmetallic. It is 50 times smaller than in K_3C_{60} ($D(E_F) \approx 0.3$ states/eV/atom [1]) and is comparable to the low DOS of pristine graphite ($D(E_F) \approx 5 \times 10^{-3}$ states/eV/atom [34]). With the above DOS, we obtain that a typical 2 mg SWCNT sample gives a practically detectable signal-to-noise ratio of $S/N = 10$ for a spectrum measured for 1000 seconds provided the ESR line is not broader than 110 mT. To obtain this value, we considered that the state-of-the-art ESR spectrometers give a $S/N = 1$ for 10^{10} $S = 1/2$ spins at 300 K provided the ESR linewidth is 0.1 mT and each spectra points (typically 1000) are measured for 1 sec. We also took into account that the S/N drops with the square of the linewidth for broadening beyond 1 mT.

The above calculated homogeneous broadening of the ESR line of a LL is $2\pi\gamma k_B T/g\mu_B$ in units of the magnetic field. Thus at 4 K, which is the lowest available temperature for most ESR spectrometers, one has a broadening of $\gamma \times 18.7$ T. This, together with the above detectability criterion gives an upper limit of $\gamma = 6 \times 10^{-3}$ for the detection of the ESR signal. Clearly, the above conservative estimate of $\gamma = 4.5 \times 10^{-3}$ based on the $K_s = 1.1$ value is close to this limit, which explains why careful studies have not yet yielded a conclusive ESR signal of itinerant electrons is SWCNTs. This argument might be also turned around: the fact that no ESR signal of the itinerant electron has been observed in the SWCNTs means that the line is broadened beyond observability, which is translated to $\gamma > 6 \times 10^{-3}$, putting also $K_s > 1.1$. However, other factors, such as, e.g., limited microwave penetration into the SWCNT sample further limits ESR experiments, leading to the unobservability of ESR for smaller values of γ and K_s as well.

We finally comment on the future viability of this observation. Clearly, ESR spectrometers operating to sub Kelvin temperatures are required. Observation of linearly temperature dependent ESR linewidth would be an unambiguous evidence for the observation of the ESR signal of itinerant electrons in the LL state. Such a temperature dependence is fairly unusual as ESR linewidth in metals normally tends to a residual value similar to the resistivity.

In summary, we extended the theory of electron spin resonance in a LL for the case of broken spin symmetry with interacting spin sector. We obtain a significant homogeneous broadening of the ESR linewidth with increasing temperature, which explains the unobservability of ESR in single-wall carbon nanotubes and puts severe constraints on the usability of SWCNTs for spintronics.

The authors acknowledge useful discussions with L. Forró and an illuminating exchange of Emails with A. De Martino. Supported by the Hungarian State Grants (OTKA) F61733, K72613, NK60984, F68852, and K60576. V. Z. and F. S. acknowledge the Bolyai programme of the HAS for support.

*dora@pks.mpg.de

[1] O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997).
[2] K. S.Novoselov *et al.*, Nature (London) **438**, 197 (2005).
[3] R. Egger and A. O. Gogolin, Eur. Phys. J. B **3**, 281 (1998).
[4] C. Kane *et al.*, Phys. Rev. Lett. **79**, 5086 (1997).
[5] L. Balents and M. P. A. Fisher, Phys. Rev. B **55**, R11 973 (1997).
[6] H. Yoshioka and A. A. Odintsov, Phys. Rev. Lett. **82**, 374 (1999).
[7] Y. A. Krotov *et al.*, Phys. Rev. Lett. **78**, 4245 (1997).
[8] P. M. Singer *et al.*, Phys. Rev. Lett. **95**, 236403 (2005); B. Dóra *et al.*, Phys. Rev. Lett. **99**, 166402 (2007).
[9] M. Bockrath *et al.*, Nature (London) **397**, 598 (1999).
[10] B. Gao *et al.*, Phys. Rev. Lett. **92**, 216804 (2004).
[11] H. Ishii, *et al.*, Nature (London) **426**, 540 (2003).
[12] H. Rauf *et al.*, Phys. Rev. Lett. **93**, 096805 (2004).
[13] D. C. Vier and S. Schultz, Phys. Lett. A **98**, 283 (1983).
[14] J. B. Torrance *et al.*, Phys. Rev. Lett. **49**, 881 (1982).
[15] A. Jánossy *et al.*, Phys. Rev. Lett. **79**, 2718 (1997).
[16] P. Petit *et al.*, Phys. Rev. B **56**, 9275 (1997).
[17] A. S. Claye *et al.*, Phys. Rev. B **62**, R4845 (2000).
[18] J.-P. Salvetat *et al.*, Phys. Rev. B **72**, 075440 (2005).
[19] V. Likodimos *et al.*, Phys. Rev. B **76**, 075420 (2007).
[20] I. Žutić *et al.*, Rev. Mod. Phys. **76**, 323 (2004).
[21] F. Kuemmeth *et al.*, Nature (London) **452**, 448 (2008).
[22] A. De Martino *et al.*, Phys. Rev. Lett. **88**, 206402 (2002).
[23] A. De Martino *et al.*, J. Phys. Condens. Matter **16**, S1437 (2004).
[24] A. O. Gogolin, A. A. Nersesyan, and A. M. Tsvelik, *Bosonization and Strongly Correlated Systems* (Cambridge University Press, Cambridge, 1998).
[25] T. Giamarchi, *Quantum Physics in One Dimension* (Oxford University Press, Oxford, 2004).
[26] C. P. Slichter, *Principles of Magnetic Resonance* (Spinger-Verlag, New York, 1989), 3rd ed.
[27] T. Giamarchi and H. J. Schulz, J. Phys. (Orsay, Fr.) **49**, 819 (1988).
[28] H. J. Schulz, Phys. Rev. B **34**, 6372 (1986).
[29] M. Oshikawa and I. Affleck, Phys. Rev. B **65**, 134410 (2002).
[30] V. Gritsev *et al.*, Phys. Rev. Lett. **94**, 137207 (2005).
[31] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt Rinehart and Winston, New York, 1976).
[32] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
[33] R. Saito, G. Dresselhaus, and M. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
[34] M. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).