Nuclear Magnetism and Electronic Order in $^{13}$C Nanotubes

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Single wall carbon nanotubes grown entirely from $^{13}$C form an ideal system to study the effect of electron interaction on nuclear magnetism in one dimension. If the electrons are in the metallic, Luttinger liquid regime, we show that even a very weak hyperfine coupling to the $^{13}$C nuclear spins has a striking effect: The system is driven into an ordered phase, which combines electron and nuclear degrees of freedom, and which persists up into the millikelvin range. In this phase the conductance is reduced by a universal factor of 2, allowing for detection by standard transport experiments.

The physics of conduction electrons interacting with localized magnetic moments is central for numerous fields in condensed matter such as nuclear magnetism [1], heavy fermions [2], or ferromagnetic semiconductors [3–6]. Nuclear spins embedded in metals offer an ideal platform to study the interplay between strong electron correlations and magnetism of localized moments in the RKKY regime. In two dimensions the magnetic properties of the localized moments [7,8] depend indeed crucially on electron-electron interactions [9–13]. In one-dimensional (1D) systems such as single wall carbon nanotubes (SWNTs) electron correlations are even more important. For metallic (armchair) SWNT they lead to Luttinger liquid physics [14–16]. Recently, SWNTs made of $^{13}$C, forming a nuclear spin lattice, have become experimentally available [17–20]. Motivated by this we study here nuclear magnetism in metallic $^{13}$C SWNTs. We show that even a weak hyperfine interaction can lead to a helical magnetic order of the nuclear spins (see Fig. 1) coexisting with an electron density order that combines charge and spin degrees of freedom. The ordered phases stabilize each other, and the temperature undergradues a dramatic renormalization up into the millikelvin range due to electron-electron interactions. In this new phase the electron spin susceptibility becomes anisotropic and the conductance of the SWNT drops by a universal factor of 2.

The drastic restructuring of the electron wave functions through the renormalization is very different from the case of two [7,8] or three dimensions [1] where it is, in comparison, weak. The same renormalization leads to considerable anisotropy in the electron system: The nuclear magnetic field spontaneously breaks the spin rotational symmetry; it rotates in a plane, which we can associate with the spin $(x, y)$ directions (see Fig. 1). This plane is singled out as an easy plane through the stabilization of the electron density wave, and electron correlation functions become anisotropic between the spin $(x, y)$ plane and the spin $z$ direction. We illustrate this behavior below through the calculation of the electron spin susceptibilities. We emphasize that this anisotropy is a crucial feature of the SWNT system studied here and appears spontaneously due to strong renormalization of the RKKY interactions. This distinguishes our system, in particular, from models with built-in easy-axis anisotropy [21].

Model.—We assume that the electrons are confined in a single mode $\psi_\perp$ in the directions perpendicular to the tube axis. The nuclear spins $I = 1/2$ of the $^{13}$C ions on a circular cross section have identical overlaps with this transverse mode, and so identical couplings to the electrons. Through their indirect RKKY interaction over the electron gas they are therefore locked in a ferromagnetic alignment (see Fig. 1). This RKKY interaction, described below, overrules furthermore the direct dipolar interaction between the nuclear spins. The latter is very small [22], $\sim 10^{-11}$ eV, and shall be neglected henceforth. This allows us to treat the nuclear spins as a 1D chain of large $I = IN_\perp$ spins, composed of the sum of the $N_\perp \sim 50$ spins around a circular cross section. Because of this, Kondo physics, which requires small quantum spins, can be excluded from the beginning.

Hence, we model the SWNT by a 1D nuclear spin lattice of length $L$ coupled through the hyperfine interaction to a 1D electron gas. The Hamiltonian resembles that of a Kondo lattice $H = H_\text{el} + A\sum_i \mathbf{S}_i \cdot \mathbf{I}_i$, where $i$ runs over the 1D lattice sites with positions $r_i$, $\mathbf{I}_i = (\mathbf{I}_i^x, \mathbf{I}_i^y, \mathbf{I}_i^z)$ is the effective nuclear spin of size $I = IN_\perp$, $\mathbf{S}_i = (\mathbf{S}_i^x, \mathbf{S}_i^y, \mathbf{S}_i^z)$ is the electron spin operator at site $i$, and $A = A_0/N_\perp$ is the on-site hyperfine interaction constant $A_0$ weighted by the transverse electron mode. In contrast to the usual Kondo-lattice model, $H_\text{el}$ describes the interacting electrons and is defined in Eq. (2) below.

The precise value of $A_0$ in SWNTs is unknown. Estimates in the literature [23] provide values of $A_0 \sim 10^{-7}–10^{-6}$ eV, depending much on the curvature of the
The effective Hamiltonian for the nuclear spins [7,8], allows us to obtain an effective Hamiltonian for the nuclear spins $\mathcal{H}_n = \frac{1}{2} \sum_{ij} J_{ij}^{n} \hat{I}_i^{n} \hat{I}_j^{n} = \frac{1}{2} \sum_{ij} J_{ij}^{n} \hat{I}_i^{n} \hat{I}_j^{n}$, where $a = x, y, z$, and $J_{ij}^{n} = A_0^2 A_{ij}^{a} a / 2$ is the effective RKKY [25] interaction between nuclear spins. $a$ is the lattice spacing and provides the short distance cutoff of the continuum theory. The sum over $q = n \pi / L$ for integer $n$ runs over the first Brillouin zone. $\chi_{ij}^{a} = -i a^{-1} \int_{0}^{\infty} dt [\langle \hat{S}_i^{a}(t), \hat{S}_j^{a}(0)\rangle] e^{-\eta t}$ (for an infinitesimal $\eta > 0$) is the static electron spin susceptibility. We also have defined $J_{ij}^{q} = \sum \hat{e}_{ij} \hat{S}_i^{a} \hat{S}_j^{a}$ and $J_{ij}^{q} = \int dt e^{-i t q} J_{ij}^{a}(r)$. The effective electron Hamiltonian, on the other hand, includes the effect of the feedback of the nuclear field on the electrons. Since the spins $\hat{I} = IN_\perp$ are large, we can choose $H^n_{\text{eff}} = H_{\text{el}} + H_{\text{OV}}$, with $H_{\text{OV}} = \sum \hat{h}_i \cdot \hat{S}_i$ and $\hat{h}_i = A(\hat{I})$ the nuclear Overhauser field.

Interacting electrons as Luttinger liquid.—We use a bosonized Hamiltonian to describe the interacting electron system of the armchair SWNT, which is naturally in the Luttinger liquid state due to the linear electron dispersion [14,15]. The unit cell of a graphite sheet contains two carbon atoms, which results into a two-band description of the bosonized system. Since mixing between the bands is essentially absent [14,15] we shall, however, focus on a single band only in order to avoid a heavy notation. The bosonized single-band Hamiltonian reads [14,15,26]

$$H_{\text{el}} = \sum_{\nu = c,s} \int \frac{dr}{2\pi} \left[ \frac{v_F}{K_{\nu}} (\nabla \phi_{\nu}(r))^2 + v_{\nu} K_{\nu} (\nabla \theta_{\nu}(r))^2 \right],$$

where $\phi_{c,s}$ are boson fields such that $-\nabla \phi_{c,s} \sqrt{2}/\pi$ express charge and spin density fluctuations, respectively. $\theta_{c,s}$ are such that $\nabla \theta_{c,s} / \pi$ are canonical conjugate to $\phi_{c,s}$. $v_{c,s} = v_F / K_{c,s}$ are charge and spin wave velocities, and $K_{c,s}$ are the dimensionless Luttinger liquid parameters. For SWNTs [14,15], $K_c = 0.2$. If the electron spin SU(2) symmetry is maintained, $K_t = 1$, otherwise $K_t \neq 1$.

Without feedback from nuclear magnetic field.—Let us first assume that there is no feedback from the Overhauser field on the electrons and set $\hat{h}_i = \hat{0}$. The electron system forms a Luttinger liquid, for which the zero temperature spin susceptibility has a singularity at momentum $q = \pm 2k_F$ induced by backscattering processes [26,27]. At $T > 0$ this singularity turns into a steep but finite minimum: The backscattering part of the spin operator $\hat{S}_i^{a}$ is expressed in the bosonization language by the operators [26] $\hat{S}_{\text{SDW}}^{a} = e^{-i q} e^{i \phi_{\nu}} \cos(\sqrt{2} \theta_{\nu})$, such that $\hat{S}^{a} = \hat{S}_{\text{SDW}}^{a} + \hat{S}_{\text{SDW}}^{a+1} / 2$ plus forward scattering terms. Similar expressions [26] hold for $\hat{S}$ and $\hat{S}^{c}$. We further assume that $J_{ij}^{q} = J_{ij}^{q}$ is isotropic and in particular $K_t = 1$. The correlators between those operators can be evaluated in the standard way and we obtain (for $q > 0$)

$$J_q(g, v_{\nu}) = -C(g, v_{\nu})(k g T)^{2 g - 2} |\Gamma(\kappa) / \Gamma(\kappa + 1 - g)|^2,$$

where $g = (K_c + K_s^2) / 2$, $\kappa = g / 2 - i \lambda_T (q - 2k_F) / 4 \pi$, depending on the thermal length $\lambda_T = v_F / k_B T$ with $k_B$ the Boltzmann constant. $\Gamma$ is Euler's Gamma function and $C(g, v_{\nu}) = A_0^2 a \sin(\pi g) / 2 \pi a / v_F / 8 \pi^2 v_{\nu}$. We have made the inessential assumption $v_{\nu} = v_q = v_{\nu}$. Note that $J_q$ is independent of $k_F$ for a linear dispersion. A density dependence of $J_q$ requires a curvature of the electron dispersion, which partially restores Fermi liquid properties [28], a scenario which we disregard for metallic SWNTs. A sketch of $J_q$ is shown in Fig. 2.
At temperatures $T < T_0^*$ [defined in Eq. (6) below], $|J_{2k_y}(T)| > k_BT$ and the nuclear spins can—classically—minimize the RKKY energy by aligning in a spiral order $\mathbf{I}_L = h^\dagger \mathbf{e}_x + \sin(2k_FR) \mathbf{e}_y$, where $\mathbf{e}_{x,y}$ are vectors defining the spin $(x,y)$ plane. We shall henceforth assume that this order is established, and show that this assumption is self-consistent. Fluctuations reduce this maximal polarization, and in general $|\langle L_y \rangle | < \langle N_L \rangle$. The lowest lying excitations (to order $1/N_L$) in the nuclear spin system are magnons. Since $J_{2k_y}$ is long ranged the energy cost of local defects, like kinks, scales with the system size and is very high.

For a helimagnet, there exists a gapless magnon band with the dispersion \cite{8} $\omega_q = 2(IN_L)(J_{2k_y+q}/N_L^2 - J_{2k_y}/N_L^2)$. Let $m_i = \langle \hat{L}_i \rangle \cdot \mathbf{I}_L^2/(IN_L^2)$ measure the component of the average magnetization along $\mathbf{I}_L^2$, normalized to $0 \leq m_i \leq 1$. Its Fourier component $m_{2k_y}$ acts as an order parameter for the spiral phase. Magnons decrease this order parameter and we have \cite{8}

$$m_{2k_y}(T) = 1 - \frac{a}{(IN_L)^2} \sum_q \frac{1}{e^{\omega_q/k_BT} - 1}.$$  

where the sum represents the magnon occupation number. In the continuum limit $L \rightarrow \infty$ the integrand diverges as $1/q^2$ for $q \rightarrow 0$ (the $q = 0$ mode is absent because the system is not a ring), showing the absence of true long range order in the 1D system. Despite its appearance the divergence is not a consequence of the Mermin-Wagner theorem \cite{29,30}, which forbids long range order in low-dimensional systems for sufficiently short ranged interactions. Since $J_{2k_y}$ is long ranged this theorem does not apply.

The present situation, however, is very different in that the system has a finite length $L \sim 2 \mu m$ imposed either through the natural length of the nanotube or through an external confining potential. At temperatures $T < T_0^*$ we find that $L \ll A_T$, and so the cost of exciting the first magnon is already very high $\omega_q = \pi/L \approx 2|J_{2k_y}(T)|/N_L$. We can define a temperature $T_{M0}$ providing the scale of the excitation of the first magnons by imposing $\omega_q/k_BT = 2|J_{2k_y}(T)|/N_L k_BT$. For $T > T_{M0}$ we can then simplify Eq. (4) to

$$m_{2k_y}(T) = 1 - \frac{1}{\langle N_L \rangle^2 \sum_q \frac{1}{e^{\omega_q/k_BT} - 1}} \approx 1 - \left( \frac{T}{T_0^*} \right)^{3-2g}.$$  

where we have defined

$$k_BT_0^* = \left[ 2I^2C(g, \nu_F) \Gamma^2(g/2) \Gamma^{-2}(1 - g/2) \right]^{1/(3-2g)}.$$  

For the SWNT this temperature satisfies the self-consistency condition $k_BT_{M0} < k_BT_0^* \ll \nu_F/L$. We use $T_0^*$ as an estimate for the critical temperature. For a typical SWNT $T_0^*$ is very low. With the values given with Fig. 3 we obtain $T_0^* \sim 10 \mu K$, too low for experimental detection. Yet this analysis completely neglects the feedback of the magnetic field on the electron gas. This leads to a strong renormalization of $T_0^*$.

**Feedback of nuclear magnetic field on electrons.**—The ordering of the nuclear spins leads to a spatially oscillating Overhauser field $\mathbf{h}_i = A\langle \hat{L}_i \rangle$ that acts back on the electrons. We choose the electron spin axis such that $\hat{S} \cdot \mathbf{e}_y = S^x$ and $\hat{S} \cdot \mathbf{e}_x = S^y$. The spatial oscillations of $\mathbf{h}_i \propto e^{2ik_F r_i}$ in $H_{OV}$ perfectly cancel some of the spatial oscillations of the $\hat{S}^{x,y}$ operators of the $\hat{S}^z$. Neglecting the remaining (irrelevant) oscillating terms we obtain $H_{OV} = \sum A_{ij} Im_{2k_y} \cos(\sqrt{2}K \phi_j(r_j))$, where we have introduced \cite{31} $\phi_+ = (\phi_r + \theta_r)/\sqrt{K}$ with the normalization $K = K_r + 1/K_s$. The Hamiltonian becomes of the sine-Gordon type and $H_{OV}$ is relevant in the sense of the renormalization group (RG): The $\phi_+$ field is pinned at a minimum of the cosine term of $H_{OV}$. The result is a density wave that combines charge and spin degrees of freedom. Fluctuations about the minimum are massive, with a mass associated to an energy scale $\Delta$. At commensurate electron filling fullkllaps processes would become relevant too, and lead to fully gapped charge and spin sectors. For SWNTs, however, this would require high electron densities leading to $\nu_F = 1.4 eV$. This case is not considered here.

Within a perturbative RG approach we find that

$$\Delta \sim \left( A_0 Im_{2k_y}/\nu_F \right)^{1/(2-g)} \nu_F/a.$$  

This mass gap $\Delta$ is the first important consequence of the feedback. The second important consequence is the spontaneous generation of anisotropy because the spin $(x,y)$ plane is singled out by the Overhauser field. This is seen, for instance, in the spin susceptibilities $\chi^{xx}$. Those can be calculated in the same way as before (details are provided in \cite{31}) if we notice that the massive $\phi_+$ field does not contribute to the long-wavelength asymptotics. The finite temperature expressions for the $\chi^{xx}$ are otherwise identical to the case without feedback, and the RKKY couplings $J_0^a$ can be obtained from Eq. (3) upon the following modifications: For $\chi^{xx}$ and $\chi^{xy}$ the exponent $g$ is replaced by

![FIG. 3. (a) Magnetization $m_{2k_y}(T)$ [Eq. (5)]. Dashed line: without feedback. Solid line: with feedback. Parameters for the curves are $[14,15,23,24] \nu_F = 0.1 eV, A_0 = 10^{-7} eV, \nu_F = 8 \times 10^5 m/s, a = 2.46 \AA, K_s = 1, K_r = 0.2$ (leading to $g = 0.6, g_r = 0.33$), and $L = 2 \mu m$. The vertical lines mark the temperatures written next to them. (b) Characteristic temperature $T^*$ [Eq. (9)] as a function of the hyperfine constant $A_0$. The curve follows a power law $T^* \approx A_0^{8/3} = A_0^{8/3}$, and is plotted up to the self-consistency limit $T^* < v_F/Lk_B = 3 K$.](116403-3)
$g' = 2K_c/K_sK$ and the amplitude is reduced by a factor 2 because a term depending on $\phi_+$ only drops out. For $\chi^2$ the exponent becomes $g'' = (K_c/K_s + K_sK_c)/2K$ while the amplitude remains unchanged. $v_F$ is replaced by $v_- = (v_c/K_s + v_cK_s)/K$. This leads to

$$J_0^{g'}/J_0^{g''} = J_0^{g'}(g', v_-)/2, \quad J_0^{g''} = J_0^{g''}(g'', v_-). \quad (8)$$

For $K_c = 0.2$ and $K_s = 1$ we have to compare $g = 0.6$ with the strongly renormalized $g' = 0.33$ and $g'' = 0.17$.

Let us finally note that correlators between $\phi_+$ and $\theta_+$ can only be neglected as long as $k_BT < \Delta$, i.e., $\lambda^2 \xi^{-1} < \xi^{-1}$ with $\xi = v_F/\Delta$ the correlation length. In Eq. (9) below we define a critical temperature $T^*$ similarly to $T_0^*$ before.

For $T \ll T^*$, $m_{2k_f} = 1$ (see Fig. 3), and we find that $\Delta \gg k_BT$. At $T \rightarrow T^*$, however, $m_{2k_f}$ vanishes and so does $\Delta$.

The order furthermore modifies the transport properties of the system. With the opening of the mass gap in the $\phi_+$ channel, half of the conducting modes are blocked and the conductance decreases by the universal factor of 2. As an illustration we consider a SWNT connected to metallic leads. The conductance is given by $[32-34]$: $G = 4e^2/h$, where $e$ is the electron charge, $h$ the Planck constant, and where 4 is the number of conducting channels (2 spin projections and 2 bands). The pinning of the $\phi_+$ field (in each band) blocks 2 conductance channels and so reduces the conductance precisely by the factor 2 (see [31] for details). Such a reduction is a direct consequence of the nuclear spin ordering and the Luttinger liquid physics of the electrons, and should be detectable experimentally in standard transport setups.

As a conclusion, we emphasize that the physics described here is quite general and is also relevant for other 1D systems of the Kondo-lattice type.

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