Unusual Magnetic State in Lithium-Doped MoS_2 Nanotubes

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We report on the very peculiar magnetic properties of an ensemble of very weakly coupled lithium-doped MoS_2 nanotubes. The magnetic susceptibility χ of the system is nearly 3 orders of magnitude greater than in typical Pauli metals, yet there is no evidence for any instability which would alleviate this highly frustrated state. Instead, the material exhibits peculiar paramagnetic stability down to very low temperatures, with no evidence of a quantum critical point as $T \to 0$ in spite of clear evidence for strongly correlated electron behavior. The exceptionally weak intertube interactions appear to lead to a realization of a near-ideal one-dimensional state in which fluctuations prevent the system from reordering magnetically or structurally.

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An idealized one-dimensional (1D) system, even with strong interactions between electrons, is fundamentally constrained by fluctuations and disorder from forming a long-range ordered state at finite temperature [1]. However, such an idealized state has never been realized in practice because in typical quasi-1D solids, interactions between 1D subsystem units lead to the formation of three-dimensionally (3D) ordered states at low temperatures. These exhibit a rich phenomenology of low-temperature broken symmetry charge- and spin-ordered states and have been the subject of intense investigations for many years [1]. In an apparent realization of the near-ideal 1D state in a bulk system, we report on the magnetic properties of Li-doped MoS_2 nanotubes (NTs). The material is exceptional because of its inherently extraordinarily weak coupling between 1D subunits (i.e., individual nanotubes) which we find leads to some remarkable quantum properties.

One of the fundamental reasons why 1D systems typically behave quite differently from two- or three-dimensional ones arises from the very different energy dependence of the electronic density of states: 1D systems have Van Hove (VH) singularities in $N(E)$ which cause strong coupling of electrons or spins to phonons resulting in Peierls-type instabilities. Another peculiar aspect of 1D systems is that single-particle excitations do not exist in the same way as they do in higher dimensions, while the collective excitations exhibit characteristic 1D quantum fluid behavior, and are generally discussed in terms of excitations of Tomonaga-Luttinger liquids. Importantly, fluctuations—both classical and quantum—have a much more pronounced effect in 1D than in higher dimensions and act to stabilize high-entropy states, counteracting the tendency to form an ordered state [1]. Such fluctuations are found to play a crucial role in stabilizing the strongly correlated high-susceptibility state of the system described here: magnetic measurements of Li-doped chalcogenide nanotubes Li_xMoS_2 [2] show a nearly T-independent susceptibility $\chi \sim 10^{-2}$ emu/mol, which is some 500 times larger than for Li metal [3] and more than 100 times larger than in archetypal linear-chain quasi-1D compounds such as $K_{0.3}MO_3$ or $(TaSe_4)_2I$ [4], which persists down to low temperatures.

The recent discovery of transition metal chalcogenide (TMC) nanotubes (MoS_2) [5] with exceptionally weak internanotube interactions, gives new opportunities to study electronic properties of near-ideal model 1D systems (the structure is shown in Fig. 1). These interactions are measured rather accurately by mechanical shear measurements on NT bundles [6] and have been shown to be more than 10 times weaker than those between carbon nanotubes in ropes, which are in turn at least an order of magnitude weaker than in other quasi-1D solids which exhibit 3D ordering transitions at low temperatures [1]. Just on the basis of comparing the inter-1D subsystem interactions, one may expect any 3D ordering temperature in the present system to be well below 2 K, implying that the system might remain effectively one dimensional well into the low-temperature quantum fluctuations regime.

MoS_2 NTs were prepared as reported previously [5]. The material was electrochemically doped to a nominal concentration of $x = 2.5$ according to the formula Li_xMoS_2. x was determined by monitoring the potential between the TMC electrode and a reference electrode [2]. $x = 2.5$ corresponds to a doped electron concentration of $\sim 40e^-/\text{nm}$, in linear dimension measured along the nanotube. The magnetization $M(H)$ and susceptibility χ of the doped material (which was kept in an inert

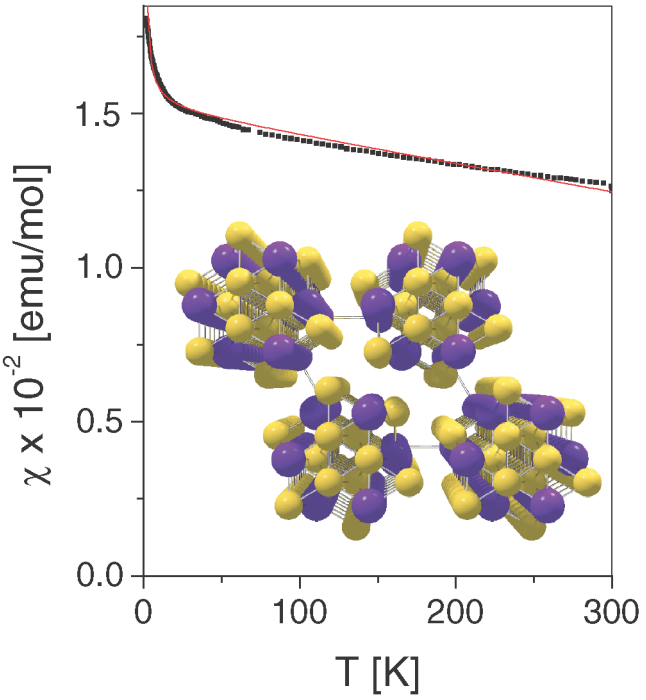

FIG. 1 (color online). The susceptibility of Li_xMoS_2 ($x = 2.5$) NTs at 1000 Oe. The inset shows the cross-sectional structure of the NT bundles [5]. The solid line is a fit to the data using Eq. (1).

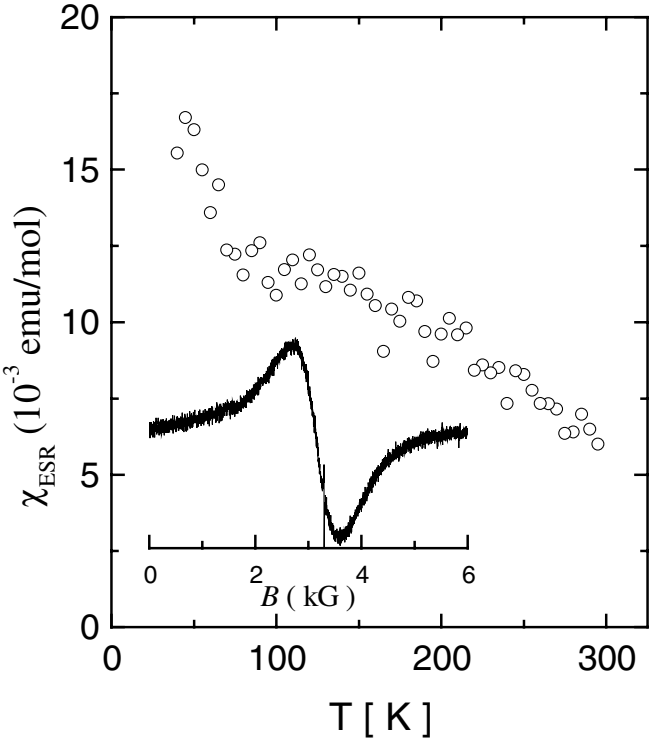

FIG. 2. χ_{ESR} (ESR intensity) of the broad line as a function of temperature. Inset: the ESR spectrum at room temperature with $g \approx 2.15$.

atmosphere at all times) was measured with a Quantum Design SQUID magnetometer. The static susceptibility χ_{ESR} was also measured using an ESR spectrometer (Bruker 300 with a Varian dual resonator). The magnetization measurements were performed on five different samples doped from three different growth batches of NTs. Control experiments were performed with samples in different containers to ensure that background subtraction procedures were accurate. The absolute values of χ and χ_{ESR} were calculated by weighing the sample after the measurements.

The typical susceptibility χ on Li_xMoS_{2-y} is shown in Fig. 1. Between 50 and 300 K, χ is weakly T dependent. Below 50 K, we usually observe an upturn, which is in some samples more pronounced than in others. The data can be fit quite well using a sum of a Curie-like susceptibility χ_C and a linearly T-dependent Pauli-like susceptibility χ_P (see fit in Fig. 1):

$$\chi = \chi_C + \chi_P = C/(T + \theta) + (\chi_0 + \chi_1 T), \qquad (1)$$

where $\chi_0 = 1.4 \times 10^{-2}$ emu mol^{-1}, $\chi_1 = -6.8 \times 10^{-6}$ emu mol^{-1} K^{-1}, $\theta < 2$ K, and $C = 2 \times 10^{-2}$ emu mol^{-1}.

Very similar behavior is observed in ESR measurements. The ESR spectrum of the Li_xMoS_2 is shown in Fig. 2. Two ESR lines are typically observed: one very broad, with $\Delta H > 1000$ G, and one narrow ($\Delta H \simeq$ 3–5 G), which we discuss in detail elsewhere [7]. The static susceptibility χ_{ESR} (i.e., ESR intensity) has a rather weak T dependence, similar to χ_P measured by the SQUID magnetometer, with excellent *quantitative* agreement between χ_{ESR} and χ_P (Figs. 1 and 2).

The magnetization $M(H)$ of Li_xMoS_{2-y} as a function of applied magnetic field H is shown in Fig. 3(a). The ubiquitous feature of the data at all temperatures is the predominantly linear magnetization with no signs of saturation above 5 kOe together with weak, but unambiguously nonlinear behavior below 5 kOe. At 50 kOe, the $M = 1.5 \times 10^{-3}$ emu corresponds to a magnetic moment of approximately $0.05\mu_B$ per mole, suggesting full saturation is not reached up to fields in excess of 100 T (10^6 Oe).

Following the suggestion from (1) that the system can be described in terms of the sum of contributions from Pauli and Curie-like terms, we fit the magnetization data to

$$M(H) = \chi^* H + M_0 \mathcal{B}[S, H, T], \qquad (2)$$

where the dominant contribution $\chi^* = 2 \times 10^{-3}$ emu mol^{-1} Oe^{-1} and is nearly T independent. $\mathcal{B}[S, H, T]$ is the Brillouin function and $M_0 = 2 \times 10^{-4}$ emu. Remarkably, the data *cannot* be fit with $S = 1/2$ [Fig. 3(b)]. Rather, the behavior of $\mathcal{B}[S, H, T]$ for $H < 5$ kOe is more typical of a superparamagnet, with $S = 10$–100, depending on the sample. The value

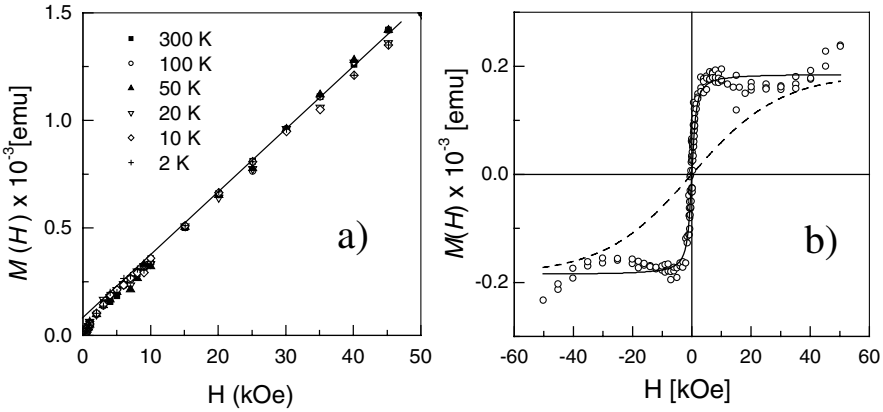

FIG. 3. (a) The magnetization M as a function of magnetic field H at different temperatures. The line is a linear fit to the data, which has a nonzero intercept at all T. (b) A fit to $M(H)$ using $S = 1/2$ (dashed line) and $S = 25$ (solid line). (The linear contribution to $M(H)$ has been subtracted.)

of M_0 corresponds $\sim 5 \times 10^{-3} \mu_B \, \mathrm{mol}^{-1}$, suggesting only a small number of spins contribute to the second term in Eq. (2). The presence of a nonzero intercept in Fig. 3(a) indicates that these spin clusters exist from 2 K up to at least 300 K.

Before discussing the origins of this very peculiar magnetic behavior, we show that the observed magnetic properties are intrinsic, which is fortunately quite unambiguous in this case. First, *undoped* MoS_{2-y} NTs show *no detectable magnetic or ESR signal*, while the ESR signals of Li-doped material disappear entirely upon exposure to air within hours [2]. This excludes all possible contributions from magnetic impurities. Moreover, Mo metal impurities cannot be contributing to the magnetization, since Mo metal is diamagnetic. Also, Li-doped layered $2H$-MoS_2 can be excluded as it has a very different g value, with a dominant ESR line which is significantly narrower and weaker than in Li_xMoS_{2-y} NTs. Altogether, considering the excellent reproducibility from sample to sample, similar behavior of samples from different growth batches, and excellent quantitative agreement between ESR and SQUID measurements, we conclude that the data are intrinsic.

In principle, we can try and explain the large χ in terms of a quasi-1D Pauli metal with a VH singularity near E_F. From the measured χ, we can estimate $N(E) = \chi/\mu_B^2 \simeq$ 300 states eV^{-1} per formula unit (f.u.). This is some 20 times bigger than predicted by band-structure calculations [8]. The bandwidth implied by $N(E) \simeq 300$ states $\mathrm{eV}^{-1}\,\mathrm{f.u.}^{-1}$ is $W \sim 1/N(E) \approx 3$ meV (25 K) indicating that the susceptibility should be strongly temperature dependent. Such behavior is typically displayed by heavy fermion compounds, which have a rather high susceptibility at low temperatures, but a much smaller one at room temperature. This is quite contrary to the nearly T-independent behavior we observe, suggesting a serious discrepancy with a Fermi liquid-based interpretation of the magnetic susceptibility data.

Invoking a Stoner enhancement factor S to take into account strong electron-electron interactions [9], the susceptibility is given by $\chi = \chi_0 S = \chi_0[1 - IN(E)]^{-1}$ where χ_0 is the "bare" Pauli susceptibility and I is the exchange correlation integral. From the data we calculate an extremely large enhancement $S = [1 - IN(E)]^{-1} \simeq$ 20. Using $N(E) \simeq 10$ states/eV/f.u. from band-structure calculations [8], we find that $I \simeq 0.1$ eV f.u. More importantly, $IN(E) \simeq 0.95$, i.e., very close to 1. Considering Stoner's criterion for the formation of a ferromagnetic state [9], namely, $IN(E) > 1$, the implication is that the system is *very close to a ferromagnetic (FM) instability.*

An alternative approach to understanding the quantum behavior of the system would be to examine the expected behavior of a Luttinger liquid (LL). The spin susceptibility of interacting electrons in one dimension has been calculated theoretically by a number of authors for various degrees of doping [10]. The most recent predicted temperature dependence of a LL at quarter filling is predicted by Nelisse *et al.* [11] to show a weakly T-dependent susceptibility at high T. The predicted susceptibility has a magnitude given by $\chi_{\mathrm{LL}} \simeq \mu_B^2/t$, where t is the electron hopping integral. With $t \simeq 0.1$ eV, this gives $\chi_{\mathrm{LL}} \sim 1.5 \times 10^{-4}$ emu $\mathrm{mol}^{-1}(\mathrm{Oe}^{-1})$. This is not much different from the value of the bare Pauli susceptibility χ_0 and is 2 orders of magnitude too small to account for the observations.

A more realistic approach to analyzing the data may be to assume that the system is inhomogeneous and to discuss the two contributions to the magnetization in Eqs. (1) and (2) separately. The nonlinear low-field magnetization and Curie-like susceptibility seem to arise from a relatively small number of FM spin clusters with $M_0 \sim 5 \times 10^{-3} \mu_B$/mol and $S = 10$–100. When this is subtracted from $M(H)$ and $\chi(T)$, we are left with an "intrinsic" susceptibility of the 1D system, characterized by a still very large $\chi^* = \partial M/\partial H = 2 \times 10^{-3}$ emu mol^{-1}. With this value of χ^* and the band-structure value of

$N(E) \simeq 10$ states/eV/f.u., the calculated Stoner enhancement would still be large, but not unphysically so, with $S = 3.3$.

Clearly, in the presence of such strong electronic correlations which the magnetic data imply, the conspicuous absence of any anomaly which would signify a transition to a lower-energy ordered state at low temperatures is quite extraordinary. The system exists in a state very close to a FM instability, but is stabilized in the paramagnetic state because 1D fluctuations—including spin and structural ones—overcome any weak internanotube interactions which might act to form a 3D FM ordered state. Of course, topological defects would aid the formation of some local spin clusters, as we indeed observe. However, the rest of the ensemble composed of extremely weakly coupled nanotubes appears to exist in an inherently stable high-susceptibility paramagnetic state which is fundamentally constrained by fluctuations from undergoing a transition to a magnetically ordered state. It should be noted that similar susceptibility behavior—albeit smaller in magnitude—has been observed in K-doped WS_2 fullerenelike nanoparticles [12], implying that confinement due to nanosize particles may be relevant. We thus conclude that the Li-doped MoS NTs appear to be a realization of a near-ideal 1D system displaying qualitatively new strongly correlated behavior not hitherto observed. Whether quantum fluctuations prevent the system from reaching a quantum critical point (QCP) at ultralow temperatures approaching $T = 0$ is a fundamental question which still remains to be answered, but in the present data down to 2 K there is nothing to suggest the presence of a QCP as $T \rightarrow 0$. The answer to another fundamental question, namely, why the system prefers ferromagnetic correlations in the first place—rather than the more usual antiferromagnetic correlations, or a superconducting [13] pairing instability—still remains to be answered.

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