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Magnetic properties of MoS_2 nanotubes doped with lithium

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Abstract

DC magnetization measurements of lithium-doped molybdenum sulfide nanotubes (Li_xMoS_2, $2.2 < x < 2.5$) reveal a very large, nearly linear temperature-dependent susceptibility. The susceptibility in the temperature interval from 300 to 2 K is more than 10^{-2} emu mol^{-1}, which is more than 100 times larger than the susceptibility of Li metal. The $M(H)$ curves (0 kOe $\leq H \leq$ 50 kOe) measured at several temperatures between 2 and 300 K show a very small temperature dependence. Besides the linear part of $M(H)$ for $H > 10$ kOe, the nonlinear part in $H < 5$ kOe with saturation at approximately 10 kOe can be observed. This suggests a formation of ferromagnetic clusters even at room temperature. No magnetic phase transition between 2 and 300 K has been detected.

Keywords: Li_xMoSo_2; Magnetic properties; Susceptibility; Nanotubes

1. Introduction

The discovery of microscopic one-dimensional molecular structures (e.g. nanotubes of carbon) has attracted a great deal of attention because of various interesting properties associated with their small dimensions, high anisotropy, and tube-like structures. Nanoparticles exhibit magnetic phenomena usually different from the properties of the individual constituents, e.g. magnetoresistance effects, magnetocaloric effects and high magnetic susceptibilities.

The synthesis of subnanometer-diameter monomolecular MoS_2 single-wall nanotubes and a proposed structure were reported recently [1]. MoS_2 nanotubes can be doped with large amounts of Li atoms and it has been proposed that they might be used as the electrodes for Li-ion batteries [2]. On the other hand, this system offers new possibilities to study low-dimensional magnetic phenomena, particularly because the forces between individual tubes appear to be very weak. We present here DC magnetization and susceptibility measurements of the Li-doped MoS_2 nanotubes in the temperature interval from 2 to 300 K as a function of temperature and magnetic field.

2. Experimental

MoS_2 nanotubes were grown by a catalyzed transport method using C_{60} as a growth promoter in the reaction. The C_{60} (5 wt.%) was added to MoS_2 powder in the transport tube as catalyst [1]. The material was then electrochemically doped by Li to a nominal concentration of $2.2 < x < 2.5$ in Li_xMoS_2 [2]. The Li concentration was determined by monitoring the potential between the MoS_2 nanotube electrode and a reference electrode. The doped material was then transferred to a quartz ampoule and sealed in an inert atmosphere.

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The magnetization was measured with a Quantum Design SQUID magnetometer, equipped with a 5-T superconducting magnet.

We have measured the magnetization of several different samples doped in different growth batches of nanotubes from 300 to 2 K in magnetic field $H = 1000$ Oe. All samples were sealed in quartz tubes (5 cm in length, 5 mm in diameter). In order to obtain as much as possible symmetrical configuration inside the susceptometer, an additional empty quartz tube with the same dimensions as the sample tube was attached to the bottom part of the sample tube. With such arrangement, the SQUID response on the sample movement along the detection coil was symmetrical and the calculated magnetization of the sample was reliable and reproducible. After each measurement, the tubes were inverted. The inversion did not change the configuration of the quartz tubes, while the sample fell out of the SQUID sensitivity area. In this way, we were able to measure the background signal due to quartz tubes. The SQUID response without the sample inside its sensitivity area was negligible and we did not need to subtract it from the signal of the sample.

All tubes contained approximately the same amount of sample. The measured magnetizations of the four samples in $H = 1000$ Oe as a function of temperature are shown in Fig. 1.

One sample (sample 4 in Fig. 1) was moved from the quartz tube into a small pharmaceutical plastic capsule which is usually used as a sample holder for SQUID magnetization measurements. The rearrangement of the sample was done in the helium-filled dry box. The measured magnetization of this sample in the plastic capsule was even slightly larger than the magnetization of the same sample measured in the quartz tube. This can be explained by the different arrangement of the sample in two holders. In the plastic capsule, the sample occupies a smaller volume and behaves more like a magnetic dipole, while in the quartz tube, because of its small inner diameter, the sample occupies larger linear range. This "linearly extended" sample, while moving along the SQUID gradiometer coil arrangement, produces smaller peak-to-peak signal than the magnetic dipole, even if their magnetization was the same.

However, the temperature dependence of the magnetization was practically the same regardless on the sample holder. This and the similarity of the emu values of the magnetization in all five samples convinced us that the data are correct and reproducible. Following all measurements, the sample in the plastic capsule was weighted.

We have also measured the magnetization M as a function of magnetic field H (0 kOe $\leq H \leq$ 50 kOe) at several temperatures. Some of these measurements are shown in Fig. 2. The magnetization is linear in magnetic field up to 1000 Oe and the susceptibility $\chi = M/H$ is shown in Fig. 3.

A large susceptibility of this system has also been obtained from ESR measurements. Two ESR lines are typically observed: one very broad and one narrow. The broad line is very intense and has similar T-(in)depen-

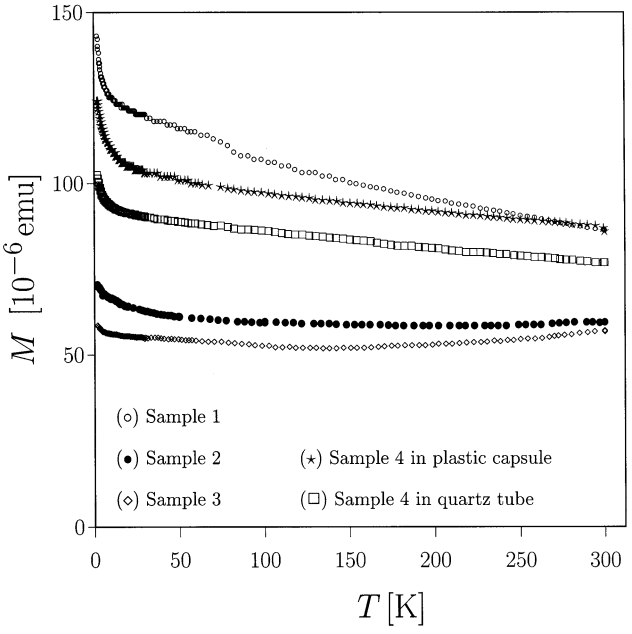

Fig. 1. The magnetization of four Li_xMoS_2 nanotubes measured in magnetic field of 1000 Oe. In all cases approximately 1 mg of the sample was used.

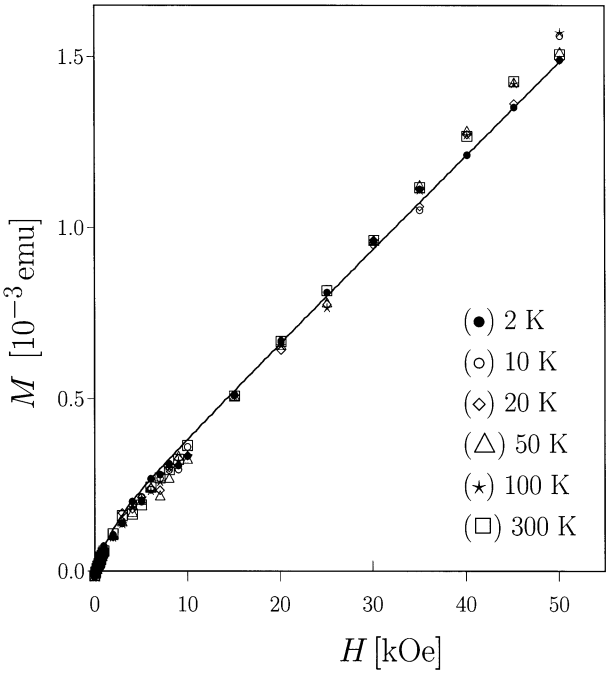

Fig. 2. The magnetization M as a function of magnetic field H at different temperatures. The solid line is a fit to the data at 2 K (●) using $M = kH + M_0$ Brillouin $f(S,H,T)$.

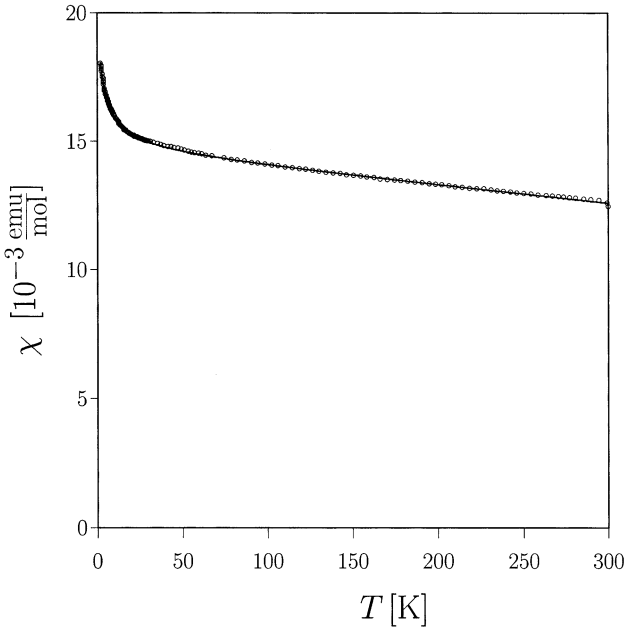

Fig. 3. The susceptibility of the Li_xMoS_2 nanotubes measured in plastic capsule. The solid line is a fit to the data using Eq. (1).

dence as DC-susceptibility measured by the SQUID susceptometer. There is also excellent quantitative agreement between these two susceptibilities [4].

3. Discussion and conclusions

The measured susceptibility $\chi(T)$ as a function of temperature can be described well with a sum of a Curie-like susceptibility χ_C and a linearly temperature-dependent term χ_P:

$$\chi = \chi_C + \chi_P = \frac{C}{T+\theta} + \chi_0 + \chi_1 T \quad (1)$$

In our case, the fitting parameters C, θ, χ_0 and χ_1 still depend on the mass of sample, since only the mass of one sample is known exactly. However, the masses of all five samples are comparable and the calculated fitting parameters are of the same order of magnitude for all measurements. The temperature-independent susceptibility χ_0 and the linearly dependent term $\chi_C T$ can be described in the form of Pauli-like susceptibility of conduction electrons. Using magnetization data, obtained from the weighted sample, we calculated for susceptibility, $\chi_0 = 1.4 \times 10^{-2}$ emu mol^{-1}. This value is more than 100 times larger than the susceptibility of Li metal [3] and we attribute this large susceptibility to the nanotubes themselves rather than to Li metal.

From the Pauli relation between the susceptibility of conduction electrons and the density of states at Fermi energy, $\chi_0 = \mu_0 \mu_B^2 N(\varepsilon_F)$ [5], where μ_0 is the permeability of vacuum, μ_B the Bohr magneton and $N(\varepsilon_F)$ the density of states at Fermi energy, $N(\varepsilon_F)$ can be calculated. We obtain for the density of states at Fermi energy approximately 300 levels per molecule MoS_2 per eV. Such large density of states would lead to lattice instability which is seriously challenging the Pauli-like interpretation of the measured susceptibility.

The temperature-independent magnetization curve $M(H)$ (Fig. 2) is compatible with the Pauli-like temperature (in)dependence of $\chi(T)$. While the linear $M(H)$ dependence (for $H > 10$ kOe) is expected for Pauli-like susceptibility, the $M(H)$ in smaller field ($H < 5$ kOe) is obviously nonlinear. This part of $M(H)$ resembles more to (super)paramagnetic behaviour with saturation at around 10 kOe. Indeed, the nonlinear part of $M(H)$ can be well fitted with Brillouin function with spin S between 10 and 100, depending on the sample. This large S implies the formation of ferromagnetically coupled spins in clusters. The nonlinear behaviour of $M(H)$ with large spin S remains present even at room temperature which means that the formation of the clusters takes place already at high temperatures. The temperature independence of this nonlinear part of the $M(H)$ in small magnetic field suggests possibility of a ferromagnetically ordered state even at room temperature.

To conclude, Li-doped MoS_2 nanotubes show a very large, nearly temperature-independent Pauli-like susceptibility. The susceptibility is more than 100 times larger than for Li metal and appears to be an intrinsic property of the doped nanotubes. Measured $M(H)$ dependencies at several temperatures can be explained by the formation of small ferromagnetic clusters above room temperature.

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