Low-energy excitations in Mo-S nanotubes:

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Why should we be interested?

- Mo-chalcogenide nanotubes are a new class of 1-D objects, in many respects similar to carbon NTs - potentially better:
  - they are all the same,
  - easily dispersed
  - no problem with sorting different tubes
  - they can be doped, etc.

- In bundles, they are very weakly coupled to each other: leading to enhanced 1D properties

- They exhibit very peculiar magnetic properties when doped with Li

- ....
Why should we be interested?

Potential applications

Li batteries

Composites

Field emission

Commercially available in near future
Outline

• Brief introduction
  – structure
  – transport (resistivity and infrared)
• Li doping
• Peculiar magnetic properties
Electron microscopy images of MoS$_{2-y}$ NTs

Remskar et al, Science 2001
MoS$_{2-y}$I$_{y}$ NTs - structure

Simulation

Space group $P6_3$ ($C_6^6$)

Unit cell: 18 atoms

$a = b = 0.96$ nm, $c = 0.4$ nm

Shear modulus of $\text{MoS}_2$ nanotube bundles

\[ F = 1 \text{nN} \]

Shear modulus $G = 17 \text{ MPa}$

The forces between the NTs are extremely weak!

A. Kis and L. Forro
Some predicted band structures
(DFT calculations; M. Verstraten and J-C. Charlier, Leuven)

zigzag, I interstitial

armchair, I centered
MoS$_{2-y}$ Resistivity measurements on “mats”

Some experimental details:
• 4 and 2-probe measurements gives similar results
• Gold and silver contact paste gave same results

$\rho = \rho_0 \exp[T_a/T^{1/4}]$ gives a relatively good fit, where $\rho_0$ differs significantly from sample to sample, but $T_a$ does not!

VRH implies a finite DOS at $E_F$
STM measurements

Hassanien et al (2002)
MoS$_2$ Nanotube bundles on 10 nm SiO$_2$ with Ti electrodes

P.Avouris and V.Derycke, IBM

sample: Jozef Stefan Institute
Resistivity appears metallic at 300K

I-V characteristic at 300 K

Effect of annealing: contact improvement

Gating effect

P. Avouris and V. Derycke, IBM
MoS$_{2-y}$ NTs: I-V measurements on individual tubes

Shadyar Farhangfar and Christian Schoenberger, University of Basel, unpub. 2002
Reflectivity measurements

L. Degiorgi (ETHZ)
Li doping
Electrochemical Li insertion into MoS$_2$ NTs

**Li-MoS-NT - Li charging/discharging performance**

Where does the Li go?

Effect of dispersion and de-iodination
Magnetic susceptibility of $\text{Li}_x\text{MoS}_2$-

\[
\chi = \chi_{\text{Curie}} + \chi_{\text{Pauli}}
\]

where

\[
\chi_{\text{Curie}} = \frac{C}{(T+\theta)}
\]

\[
\chi_{\text{Pauli}} = \chi_0 + \chi_1 T
\]

$\chi_{\text{Pauli}} = 1.4 \times 10^{-2} \text{ emu mol}^{-1}\text{Oe}^{-1}$

($\chi_{\text{Li}} = 2.4 \times 10^{-5} \text{ emu mol}^{-1}\text{Oe}^{-1}$)
Magnetic susceptibility of Li$_x$MoS$_{2-y}$ sample-to-sample variations
Magnetisation of Li$_x$MoS$_{2-y}$ NTs in large field

\[ M(H) = kH + M_0B[S, H, T] \]

\[ k = 2 \times 10^{-3} \text{ emu/mol-Oe} \]
Magnetisation of $\text{Li}_x\text{MoS}_2-y$ NTs
sample-to-sample variations

$M(H) = kH + M_0\mathcal{B}[S, H, T]$
Magnetisation of Li\textsubscript{x}MoS\textsubscript{2-y} NTs in small field* 

\[ M(H) \times 10^{-3} \text{ [emu]} \]

\[ H \text{ [kOe]} \]

\[ S = 1/2 \]

\[ S = 25 \]

\[ B[S, H, T] \]

(*The linear term is subtracted)
Static susceptibility $\chi_0$ on Li$_x$MoS$_{2-y}$ NTs (from ESR intensity)

Denis Arcon et al (2002)
Experimental arguments for an intrinsic FM state:

- Undoped MoS$_2$ NTs show a very small (unmeasurable) susceptibility
- Magnetic properties disappear when exposed to air (Li reaction).

- Mo (metal) is diamagnetic
- Li has a small Pauli susceptibility $\chi \sim 10^{-5}$ emu/mol (not FM)
- Mo does not usually form FM compounds
  (some Mo spinels exist with $T_c$s 10-28K)
How can we understand the unusual magnetic behaviour?
Magnetic properties of carbon nanotubes

Chauvet et al., PRB 1995

Ajiki and Ando (1993)
Susceptibility of quasi-1D crystals

Johnson et al, 1985
1D-metal and Pauli susceptibility

From fits to the data $\chi_0 = \mu_0 \mu_B^2 N(E)$, we would obtain:

$$N(E) \approx 300 \text{ states/eV/f.u.}$$

Stoner enhancement due to e-e interactions:

$$\chi = \frac{\chi_0}{1 - IN(E)}$$

From experiments, $1 - IN(E) \sim 10^{-3}$

(Condition for ferromagnetism : $IN(E) > 1$)
Susceptibility of Luttinger liquids

1. Dzyaloshinski and Larkin (1972)
2. Lee et al (1977)

High T (QMC):

\[ H \approx \sum_{k,\varepsilon,\mu} c_\varepsilon(k)c_\varepsilon \pi(k)c_{\varepsilon,\mu}(k) \]
\[ + \sum_{k,\varepsilon,\lambda,\mu} c_\varepsilon(k)c_{\varepsilon,\lambda}(k)c_{\varepsilon,\mu}(k) \]
\[ + \sum_{k,\varepsilon,\lambda,\mu} c_\varepsilon(k)c_{\varepsilon,\lambda}(k)c_{\varepsilon,\mu}(k) \]
\[ + \sum_{k,\varepsilon,\lambda,\mu} c_\varepsilon(k)c_{\varepsilon,\lambda}(k)c_{\varepsilon,\mu}(k) \]

Low temperature limit, as \( T \to 0, \)
\[ \partial \chi / \partial T \to \infty \]
(RG result)
Conclusions

Li-doped MoS NTs exist in a peculiarly stable high-susceptibility strongly correlated spin state with coexisting ferromagnetic spin clusters with $S=10-100$

Careful experimental considerations indicate that the state is intrinsic

Can we rely on DFT calculations to give the correct structure?