High-temperature ferromagnetism of Li-doped vanadium oxide nanotubes

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Abstract – The nature of a puzzling high-temperature ferromagnetism of doped mixed-valent vanadium oxide nanotubes reported earlier by Krusin-Elbaum et al., Nature, 431 (2004) 672, has been addressed by static magnetization, muon spin relaxation, nuclear magnetic and electron spin resonance spectroscopy techniques. A precise control of the charge doping was achieved by electrochemical Li intercalation. We find that it provides excess electrons, thereby increasing the number of interacting magnetic vanadium sites, and, at a certain doping level, yields a ferromagnetic-like response persisting up to room temperature. Thus we confirm the surprising previous results on the samples prepared by a completely different intercalation method. Moreover our spectroscopic data provide first ample evidence for the bulk nature of the effect. In particular, they enable a conclusion that the Li nucleates superparamagnetic nanosize spin clusters around the intercalation site which are responsible for the unusual high-temperature ferromagnetism of vanadium oxide nanotubes.

The quest for new materials with novel physical properties and functionalities continuously pushes forward materials’ science efforts to structure “old known” bulk solids into nano-sized low-dimensional objects (see, e.g., [1]). The magnetic and electronic properties of such nanostructures are mainly governed by their surfaces and interfaces which renders them promising materials for tailored functionalization. For oxide heterostructures the great potential of such an approach is, e.g., highlighted by recent findings of novel effects at interfaces between nonmagnetic oxide insulators where magnetism, metallic behavior and even superconductivity have been reported [2]. In order to tailor nanostructured functional elements, different design strategies are being used, such as fabrication of multilayers, heterostructures with quantum confinement (quantum wells, wires and dots) etc. Another promising approach is based on self-assembly of elementary nano- and even atomic-size building blocks. In particular, two-dimensional layers of transition metal (TM) oxides rolled up into nanosized multiwalled tubes or scrolls attract a rapidly growing attention owing to unique physical properties not occurring in the bulk parent materials (see, e.g., [3]). A recent example of such a nanostructured TM oxide is multiwalled vanadium oxide nanotubes VO_{2}-NTs [4, 5]. Vanadium ions are mixed valent in this material with an average valence count of ~ +4.4 (i.e., x ≈ 2.2) [6, 7]. This results in a roughly equal number of magnetic V^{4+} (3d^1, S = 1/2) and nonmagnetic V^{5+} (3d^0, S = 0) sites in the VO_x layers. The spins associated with the former sites act either as individual spins or strongly gapped antiferromagnetic (AF) dimers or trimers [8]. As reported by Krusin-Elbaum et al. [9], doping of VO_{2}-NTs with either holes or electrons via iodine or lithium intercalation yields a nonlinear and hysteretic magnetization response to applied magnetic fields suggesting the occurrence of ferromagnetism that persists even above room temperature. Such high-temperature ferromagnetism (HTFM) is very surprising

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and unexpected for an oxide material comprising TM ions with a small spin-1/2 and provides a remarkable example of novel functionalities in nanostructured oxides.

Since a conclusion on the HTFM in the doped VO$_x$-NTs is based in ref. [9] only on the results of the SQUID magnetometry, where artefacts due to uncontrollable ferromagnetic impurities cannot be always excluded, we have conducted a new experimental study using a combination of different techniques. Our objectives were: i) to obtain an independent evidence of HTFM in Li doped VO$_x$-NTs, and, if confirmed, ii) to obtain insights into the origin of this unusual phenomenon. To achieve these goals we have prepared a series of Li$_x$VO$_x$-NTs samples by a completely different electrochemical method of Li intercalation that as compared with the chemical method used in ref. [9] enables an accurate control of the doping level. We have performed a complex experimental investigation of these samples with three different local spin probe techniques, namely, electron spin resonance (ESR), nuclear magnetic resonance (NMR) and muon spin relaxation/rotation ($\mu$SR) spectroscopies, along with measurements of the bulk static magnetization. We find that for a particular concentration of the Li-dopant a large magnetization $M$ which can be easily saturated even at room temperature by a magnetic field $\mu_0 H$ of about 1 T is present in the sample. Thereby we reproduce and confirm the results of ref. [9] on the samples prepared by a different method. Moreover, $\mu$SR and NMR measurements give evidence for a bulk nature of the effect. NMR data suggest that the magnetization is not uniform throughout the sample and that strongly magnetic regions are formed around the intercalated Li sites. ESR experiments reveal a sharp signal that bears essential features of a superparamagnetic resonance. We argue that Li intercalation affects the charge disproportionation and hence the spin states and magnetic interactions in the rolled-up VO$_x$ layers thereby promoting, for particular doping levels, the formation of nanosized interacting spin clusters that behave similar to superparamagnetic nanoparticles.

Pristine multiwalled vanadium oxide nanotubes were synthesized by a hydrothermal technique, previously described in [6]. Electrochemical treatment that enables a precise control of the Li doping was done by means of two-electrode Swagelok-type cells, each including 83.3 wt% of active material (VO$_x$-NT), 16.7 wt% of Carbon SP (Timcal), a Li metal anode, and 1:1 ethylene carbonate/dimethyl carbonate solution of 1 M LiPF$_6$ (LP30-Ferro) that was used as electrolyte. The electrochemical doping was done using a VMP controller (Ametek Princeton Applied Research), in galvanostatic mode, with a discharge rate of 1 Li per formula unit in 100 h. By applying the constant current mode Li ions have been intercalated to the active material until a desired composition Li$_x$VO$_x$-NT was achieved: For the present study samples with $y = 0, 0.05, 0.10, 0.15$ and 0.6 have been prepared. For all samples, magnetization has been measured in the temperature range $T = 2$–350 K and in fields up to 5 T by means of a Quantum Design MPMS. $^{51}$V NMR data were recorded on a Tecmag pulse solid-state NMR spectrometer at $T = 4.2$–300 K. The NMR spectra were acquired by a point-by-point magnetic-field sweeping. For ESR experiments we used an X-band EMX Bruker ESR spectrometer operational at $T = 3.5$–300 K. Muon spin relaxation ($\mu$SR) data on undoped and doped VO$_x$-NTs were obtained at the GPS spectrometer of PSI.

Fig. 1: (Colour on-line) $H$-dependence of the magnetization of Li$_x$VO$_x$-NT with $y = 0.1$ ($T = 300$ K, 50 K, 2 K) and $y = 0$ ($T = 300$ K). Inset: Part of the $M(H)$ loop, at 300 K, for $y = 0.1$.

Our static magnetic data show an increase of the magnetization in Li$_x$VO$_x$-NT with $0 < y \leq 0.6$ as compared with the undoped material. This observation is consistent with a higher number of paramagnetic V sites suggested by the NMR data (see below). Note, that a spin-gap feature in the $T$-dependence of the susceptibility in pristine VO$_x$-NT attributed to the presence of dimers [8,9] vanishes upon Li doping. The main result of the magnetization study is the observation of a non-linear behavior for the doping level $y = 0.1$ which strongly differs from the magnetic response at other Li contents. At 300 K, the $M(H)$ curve practically saturates in a field of ~1 T at a value of ~0.1$\mu$B per V site with a small subsequent linear increase at higher fields (see fig. 1). The data at 50 K and 2 K (fig. 1) illustrate that at low $T$ this saturation is superimposed by a stronger linear contribution to $M(H)$. Note, that the data exhibit a small hysteresis with the coercivity $2H_c \sim 23$ mT at 300 K (see fig. 1, inset).

Further insight into the magnetic properties is provided by zero field (ZF) $\mu$SR data. Selected ZF-$\mu$SR spectra obtained on Li$_x$VO$_x$-NT with $y = 0$ and $y = 0.1$, i.e. for the pristine and the magnetic materials, (see fig. 2). For $y = 0$, both at 300 K and at 20 K the data show only a small decrease of the asymmetry signal $A(t)$ at short times. This clearly implies the absence of magnetic order in this temperature range. On a longer time scale of $\mu$s, there is a decrease due to the slow relaxation which we attribute to nuclear and fast fluctuating electronic magnetic moments.

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The most important result of the ZF-μSR study on Li_{0.1}VO_{x}-NT is the observation of a significant and rapid loss of asymmetry at early times. As displayed (see fig. 2(b)), most of the relaxation occurs already during the dead time of the spectrometer (≈5 ns). The full asymmetry scale was defined by a subsequent measurement of a nonmagnetic compound. Such a rapid relaxation clearly indicates that a significant fraction of the muons experiences a local quasi-static magnetic field. The absence of an oscillating signal proves a broad static magnetic-field distribution within the compound.

Assuming for a quantitative analysis that a fraction of a muons experiences both the nuclear and the electronic static magnetic field, the data are described by

\[ A(t) = (1 - a) \cdot e^{-\sigma_{\text{nuc}} t} + a \cdot (2/3)e^{-\lambda_{T,L} t} + 1/3e^{-\lambda_{L} t}. \]

Here \( \sigma_{\text{nuc}} \) and \( \lambda_{T,L} \) are muon relaxation rates due to interaction with nuclear and electron spins, respectively [10]. This analysis implies that \( \sim2/3 \) of the muons in Li_{0.1}VO_{x}-NT experience a static magnetic field originating from a magnetic ordered volume fraction at or in the vicinity of the muon stopping site(s). The μSR data hence unambiguously prove the bulk, and not impurity related, character of the magnetism found in the static magnetization.

NMR studies on \(^{51}\text{V}\) and \(^{7}\text{Li}\) shed further light on the effect of Li doping on the local magnetic properties. The \(^{51}\text{V}\) NMR data (see fig. 3(a)) reveal a gradual increase of the relative intensity of the low-field fast-relaxing shoulder of the \(^{51}\text{V}\) signal at \(\sim9.16\) T upon doping. Since this part of the spectrum is associated with the response of the magnetic ions’ nuclei, shifted due to hyperfine interaction from the central slow-relaxing nonmagnetic \(^{51}\text{V}^+\) peak at \(\sim9.22\) T [8], its growth indicates an increasing fraction of magnetic vanadium ions upon Li intercalation and confirms that the doping process affects the whole sample. Though magnetic ordering usually creates a shift or splitting of the NMR spectrum, neither was observed for the \(^{51}\text{V}\) signal for the Li_{0.1}VO_{x}-NT sample in a sufficiently wide field range. The absence of the significant loss of its intensity suggests that the large part of V ions does sense the charge doping but not the internal field.

The situation with \(^{7}\text{Li}\) NMR is different: The resonance field of the signal steadily changes with doping. However, the line shift for \(y = 0.1\) is much larger compared to \(y = 0.05\) and \(y = 0.15\) (see fig. 3(b)). This suggests the presence of an external field at the Li sites only for the strongly magnetic Li_{0.1}VO_{x}-NT. The absence of a second unshifted \(^{7}\text{Li}\) line at the expected place between the line positions of Li_{0.05} and Li_{0.15} samples indicates that practically all Li nuclei experience internal magnetic fields.

The ESR study of undoped VO_{x}-NTs at a frequency \(\nu = 9.5\) GHz reveals, similar to other results [11], a spectrum comprising two overlapping resonance lines with slightly different \(g\)-factors of \(\sim2.0\) and \(\sim1.97\) (not shown). The first line can be assigned to quasi-free spins associated with \(^{51}\text{V}^+\) \((S = 1/2)\) ions in the tetrahedral position. The second line is due to \(^{51}\text{V}^+\) ions in the distorted octahedral coordination which are coupled magnetically into dimers and trimers [8].

In the samples of Li_{0.1}VO_{x}-NTs with \(y = 0.05, 0.1, 0.15\) and 0.6 a systematic evolution of the lines in the ESR spectrum with increasing the Li doping gives evidence for the increasing number of magnetic \(^{51}\text{V}^+\) ions, and a reduction of the contribution related to spin dimers and trimers, in agreement with the magnetization data (see above). We note that the carbon black used as a conductive additive for the preparation of Li-doped samples partially screens the penetration of microwaves into the interior of the sample thereby reducing the signal-to-noise ratio and superimposes an additional ESR line (see fig. 4, inset). The latter can be identified by measuring...
the carbon additive separately and accurately subtracted from the spectra. The central result of the ESR study is the observation of an “extra” narrow resonance line in the strongly magnetic $y = 0.1$ sample. Despite the disturbing effect of the carbon line, the “extra” line is clearly visible in the raw data (see fig. 4, inset, middle curve) and can be accurately singled out, e.g., by subtracting from the $y = 0.1$ spectrum the spectrum of a weakly magnetic sample with a different Li content (see fig. 4, inset, bottom curve). The width of this “extra” line $\Delta H \sim 70$ G is significantly smaller compared to the signals from paramagnetic $V^{4+}$ ions whereas the $g$-factor of $\sim 1.98$ is similar. Both $\Delta H$ and $g$ change little in a broad $T$-region above $\sim 40$–70 K and become temperature dependent at lower $T$ (see fig. 4). As will be discussed below, this narrow signal is directly related with the ferromagnetic-like behavior of the $y = 0.1$ sample.

Uniform long-range magnetic order in the low-spin ($S = 1/2$) vanadium oxides is not competitive at high temperatures with thermal fluctuations and/or insulator-to-metal transitions (see, e.g., [12]). A ferromagnetic-like magnetization up to room and even higher temperatures is in particular unexpected. However, in the case of VO$_2$-NTs an alternative cluster scenario of ferromagnetism is clearly corroborated by our $\mu$SR and NMR results. $\mu$SR data yield about 2/3 of the magnetic volume fraction and a broad distribution of static magnetic fields within the sample. The absence of an appreciable shift of the $^{51}$V NMR signal in the ferromagnetic sample suggests that it originates from the regions outside ferromagnetic clusters. The $^{51}$V-NMR line shift from the nuclei inside the clusters is expected to be as big as in magnetically ordered compounds, hence displacing the signal out of the observation range (see, e.g., [13]). Furthermore, owing to a possible distribution of the clusters’ size, as also suggested by the $\mu$SR data, this signal could be very broad and thus practically undetectable. On the other hand, the $^7$Li-NMR data give clear evidence that ferromagnetism is confined to regions around the lithium site which yields a shift of the $^7$Li-NMR line by the internal magnetic field inside the cluster.

Thus one can argue that the Li which is intercalated between the vanadium oxide layers in the walls of VO$_2$-NTs [7] may play a role of nucleating centers for spin clusters of different size. In fact, the magnetization data (fig. 1) bear features characteristic of a magnetic response of superparamagnetic particles with a broad size distribution, such as, e.g., samples of ultra-fine $\gamma$-Fe$_2$O$_3$ particles studied in [14]. Specifically, the small hysteresis in $M(H)$ at room temperature suggests the presence of large clusters with a blocking temperature $T_B > 300$ K. At higher external fields they are already saturated and the observed finite slope of $M(H)$ in this field regime is mainly determined by smaller unblocked superparamagnetic clusters ($T_B < 300$ K) [14]. The sharp ESR line with the spin-only paramagnetic resonance field $H_{res} = h\nu/\gamma B$ observed in the strongly magnetic Li$_{0.1}$VO$_2$-NT sample (fig. 4) can be straightforwardly assigned to a resonance response of those small unblocked clusters. Above $T_B$ the anisotropy field, that otherwise produces a shift and broadens the signal, is averaged due to thermal fluctuations yielding a narrow line at $H_{par}^{res}$ (see, e.g., [15]). At low temperatures one can consider the shift of the effective $g$-factor from the spin-only value and the increase of the width of this signal (see fig. 4) as an indication of approaching the $T_B$ of the resonating superparamagnetic clusters. According to the study of the effect of the particle size on the ESR response in [16], for small particle size ($\approx 5$ nm) the spectrum is defined by an isotropic and unshifted narrow line. In contrast, for a large particle size ($\approx 10$ nm) the associated anisotropy field is much stronger, therefore, thermal fluctuations even on a room temperature scale cannot overcome the anisotropic orientation of the magnetic moments. As a result, the spectrum is broad and shifted towards lower fields due to the influence of the remaining orientational anisotropy. Thus, in the case of a broad size distribution, the ESR response of the blocked clusters in Li$_{0.1}$VO$_2$-NT could be smeared out and become unobservable, in particular, also due to the limited sensitivity caused by the carbon additive (see above).

Obviously, local charge and structural distortions around an intercalated Li$^+$ ion as well as nanostructuralization of VO$_2$ may be crucial for the nucleation of ferromagnetic clusters in VO$_2$-NTs. In this respect one can find a striking similarity with high-temperature ferromagnetism (HTFM) with $T_C > 300$ K recently observed in nanostructured diluted magnetic semiconductors (DMS) (see, e.g., [17,18]). Adding a small percentage of magnetic TM ions to nanocrystals [17] or nanowires [18]
of nonmagnetic ZnO yields a robust HTFM that was not achieved by doping the bulk ZnO. The occurrence of structural inhomogeneities on the nanometer scale concomitant with the charge localization are the key prerequisites for this remarkable effect. For example, in Ni:ZnO nanocrystals, just by tuning the aggregation of nanocrystals, one obtains HTFM with a T-independent saturation value and a small coercivity, very similar to our findings [17]. The stabilization of HTFM in DMS has been discussed theoretically in terms of collective polaronic effects [19,20], namely that bound interacting ferromagnetic polarons may be formed due to exchange interaction of localized charges with magnetic impurities, in particular in the presence of defects. One can conjecture a possible relevance of this scenario to VO$_2$-NTs in view of some apparent similarities with DMS: i) the current-voltage characteristics of individual tubes reveals a semiconducting behavior with conductivity decreasing upon Li doping [9]; ii) electron doping due to the Li intercalation creates additional spin centers and iii) locally distorts the structure. A delicate balance between these factors controlled by the Li intercalation may be the reason for a strong sensitivity of the observed effect to the Li content. At small doping levels the amount of nonmagnetic V$^{5+}$ ions (which are the “holes” in the magnetic subsystem) is big enough to prevent the formation of spin clusters. On the other hand at large Li dopings VO$_2$-NTs turn to a uniform rolled up spin-1/2 plane with predominantly antiferromagnetic interactions which could be much less sensitive to a perturbing influence of Li-caused defects.

In summary, we have studied by means of NMR, µSR and ESR spectroscopies combined with static magnetic measurements the influence of Li intercalation on the magnetic properties of Li$_x$VO$_2$-nanotubes. We find a particular concentration of the Li dopant which turns this compound into a strongly magnetic material exhibiting ferromagnetism on the room temperature scale. The data give evidence that this very unusual for a low-spin vanadium oxide behavior is due to the formation of nanosize interacting ferromagnetic spin clusters around intercalated Li ions. Such clusters behave as an ensemble of superparamagnetic particles with a broad size distribution whose big magnetic moments can be easily aligned by a moderate magnetic field even at room temperature. The robustness of the ferromagnetic spin structure may be suggestive of its collective polaronic nature.

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