Anomalous magnetic properties of VO\textsubscript{x} multiwall nanotubes

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Abstract. Basing on the high frequency (60 GHz) electron spin resonance (ESR) and magnetic susceptibility study of the VO\textsubscript{x} multiwall nanotubes (VO\textsubscript{x}-NTs) in the range 4.2-300 K we report the ESR evidence of the presence of the antiferromagnetic V\textsuperscript{4+} dimers in VO\textsubscript{x}-NTs and the observation of an anomalous low temperature (T<50 K) growth of the magnetic susceptibility for V\textsuperscript{4+} quasi-free spins, which obey power law $\chi(T)\sim 1/T^{\alpha}$ with the exponent $\alpha\approx 0.6$. The estimates of the concentrations for various spin species (clusters) indicate that the non-interacting dimers should be an essential element in the VO\textsubscript{x}-NTs structure. The possibility of the disorder driven quantum critical regime in VO\textsubscript{x}-NTs is discussed.

Recently synthesized new nanoscale magnets, vanadium oxide multiwall nanotubes (VO\textsubscript{x}-NTs), have attracted attention due to a number of unusual magnetic properties [1]. This material demonstrates strong deviation from the Curie-Weiss law at temperatures $T>100$ K, which has been explained by the presence of antiferromagnetic (AF) dimers formed by V\textsuperscript{4+} S=1/2 magnetic ions [1]. Some features of magnetization and NMR spectra have been assigned to the trimers or other fragments of V\textsuperscript{4+} S=1/2 spin chains in VO\textsubscript{x}-NTs [1]. Thus, according to [1], the magnetism of VO\textsubscript{x}-NTs originates from different V\textsuperscript{4+} S=1/2 paramagnetic spin clusters, namely V\textsuperscript{4+} quasi-free spins (including monomers and trimers) and the dimers. At temperatures below 100 K a paramagnetic contribution from the AF dimers freezes and only monomers and trimers contribute to the total magnetization. Nevertheless, the estimates of the concentration for various spin clusters, which have been obtained in [1], seem to be controversial. For example, the fitting magnetic susceptibility $\chi(T)$ data by the superposition of the Curie-Weiss law and the model of non-interacting AF dimers in the range $T>15$ K gives ~17% and ~28% of the total V sites corresponding to the quasi-free spins and AF dimers, respectively. The rest of V sites is supposed to correspond to non-magnetic V\textsuperscript{5+} ions having the spin S=0. At the same time, the analysis of the field dependence of magnetization at $T=4.2$ K implies the concentration of the quasi-free spins being only about ~3% that was interpreted as an evidence of the antiferromagnetic coupling of the various V\textsuperscript{4+} spin chains fragments at low temperatures [1].

As long as analysis of dynamic and static magnetic susceptibility data may shed the light on the problems of detecting various spin clusters and correct separation of the various magnetic
contributions, the aim of the present work is a comparative study of the electron spin resonance (ESR) and magnetic susceptibility;

![SEM image of VOx-NTs](image)

**Figure 1.** The SEM image of the fine structure of individual VOx-NTs.

The sample preparation technique was similar to that used in [1]. VOx-NTs were synthesized by a hydrothermal treatment of orthorhombic vanadium pentoxide (SigmaAldrich) [2]. X-ray photoelectron spectroscopy experiments have shown that the average oxidation rate of vanadium in the nanotubes is +4.22 [2]. The microstructure of the resulting product has been examined by a transmission electron microscopy. The SEM images of the individual nanotubes show that the structure of these particles contains built-in disorder as long as the V–O layers are not closed concentrically (fig. 1). Moreover, the open ends and bending of the nanotubes may serve as additional sources of the structural defects (fig. 1). The ESR experiments have been performed at frequency 60 GHz in magnetic fields up to 7 T at temperatures 4.2-200 K using an original cavity magneto-optical spectrometer [3]. Magnetic susceptibility measurements were carried out in the temperature range 4.2-300 K with the help of SQUID magnetometer.

![ESR spectrum and temperature dependences](image)

**Figure 2.** Example of the ESR spectrum at 160 K (inset) and temperature dependences of the integrated intensities for the lines A and B (main panel). The digits near curves correspond to the various fitting models (1- AF dimers; 2- QC model from [6]).

It is found that in the temperature range 100–200 K the ESR spectrum consists of two lines A and B, corresponding to the temperature independent g-factors of ~1.8 and ~2.5, respectively (see the inset in fig. 2). The integrated intensity of the line B decreases with lowering temperature and this resonant feature is not observed below $T\sim 100$ K. At the same time the integrated intensity of the line A
increases at low temperatures (main panel in fig. 2). The shape of both spectral components can be fitted well with lorentzians (see solid lines at the inset in fig. 2). Interestingly, that the line widths of both resonances are temperature independent in the range 4.2-200 K. The reasons of this unusual behavior will be discussed elsewhere.

A rapid freezing out of the line B allows assigning this ESR signal to the AF dimers in a qualitative agreement with [1]. Indeed, an alternative explanation of the double peak structure in the non-oriented sample by the strong anisotropy of g-factor expectable in such low dimensional system does not meet the case as long as both peaks must exist at low temperatures. The approximation of the integrated intensity data for the line B $I_B(T)$ by the known analytical expression for the magnetic susceptibility of the noninteracting AF dimers $\chi_d(T) = C_d / T (3 + \exp(\Delta / T))$ [1] provides good description of the experimental data (see curve 1 in fig. 2). The two parameter fit gives the spin gap value $\Delta \approx 720 \pm 20$ K practically coinciding with the data reported previously $\Delta \approx 710$ K [1] and results in ~20% error in $C_d$ magnitude.

The ESR signal for the line A exists at all temperatures and increases with lowering temperature thus, according to [1], it may be caused by quasi-free spins having susceptibility $\chi_s(T)$. However, the integrated intensity $I_A(T) \sim \chi_s(T)$ demonstrate essentially non Curie-Weiss behavior, and acquires the power law $I_A(T) \sim \chi_s(T) \sim 1/T^{\alpha}$ at low temperatures $T<50$ K with the exponent $\alpha \approx 0.6$ (dashed line in fig. 2).

The onset of the power law with $\alpha<1$ for magnetic susceptibility is a fingerprint for various magnets with the disorder driven quantum criticality [4,5]. Thus it is possible to suppose that low temperature anomaly of magnetic susceptibility in VO$_x$-NTs may be caused by quantum critical (QC) effects. In the present paper our experimental data are discussed under this assumption and probable alternative explanations will be considered elsewhere. From the theoretical point of view in the disorder driven QC state the system is separated into spin clusters characterized by different exchange constants $J$. The lowering temperature “scans” over $J$ distribution and leads to the enhancement of the thermodynamical contribution of the clusters, which are correlated stronger than average [4,5]. For $T<J_m$ this results in the formation of the QC state and susceptibility power law $\chi_s(T) \sim 1/T^{\alpha}$ (here $J_m$ denotes the characteristic value of the exchange constant in spin clusters). It is possible to show [6] that the analysis of the $I_A(T) \sim \chi_s(T)$ within the QC model describing transition from the uncorrelated spins (having Curie-type susceptibility) to the correlated spin clusters allows obtaining reasonable description of experimental data (curve 2 in fig. 2) for $J_m \approx 60$ K. In the studied case the disorder in the...
magnetic subsystem of the sample may be a consequence of various structural defects in the multiwall nanotubes (fig. 1).

Comparison of the static magnetic susceptibility $\chi(T)$ measured by SQUID magnetometer with the temperature dependences of ESR integrated intensities shows that $\chi(T)$ does not follow $I(T)$ even at low temperatures, where the contribution from the dimers is negligible. Therefore it is possible to conclude, that only a part of the total magnetic susceptibility in VO$_x$-NTs is ESR active and contributes to the observed modes of magnetic oscillations. As long as the ESR signal consists of the quasi-free spins and dimers contributions, it is possible to write $\chi(T) = \chi_a(T) + \chi_d(T) + \chi_0(T)$. Here $\chi_a(T)$ denotes the background, which does not appear in electron spin resonance experiments. We found that that both Van Vleck paramagnetism of the V$^{5+}$ ions and technological impurities contribute to background, which can be described analytically as $\chi_0(T) = C/T + \chi_0$. Such background yields in $\chi(T) = (C_1 + C_2)/T + \chi_d(T) + \chi_0$ and $\chi(T) = A\cdot T^{-\alpha} + C/T + \chi_0$ for the high ($T > J_m$) and low ($T < J_m$) temperature asymptotics respectively. From the fitting of the $\chi(T)$ data in the high and low temperature regions separately and assuming known values of the parameters $\alpha$ and $\Delta$ we (i) find that both model equations give the same value of $\chi_0$ as should be expected and (ii) obtained all Curie constants $C_\alpha$, $C_\delta$ and $C$. It is worth noting that the error in determination of Curie constants from the static susceptibility is about $\sim$5% and is much less than in the ESR case. Thus the separation of various contributions to the total susceptibility may be performed. The results are summarized in fig. 3, where the total susceptibility $\chi$, background $\chi_0$, ESR active part of spin susceptibility $\chi_a + \chi_d$ and dimers contribution $\chi_d$ are shown. The validity of the performed analysis is confirmed by good agreement of the total ESR integrated intensity $I_a + I_b$ with the found $\chi_a + \chi_d$ values (fig. 3). Returning to the problem of concentration estimates we wish to mark that the concentrations of V$^{5+}$ and V$^{4+}$ ions follow from the oxidation rate, which gives 78% of the V$^{4+}$ and 22% of the V$^{5+}$ ions in the total amount of V sites for the VO$_x$-NTs studied. For the V$^{4+}$ subsystem the experimentally found ratio $C_d/C_s = 0.023$ suggests relative concentrations $\sim$98% for the non-interacting dimers and $\sim$2% for the quasi-free spins. From these estimates it is possible to conclude that the V$^{4+}$ dimers may appear as an essential element in the VO$_x$-NT and this circumstance should be taken into account in the structural models of this material.

In conclusion, we have shown that the magnetic susceptibility $\chi(T)$ of the VO$_x$-NTs has complicated structure and only a part of the total susceptibility gives a contribution to the ESR signal. The ESR-active fraction of $\chi(T)$ is contributed by the AF dimers and quasi-free spins. The estimates of the concentrations for various spin species indicate that the V$^{4+}$ non-interacting dimers should be an important element of the VO$_x$-NTs structure. This work is supported by the the programmes of RAS “Strongly correlated electrons”, “Quantum physics of condensed matter” and by the RFBR grants 07-03-00749-a, 07-03-12182-ofi, 09-03-01122-a and 09-03-00602-a.

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