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Strong reduction of V$^{4+}$ amount in vanadium oxide/hexadecylamine nanotubes by doping with Co$^{2+}$ and Ni$^{2+}$ ions: Electron paramagnetic resonance and magnetic studies

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In this work we present a complete characterization and magnetic study of vanadium oxide/hexadecylamine nanotubes (VO$_x$/Hexa NT’s) doped with Co$^{2+}$ and Ni$^{2+}$ ions. The morphology of the NT’s has been characterized by transmission electron microscopy, while the metallic elements have been quantified by the instrumental neutron activation analysis technique. The static and dynamic magnetic properties were studied by collecting data of magnetization as a function of magnetic field and temperature and by electron paramagnetic resonance. At difference of the majority reports in the literature, we do not observe magnetic dimers in vanadium oxide nanotubes. Also, we observed that the incorporation of metallic ions (Co$^{2+}$, S = 3/2 and Ni$^{2+}$, S = 1) decreases notably the amount of V$^{4+}$ ions in the system, from 14–16% (nondoped case) to 2%–4%, with respect to the total vanadium atoms (fact corroborated by XPS experiments) anyway preserving the tubular nanostructure. The method to decrease the amount of V$^{4+}$ in the nanotubes improves considerably their potential technological applications as Li-ion batteries cathodes.


I. INTRODUCTION

Oxide nanotubes (NT’s) such as SiO$_2$, TiO$_2$, ZnO, VO$_x$, and so on, have been the subject of a very active research due to their distinctive physical and chemical properties, which have promising technological applications. Among these materials are the vanadium oxide (VO$_x$) NT’s, in which the walls are constituted by alternated layers of VO$_x$ and surfactant. The surfactant or template helps to form the walls are constituted by alternated layers of VO$_x$ and CNT’s walls. Different templates have been used, as for example the NT’s present AFM dimers while the nanolayer and nanotubes. They reported that the three different samples have distinct magnetic interactions. For example the NT’s present AFM dimers while the nanolayer sample does not. They suggest that the magnetic behavior is determined by the concentration of V$^{4+}$ ions, and the presence of dimers is inherent of the tubular shape.

Recently, Demishev and co-workers performed a magnetic study of different nanomaterials that include nanorods, nanolayer and nanotubes. They reported that the three different samples have distinct magnetic interactions. For example the NT’s present AFM dimers while the nanolayer sample does not. They suggest that the magnetic behavior is determined by the concentration of V$^{4+}$ ions, and the presence of dimers is inherent of the tubular shape.

The effect of cation exchange in VO$_x$/surfactant NT’s was initially studied by the Nesper’s group and subsequently by other authors. They reported that some transition metals, alkali metals and alkali-earths can be exchanged with good preservation of the tubular shape. Azambre and Hudson have also synthesized copper nanoparticles (NP’s) within VO$_x$/dodecylamine NT’s and our group has studied nanocomposites constituted by FeO$_x$ NP’s and VO$_x$/dodecylamine NT’s.

The VO$_x$ NT’s present several potential technological applications, such as sensing elements, catalysis and Li-ion batteries cathodes. In the last case, it was found that the amount of V$^{4+}$ in the structure is critical as it affects and notably reduces the performance of the cathode.

In this context, we present a complete structural, magnetic and electron paramagnetic resonance (EPR) study on VO$_x$/hexadecylamine nanotubes in which magnetic Co or Ni...
ions are intercalated in the structure. Our experiments confirm that the incorporation of Co$^{2+}$ and Ni$^{2+}$ ions into the amine layers notably reduces the amount of the isolated and paramagnetic V$^{4+}$ ions.

II. EXPERIMENTAL

The VO$_x$/Hexa NT’s were synthesized in two steps. In the first one, 3.09 g of crystalline V$_2$O$_5$ (Aldrich) were slowly added in a beaker containing an ethanolic solution (5.7 mL) of hexadecylamine (4.55 g, Aldrich 90%). The mixture was then maintained under magnetic stirring during 2 h and, after that, 16.7 mL of deionized water were added and the material was aged during 48 h. The second step consists in a hydrothermal digestion of the gel during 7 days at 180°C in order to form the nondoped NT’s. Afterwards, to obtain the doped NT’s, the VO$_x$/Hexa nanostructures were introduced into a solution of ethanol/water (4:1 v/v) with the metallic ions, where a fraction of the amines were exchanged.$^9,17$ We used CoCl$_2$.6H$_2$O (Merck) and NiCl$_2$.6H$_2$O (Merck) in each solution, respectively, in a molar ratio excess of 4/1 (metallic cation/V$_2$O$_5$-hexadecylamine). The solution was stirred for 3 h and filtered, and the solid black product was rinsed and dried under vacuum.

The concentration of V and Co in the NT’s was determined by Instrumental Neutron Activation Analysis (INAA). The samples were irradiated in the RA-6 research nuclear reactor, located at Centro Atómico Bariloche (Bariloche Atomic Center - Argentina), in a thermalized neutron flux ($\phi_{th} \approx 8 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$). Vanadium and cobalt concentrations were determined by comparison with high purity metallic standard materials (V: Johnson Matthey, 99.7% purity, and Co: R/X Reactor Experiments, 99.95% purity). Vanadium was measured by evaluating the 1.43 MeV emission of the $^{52}$V isotope (half-life of 3.743 min), while cobalt concentrations were determined by the 1.17 and 1.33 MeV emissions of $^{60}$Co (half-life of 121.28 days). Gamma-ray spectra were collected after appropriate decaying times taking into consideration the activation products half lives. In the case of Co, the decay time was adjusted to allow complete decay of $^{59}$Co (half-life of 10.467 min) to the ground state for the sample and standard. Due to the long half-life of the $^{58}$Ni(n,p) $^{58}$Co reaction (half-life of 70.86 days) we did not quantify the amount of Ni with this technique.

The tubular shape of the products was confirmed by transmission electron microscopy (TEM) and the local composition was characterized by EDS. Both studies were performed in a CM 200 Philips microscope (LaB$_6$ cathode, 200 keV). The X-ray diffraction (XRD) patterns were acquired in a Philips PW 1700 diffractometer by using an aluminum sample holder and CuK$_\alpha$ radiation (1.5418 Å).

EPR spectra were collected with a Bruker ESP-300 spectrometer, operating at X-band (9.5 GHz) and varying the temperature between 10 and 300 K. Two additional spectra at K-band (24 GHz) and Q-band (35 GHz) were taken at room temperature to complete the energy levels involved in the magnetic transitions.

The static magnetic characterization of the samples was performed in a commercial superconducting quantum interference device magnetometer (Quantum Design MPMS-5S and MPMS-XL) with fields up to 70 kOe. The measurements as a function of temperature were performed in the 5–360 K range.

Finally, to corroborate the amount of V$^{4+}$ measured from magnetic properties, we performed a direct composition analysis measurement by X-ray photoelectron spectroscopy (XPS). We used a standard Al/Mg twin anode X-ray gun and a hemispherical electrostatic electron energy analyzer. For the measurements, the powdered samples were spread on an appropriate adhesive carbon tape.

III. RESULTS

A. Morphology and composition

In order to understand the nanotube formation mechanism, we show isolate cases of incomplete scrolling that can be appreciated in the TEM images of Fig. 2(a) and 2(b). Schematic representations of the rolling-up of planes are presented in Fig. 2(c) and 2(d). These photographs confirm the
previous rolling hypothesis mentioned by Nesper and Muhr.\textsuperscript{18}

A typical TEM image of nondoped NT is presented in Fig. 3(a). The dark and bright lines are associated to the alternated layers of VO\textsubscript{x} and Hexa thus showing the multi-wall characteristics of these NT’s, present in all the studied samples. By comparing with the nondoped NT’s, we observed an increment of defects in the doped samples like loss of definition and a waving in the external surface of the walls. These defects can be a consequence of the doping process when the Hexa was partially exchanged by the metallic ions. Additional micrographs of the three samples are shown as supplementary material\textsuperscript{19} (Fig. S1). The collected TEM images corroborate that the tubular shape is maintained in both doped samples. In the central picture [Fig. 3(b)] the EDS spectra of the samples is shown. In the Co and Ni doped NT’s, an extra peak can be clearly detected due to the presence of each doping element. The V and Co amounts, determined by INAA, are presented in Table I. The atomic mol ratio between the Co and V amounts, by using both techniques, local (EDS) and global (INAA), are in good agreement, yielding the value Co/V = 0.14. With the EDS technique we obtain 0.16 for the Ni/V ratio. The XRD patterns are presented in Fig. 3(c). We can considerer two regions in the patterns: the low angle (LA, 1.5° ≤ 2θ ≤ 15°) and high angle (HA, 15° ≤ 2θ ≤ 20°) region.

The reflections in the LA data have been indexed as 00\textsubscript{l}, which provides information about the interlamellar distance (d). On the other hand the HA measurements show the hk0 reflections, which provide the VO\textsubscript{x} cell parameters; these last peaks have lower intensity than the LA peaks. In order to index the cell we assumed a planar square lattice.\textsuperscript{2} The interlamellar distances decrease with doping, which is in agreement with the exchange of Hexa by Ni or Co ions. The values of d are presented in Table I. The hk0 reflections do not vary with the incorporation of Ni and Co, which indicates that the samples have practically the same cell parameters. This result is an indication that the metallic ions are not incorporated to the VO\textsubscript{x} double layered structure. In this way, we assume that either the doped ions are incorporated to the structure or that they replace the amines in the skeleton of the NT’s. The calculated cell parameter is a ≈ 5.93(2) Å for the three samples.

### B. EPR measurements

The X-band EPR spectra measured at room temperature are shown in Fig. 4. From the bottom to the upper plot, the resonance lines for the three studied samples correspond to: nondoped (only magnetic vanadium ions), Co-doped (magnetic vanadium and cobalt ions), and Ni-doped (magnetic vanadium and nickel ions).

The three X-band EPR spectra can be described by the following spin Hamiltonian:

\[
H = H_{V^{4+}} + H_{i=Co^{2+},Ni^{2+}},
\]

where \(H_{V^{4+}}\) is the Hamiltonian given by the V\textsuperscript{4+} ions and \(H_{i=Co^{2+},Ni^{2+}}\) is the contribution of the transition metal doped ion (\(i = Co^{2+}\) or Ni\textsuperscript{2+}). In the nondoped sample only the Hamiltonian of the V\textsuperscript{4+} contributes to the resonance, while

<table>
<thead>
<tr>
<th>% V (INAA)</th>
<th>% metal (INAA)</th>
<th>metal/V ratio</th>
<th>d [nm] (XRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nondoped VO\textsubscript{x}/Hexa</td>
<td>37.4 (9)</td>
<td>- - -</td>
<td>- -</td>
</tr>
<tr>
<td>Co-doped VO\textsubscript{x}/Hexa</td>
<td>30.9 (5)</td>
<td>4.2 (3)</td>
<td>0.14</td>
</tr>
<tr>
<td>Ni-doped VO\textsubscript{x}/Hexa\textsuperscript{a}</td>
<td>32.6 (7)</td>
<td>- - -</td>
<td>0.16</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Previously reported in Ref.\textsuperscript{11}.
for the doped samples we have to include the extra term of metal dopants to describe the absorption.

The X-band spectra of the nondoped sample can be adjusted with a single line centered at \( g = 1.96 \) and that can be associated with the \( V^{4+} \) (\( S = 1/2 \)) ions. However, when the spectra are measured at higher frequencies (K and Q bands), the lines become asymmetric (different heights between the maximum or minimum and the baseline). This asymmetry means that the sample presents crystalline anisotropy. The Hamiltonian which describes this anisotropy is presented in Eq. (2). This expression also includes the hyperfine interaction between the electronic and nuclear spin of \( ^{51}V \) (abundance 99.76%, \( I = 7/2 \)).

\[
H_{V^{4+}} = \mu_B [ g_{\|} H_z S_z + g_{\perp} (H_x S_x + H_y S_y) ] \\
+ [ A_{\|} (S_z I_z) + A_{\perp} (S_x I_x + S_y I_y) ],
\]

(2)

where \( \mu_B \) is the Bohr magneton, \( S_j \) and \( I_j \) (\( j = x, y, z \)) are the projections in the \( j \) direction of the electronic spin and nuclear spin operator respectively; \( g_{\|} \) and \( g_{\perp} \) are the parallel and perpendicular (respect to magnetic field - \( H \)) components of the \( g \)-factor, and finally \( A_{\|} \) and \( A_{\perp} \) are the principal (parallel and perpendicular) components of the hyperfine tensor in magnetic field units (G).

In order to correctly fit the EPR spectra it was necessary to consider a random distribution of crystalline orientations (powder distribution) and we only took into account the Zeeman term [first term of the Eq. (2)]. The experimental and theoretical fittings are presented in Fig. 5. The obtained \( g \) components of the nondoped NT’s are shown in Table II. Now, when we subtracted the calculated powder line from the experimental resonance, a low intensity spectrum formed

\[ H_0 = -483 (5) \text{ G and } D = 433 (20) \text{ G}. \]

<table>
<thead>
<tr>
<th>Metal</th>
<th>( g_{|} )</th>
<th>( g_{\perp} )</th>
<th>( &lt;g&gt; )</th>
<th>( A_{|} \text{ [G]} )</th>
<th>( A_{\perp} \text{ [G]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nondoped VO(_x)Hexa</td>
<td>1.96 (1)</td>
<td>1.95</td>
<td>1.96</td>
<td>188 (5)</td>
<td>92 (2)</td>
</tr>
<tr>
<td>Co-doped VO(_x)Hexa(^a)</td>
<td>1.96 (2)</td>
<td>1.98 (5)</td>
<td>1.95</td>
<td>185 (5)</td>
<td>74 (1)</td>
</tr>
<tr>
<td>Ni-doped VO(_x)Hexa</td>
<td>2.22</td>
<td>1.96 (5)</td>
<td>1.96</td>
<td>192 (5)</td>
<td>79 (4)</td>
</tr>
<tr>
<td>( V_2O_5 ) single crystal(^{24})</td>
<td>1.923</td>
<td>1.986</td>
<td>1.965</td>
<td>187 (5)</td>
<td>67 (4)</td>
</tr>
<tr>
<td>( V_2O_5 ) amorphous(^{24})</td>
<td>1.926</td>
<td>1.984</td>
<td>1.965</td>
<td>211 (5)</td>
<td>79 (4)</td>
</tr>
</tbody>
</table>

\( ^a H_0 = -483 (5) \text{ G and } D = 433 (20) \text{ G}. \)
by equally spaced lines remains. These absorptions correspond to the hyperfine structure (hfs) produced by the interaction between the electronic and nuclear spins of $^{51}$V [both terms of Eq. (2)]. Contrary to those vanadium ions that produce the subtracted powder line, the hfs is an indication that some $V^{4+}$ ions are practically isolated without interacting with other $V^{4+}$ ions. In the case of the V ions which contribute to the powder line, the hfs collapses into a single line (width 150 G, X-band). This effect can be explained by the exchange interaction between near $V^{4+}$ ions (exchange-narrowing). This effect was studied by Deigen and co-workers in Mn$^{2+}$ ions and by Wiench et al. in $V^{4+}$ ions.

In order to describe the $^{51}V^{4+}$ EPR in our experiments, the magnetic field positions of the hfs satellites lines can be expressed as:

$$H_\perp (m_l) = \left( \frac{h v}{g_\perp \mu_B} \right) - A_\perp m_l - \left( \frac{63}{4} - m_l^2 \right) \times \left( A_\parallel^2 + A_\perp^2 \right) \frac{1}{4} \left( \frac{g_\parallel \mu_B}{h v} \right),$$

$$H_\parallel (m_l) = \left( \frac{h v}{g_\parallel \mu_B} \right) - A_\parallel m_l - \left( \frac{63}{4} - m_l^2 \right) \frac{1}{2} \frac{g_\parallel \mu_B}{h v},$$

where $h$ is the Plank’s constant, $v$ the microwave frequency, and $m_l$ is the nuclear magnetic quantum number ($m_l = \pm 7/2, \pm 5/2, \pm 3/2, \pm 1/2$). From the fit of the data, we obtained $A_\parallel$ and $A_\perp$, they are presented in Table II along with bibliographic results for comparison.

Our EPR spectra in nondoped VO$_x$ NT’s show only an enveloping line centered at $g \approx 1.96$ with equidistant hfs lines. However, Kweon, et al. and Demishev, et al. reported a second and broad resonance associated by both to $V^{4+}$-$V^{4+}$ dimers. This extra line is not observable in the NT’s studied in the present work. A similar EPR result, an only one resonance line, has been previously reported by us in VO$_x$/Polianiline NT’s. By taking into account both systems studied by us, we can conclude that the presence of AFM dimers is not a necessary condition to have VO$_x$ NT’s as has been recently reported by Demishev.

The doped samples present more complex spectra because, in addition to the $V^{4+}$ lines complexity, they also present the resonance lines provided by the magnetic doped ion.

Our first studied case is the EPR in X-band of Ni-doped NT’s (Fig. 6), where two contributions are easily visible. These contributions are described by the $V^{4+}$ and Ni$^{2+}$ Hamiltonians ($H = H_{V^{4+}} + H_{Ni^{2+}} = H_{Ni^{2+}} + g_{Ni^{2+}} \vec{H} \cdot \vec{S}$). In the spectrum both contributions are presented; the first is a signal with a superstructure centered at $g \approx 1.96$ with a well resolved hfs. This signal corresponds to the $V^{4+}$ ions. The other broad line ($\approx 1400$ G) is well described by a Lorentzian line shape centered at $g_{Ni^{2+}} \approx 2.22$ which is in agreement with the expected value for Ni$^{2+}$ paramagnetic ions. In order to adjust the EPR parameters of the Ni contribution we fitted the spectrum keeping the width and center field as free parameters. To describe the $V^{4+}$ contribution it is necessary to include $g_{V^{4+}}$, $g_{Ni^{2+}}$, $A_{V^{4+}}$, and $A_{Ni^{2+}}$ due to any possible crystalline anisotropy present in the system. Although the NT’s are randomly distributed in a typical powder, the low $V^{4+}$ content makes that we need only to consider the perpendicular and parallel contribution described by Eq. (3). The parameter results of the EPR fit, for both contributions, are in Table II.

The Co-doped vanadium oxide NT’s also present an extra broad line. We assume the responsible Co ions of this resonance are associated with Co$^{2+}$ ions. This assumption is based on the fact that in general, at the microwave frequencies used by our EPR technique, Co$^{3+}$ ions cannot be detected and submillimeter-waves are necessary for the EPR detection.

This resonance is more complex than the previous Ni case and we need to consider crystalline anisotropy ($g_\parallel$ and $g_\perp$) in order to describe the EPR Co$^{2+}$ behavior. On the other hand, we also need to add a crystal field term, which supports that the spin state of the Co$^{2+}$ must be $S = 3/2$. Instead, the other possible spin state ($S = 1/2$) can be discarded because it is not affected by the crystal field effect. Then, the Co EPR resonance can be calculated by considering quantum transition probabilities between the energy levels, the crystal field effect on these levels and its angular distribution. To describe the asymmetric Co resonance, we use a powder line-shape to fit the spectrum for each employed microwave frequency.

To obtain the position of the resonance field for each angle, we have to solve the following Hamiltonian:

$$H_{Co^{2+}} = H_{eff} \mu_B \left( (g_\perp - g_\parallel) \sin \theta \cos \theta S_z + (g_\perp \sin^2 \theta + g_\parallel \cos^2 \theta) S_z \right) + D \left( \cos^2 \theta - \frac{1}{2} \sin^2 \theta \right) \left( S_z^2 - \frac{1}{3} S(S + 1) \right) + \cos \theta \sin \theta \left( S_z S_x + S_x S_z \right) - \frac{1}{2} \sin^2 \theta \left( S_x^2 - S_y^2 \right),$$

where $H_{eff} = H - H_0$ is the effective magnetic field with $H_0$ being an internal field and $H$ the external magnetic field; $D$ is the orthorhombic crystal field parameter and $\theta$ is the angle.
between the z direction of the crystal and the external magnetic field ($\theta = 0^\circ$, parallel and $\theta = 90^\circ$, perpendicular).

Finally, the Co line [$Y(\theta, H_0)$] was calculated by adding each angular contribution weighted by the angle position ($\sin \theta$):

$$Y(\theta, H_0) = \sum_0 \sum_{i \neq j} I_{ij}(\theta, H_{ij}) f(\theta, H_{ij}, H_0) \sin \theta,$$

where $f(\theta, H_{ij}, H_0)$ is the Lorentzian line describing the absorption as a function of the polar angle ($\theta$), the resonance field ($H_{ij}$) and the internal field ($H_0$); $I_{ij}(\theta, H_{ij})$ is the intensity for each transition and angle, calculated from the eigenvectors of the Hamiltonian matrix. $H_{ij}$ is the magnetic field where the difference between the two energies ($E_i$ and $E_j$) is equal to $\hbar \mu_B$. The energy levels are the eigenvalues of the Hamiltonian matrix.

In Fig. 7(a) and 7(c) we show the magnetic field dependence of the energy levels for the two extreme cases, $\theta = 0^\circ$ and $\theta = 90^\circ$. In Fig. 7(b), the magnetic field dependence for intermediate polar angles is represented. The calculated intensities ($I_{ij}$) of the low field transitions (1–3, 1–4, and 2–4, see left vertical lines in Fig. 7) are negligible, while the high field lines contribution to the total resonance is much stronger. The envelope curves, for the three frequency bands, can be well fit with the proposed cobalt model [see solid line in Fig. 8(a)–8(c)].

The superstructure of the $V^{4+}$ was described by both terms of $H_{\text{coul}}$ [Eq. (2)] and the hfs resonance positions were fitted by Eqs. (3a) and (3b), as we assumed in the Ni doped sample by using only the perpendicular and parallel contribution.
In the inset of Fig. 8(a) we show the experimental and calculated magnetic field position \((H_i)\) for parallel and perpendicular hfs vanadium lines as a function of \(m_i\). On the other hand, in the inset of Fig. 8(b), we plot the residual experimental data after subtracting the model for the Co contribution \([\text{fitted by Eq. (5)}]\). The upper and lower bars in this inset indicate resonance fields of the perpendicular and parallel contribution of the hfs of the vanadium ions and we show how these bars coincide with the position of the resonances in the spectrum. The fitting parameters are shown in Table II.

We remark that Co-doped NT’s and Ni-doped NT’s systems, after the subtraction of the doping ion resonance, show the same residual lines in respect to intensity, width and magnetic field positions which can be directly associated to the hfs contribution of \(V^{4+}\) ions. Indeed, \(^{58}\)Ni (68.0% abundance) and \(^{59}\)Ni (23.2% abundance) with \(I = 0\) do not present hfs resonances. On the other hand, although \(^{57}\)Co has nuclear spin \((I = 7/2)\) and approximately a 100% of abundance, no hfs corresponding to these atoms was detected due to the exchange narrowing effect. These features constitute good evidence that the observed residual lines are only produced by the hfs \(^{51}\)V in both doped samples (Co and Ni). Also, we can assert that the observation of the well-resolved \(V^{4+}\) hfs resonances indicates: (i) the presence of isolated \(V^{4+}\) magnetic ions and (ii) that these doped samples have a considerable smaller \(V^{4+}\) amount than the nondoped VO\(_x\) NT’s.

**C. dc-magnetic characterization**

The dc-magnetization as a function of temperature of nondoped and doped NT’s measured with an applied field of 10 kOe is presented in Fig. 9. In a previous work we have described the magnetic behavior of Ni-VO\(_x\) NT’s as a paramagnet which follows the law: \(\chi(T) = C(T - \Theta) + \chi_0\) (Curie-Weiss model plus a temperature independent term), where \(C\) is the Curie constant, \(\Theta\) is the Curie’s temperature, \(\chi_0\) is a temperature independent contribution, which has been calculated following the procedure previously described in Ref. 27. In the studied temperature range the samples did not present antiferromagnetic dimers, as was reported by other authors.\(^6\) In the Ni and Co doped samples we assume that \(C\) has two contributions: one from the paramagnetic doping species (\(\text{Ni}^{2+}\) or \(\text{Co}^{2+}\)) and the other from to the \(V^{4+}\) ions. As the experimental results were normalized by the moles of \(V\), the units of \(C\) are expressed in moles of \(V\) too. Then the Curie constant can be written as:

\[
C = \sum_{i=V^{4+},Co^{2+},Ni^{2+}} \frac{N_A g_i^2 (g_i^\ast)^2}{3k_B} S_i(S_i + 1) F_i/V, \tag{6}
\]

where \(k_B\) is the Boltzmann constant \(<g_i^\ast>\) is the mean value of the \(g\)-factor, \(S_i\) is the spin of the \(i\)th magnetic ion and; \(F_i/V\) is the ratio \(i\)-mole/V-mole. From the Curie constant we calculated the \(V^{4+}\) percentage in the nondoped NT’s to be 16(2)%. Alternatively, for the doped case, the amount of \(V^{4+}\) cannot be estimated directly from \(C\) and to obtain this we need to subtract the Co or the Ni contribution. In this context, we take into account our EPR results that the ions are as \(\text{Co}^{2+}\) \((3d^7; S = 3/2)\) and \(\text{Ni}^{2+}\) \((3d^8; S = 1)\) and their corresponding \(<g>\)-factors (Table II). These considerations allow us to estimate the \(V^{4+}\) amount in the NT’s, which are presented in Table III.

The processing of the second integral of the experimental EPR spectra from liquid He to room temperature (Fig. S2 in the supplementary material\(^{19}\)) is the EPR susceptibility (\(\chi_{\text{EPR}}\)). In the inset of the Fig. 9 it is presented the inverse of the EPR susceptibility \((1/\chi_{\text{EPR}})\) normalized by the dc-susceptibility at 10 K. The \(1/\chi_{\text{EPR}}\) curve of nondoped NT’s presents a linear behavior with the temperature, which confirms a paramagnetic Curie–Weiss behavior and there are not observable typical features indicating the existence of dimers.

To verify the amount of \(V^{4+}\) obtained for the three samples from the temperature experiments we performed measurements by varying the magnetic field at low temperatures. The \(\chi\) vs \(H/T\) curves (see Fig. 10) follow a typical Brillouin behavior of diluted paramagnetic ions, which are partially saturated by \(H/T\). However, we obtained a very good fit with the model presented in Eq. (7). In all cases we have to take into account two terms: the linear contribution [second term in Eq. (7)] and a Brillouin function\(^{31}\) corresponding to \(V^{4+}\) ions. When we consider the \(\text{Co}^{3+}\) or \(\text{Ni}^{2+}\) case, we need to add an extra Brillouin contribution for the transition metal doped ion. Then magnetization can be described by:

![FIG. 9. (Color online) Magnetic susceptibility as a function of temperature (solid circles: nondoped VO\(_{x}\)/Hexa NT’s; open circles: Co-doped NT’s; stars: Ni-doped NT’s). Inset: \((f/\chi)^{-1}\) vs temperature. \(\chi_0\) contains all diamagnetic contributions and its calculation is mentioned in the text.]

| TABLE III. Fitting parameters obtained from the magnetic \(\chi\) vs \(T\) and \(M\) vs \(H/T\) curves. |
| --- | --- | --- | --- | --- | --- |
| Magnetic susceptibility curve* | \(C\) [emu.K/V mole Oe] | \(\Theta\) [K] | %\(V^{4+}\) | %\(V^{4+}\) Metal/V (R) |
| Nondoped VO\(_{x}\)/Hexa | 0.0606 (2) | -3.90 (4) | 16 (2) | 14 (1) | - |
| Co-doped VO\(_{x}\)/Hexa | 0.269 (9) | 2.26 (6) | 4.6 (4) | 2 (1) | 0.12 (1) |
| Ni-doped VO\(_{x}\)/Hexa | 0.2128 (5) | -1.74 (5) | 4 (2) | 2 (1) | 0.13 (1) |

*We assume the Co/V ratio measured by INAA and EDS (0.14 for Co and 0.16 for Ni).

*previously reported in Ref. 11.
Curie and 16% of quasifree spins, which are responsible of the NT’s are consistent. In both cases we obtained between 14% temperature and varying the magnetic field) in the nondoped tal EPR and magnetization results of the quasifree V4 their vanadium neighbors. Both our quantitative experimen-
tically uncoupled because they are practically isolated from other hand, the ions which occupy the V(3) sites are magnet-
1/7 of the total vanadium sites present in the unit cell. On the with the vanadium percentage that occupies the V(3) sites, 1/7 of the total vanadium sites present in the unit cell. On the other hand, the ions which occupy the V(3) sites are magnetically uncoupled because they are practically isolated from their vanadium neighbors. Both our quantitative experimental EPR and magnetization results of the quasifree V4 ions and those reported by Krusin-Elbaum5 and Vavilova6 in similar VOx NT’s, suggest that this percentage is a general characteristic of the VOx system and this not depend on the type of amine located between the oxide planes.

D. X-ray photoemission spectroscopy

Figure 11 presents the XPS spectra (in the energy region 510–530 eV) of nondoped and Co-doped NT’s. In this region the spectra present two peaks originated by the spin-orbit splitting of V2p3/2 (~517 eV) and V2p1/2 (~524 eV). The V2p3/2 peak is located in both spectra at around 13 eV from the O1s peak, which allows to assign that peak to V5+ ions.32,33 To determine the presence of V4+ ions we have fitted the spectra with two identical components separated by 1.3 eV. The fittings yield V4+ /VTotal ratios of 0.05 for the Co-doped sample and 0.09 for the nondoped NT’s. Therefore, the percentage of V4+ ions is much smaller than that of the nonmagnetic V5+ ions. The obtained amounts of V4+ ions are in agreement with the amount determined by the magnetic measurements.

Unfortunately due to the small amount of Ni-doped material we cannot perform XPS studies.

IV. CONCLUSIONS

We observed in doped and nondoped samples that a fraction of the V ions that constitute the VOx NT’s is in the V4+ state. This fraction is reduced significantly in the Co- and Ni-doped samples which present sharp residual hyperfine V4+ EPR resonances that are due to isolated V4+ ions. In these samples a broad line is also detected, corresponding to the doped metal ion in each case. The broad Co-doped line is well described by a model which considers the powder resonance of Co5+ ions with S = 3/2 in an axial angular dependence of the crystal field, perpendicular and parallel g-factors and Zeeman contribution. On the other hand, the broad Ni-doped line can be described by a single Lorentzian line of Ni2+ ions with <g> = 2.22.

The dc-magnetization studies (M vs H curves), confirm the presence of S = 3/2 coming from Co5+ ions (in Co-doped NT’s) and S = 1 corresponding to Ni2+ (in the case of Ni-doped samples). In addition the dc-magnetization allowed us to quantify the percentage of paramagnetic V4+ ions present in both samples. The VOx/Hexa NT’s have a fraction of V4+ between 14–16% while in the Co-doped sample it is reduced to 5%–2% and close to 4–2% for Ni-doped NT’s.
This result is in good agreement with the observable $^{51}$V hfs in both doped NT’s. In the case of nondoped and Co-doped NT’s, this percentage was confirmed by direct measurement of the amount of $V^{4+}$ and $V^{5+}$ by XPS.

Finally, we have presented an alternative method for doping vanadium oxide/hexadecylamine nanotubes with $Co^{2+}$ and $Ni^{2+}$, which allows to reduce the concentration of $V^{4+}$ ions keeping the tubular structure. The presence of these dopants can lead toward some interesting modifications in order to minimize the $V^{4+}$ amount in the nanotubes and consequently this material provides new options for Li batteries cathodes.

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17 See supplementary material at E-JAPIAU-109-029108 for micrographs of non- and doped samples showing the tubular shape and EPR spectra at different temperatures of non-doped sample.

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