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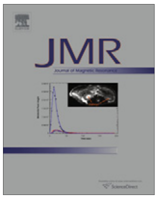

Deconvolution of the EPR spectra of vanadium oxide nanotubes

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ABSTRACT

In this work we report results of continuous wave (CW) electron paramagnetic resonance (EPR) spectroscopy of vanadium oxide nanotubes. The observed EPR spectra are composed of a weak well-resolved spectrum of isolated V^{4+} ions on top of an intense and broad structure-less line shape, attributed to spin–spin exchanged V^{4+} clusters. With the purpose to deconvolute the structured weak spectrum from the composed broad line, a new approach based on the Krylov basis diagonalization method (KBDM) is introduced. It is based on the discrimination between broad and sharp components with respect to a selectable threshold and can be executed with few adjustable parameters, without the need of *a priori* information on the shape and structure of the lines. This makes the method advantageous with respect to other procedures and suitable for fast and routine spectral analysis, which, in conjunction with simulation techniques based on the spin Hamiltonian parameters, can provide a full characterization of the EPR spectrum. Results demonstrate and characterize the coexistence of two V^{4+} species in the nanotubes and show good progress toward the goal of obtaining high fidelity deconvoluted spectra from complex signals with overlapping broader line shapes.

1. Introduction

Vanadium oxide nanotubes (VO_x-NTs) have attracted considerable attention in the lasts years because of their potential importance for electrochemical applications, as catalyst systems [1], gas sensors [2,3], supercapacitors [4] and lithium batteries [5,6]. These nanostructures consist of vanadium oxide sheets with alternating layers of long-chain alkyl amines as surfactant, which bend to form one-dimensional tubular products [7–9]. The layers of the nanotubes are constituted by vanadium ions in two different oxidation states, magnetic V^{4+} with spin $S = ½$ and non-magnetic V^{5+} with $S = 0$. Vanadium oxide nanotubes are supposed to be antiferromagnets and their magnetic properties have been widely investigated [10–12].

Electron paramagnetic resonance (EPR) spectroscopy is a powerful characterization method for tetravalent vanadyl species, V^{4+}, since they give unambiguous information about the valence state, the local coordination environment and the site symmetry of paramagnetic centers. Since the V^{4+} ion has an electronic spin $S = 1/2$ and the nuclear spin for the ^{51}V isotope (natural abundance 99.5%) is $I = 7/2$, the isotropic EPR spectrum of isolated V^{4+} species consists of a set of eight hyperfine lines due to the dipole–dipole interaction between the magnetic moment of the ^{51}V nucleus and the electronic moment of the unpaired V^{4+} electron [13,14].

In recent years, a number of EPR studies have addressed the presence and coordination geometry of the paramagnetic V^{4+} ions on vanadium oxide nanotubes [15–17]. The reported X-band EPR spectra consisted of a very weak hyperfine structure arising from the isolated V^{4+} ions superposed on a broad resonance line, which is attributed to spin–spin exchange interactions between neighboring V^{4+} sites. In order to derive the *g* and hyperfine (hfs) tensors parameters of such isolated species, Lee et al. obtained a resolved hyperfine spectrum by subtracting one or two broad Lorentzian lines from the experimental spectra. These Lorentzians lines were assigned to spin dimers and trimers in octahedral vanadium sites of the VO_x structure [15,16]. A similar procedure was used by Saleta et al. who fitted the EPR spectra of VO_x-NT by using a single powder line shape for $S = 1/2$ ions and obtained the hyperfine structure by subtracting the calculated powder line from the experimental spectrum [17].

In any case, the deconvolution of the EPR spectrum into two parts that correspond to the spin–spin exchanged species (intense broad spectrum) and isolated ones (weaker structured spectrum) constitute a first step in the pre-processing of the EPR spectrum of V^{4+} ions. The structured spectrum can give information about the local coordination of vanadyl species while the broad components can be used as a monitor for analyzing relations between the different nanostructures.

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In this respect, we have been motivated by a recent numerical procedure popularized by the physics–chemistry community since 1995 [18,19] that was initially designed for the diagonalization of large sparse matrices in quantum dynamics calculations and, then, reformulated to be applied to spectral analysis of experimentally measured transient time signals. The method was named filter diagonalization method, FDM, and has become a powerful tool for the analysis of nuclear magnetic resonance (NMR) transient experimental data. A comprehensive review of the FDM with applications for 1D and 2D NMR was published in 2001 [20].

Besides established NMR applications, FDM has also been employed in different scientific fields [21–25] and, with close relation to the present work, FDM was recently used to selectively remove broad solvent signals from complex NMR spectra without affecting overlapping or nearby narrow signals [26]. They have shown that FDM can efficiently model the broad signals in the time domain for subsequent subtraction from the original transient signal, resulting in a high fidelity separation of the underlying structured spectrum.

In this work we report results from EPR spectroscopy of vanadium oxide nanotubes emphasizing a numerical approach based on the FDM for the deconvolution of the experimental spectra. Interestingly, a predecessor of the FDM named Krylov basis diagonalization method [20], KBDM, was used instead because it is more appropriate to the CW-EPR situations under analysis. The method is already well known and established in NMR but has never been applied to CW-EPR before.

2. Theory

This section briefly explains the basic mathematical concepts and developed algorithm used for the deconvolution of the EPR spectra.

To start with, we remember that most of the CW-EPR experiments, as well as those presented in this work, detect the first derivative of the absorption spectrum and the detected signal is given by an array of real numbers, $\{y_k\}$, with $k = 0,\ldots,N-1$, measured at different magnetic field values within the interval (H_1,H_2), with $H_2 > H_1$ and $\Delta H = H_2 - H_1$ defined as the field sweep-range. Usually, N is of the order of few thousands and the field sweep follows an equidistant grid. While in simple cases the observed line shapes can be Lorentzian, Gaussian or a combination of both, for materials in the solid state, however, the spectrum may correspond to a summation of an infinite number of individual spin-packet line shapes with different positions, amplitudes and widths. Therefore, the resulting spectrum may assume a final shape that cannot be fitted by a simple mathematical expression.

Nevertheless, the method proposed here assumes that the whole EPR absorption spectrum can be fitted by a limited sum of Lorentzian lines. This hypothesis does not represent an exact description of general line shapes but, despite this fact, we will show that the algorithm is capable to provide a useful mathematical spectral deconvolution of our EPR spectra in a stable, efficient and fast way.

The method considers the harmonic inversion problem, HIP [20], and, under certain special conditions, i.e., small amount of experimental noise and exact arithmetic, the associated spectral estimation has a unique solution. Although such ideal conditions can never be reached experimentally, the method can still be successfully applied for real experiments and with personal computers, as long as the experimental signals are not too noisy and obey approximately the above formulated hypothesis.

The first step of the method is to define the HIP. For this we have chosen to consider the array $\{c_n\}$, with $n = 0,\ldots,L-1$ and $0 < L \leqslant N$, that reproduces the discrete inverse Fourier transform of the absorption spectrum. Since the absorption spectrum is not measured directly, the data $\{c_n\}$ must be calculated from the available array $\{y_k\}$, resulting in:

$$c_n = \frac{i}{2\pi n\tau}\left[y_0 + y_{N-1}(-1)^n + \sum_{k=1}^{N-2} y_k \cos\left(\frac{\pi k n}{N-1}\right)\right]\frac{1}{2(N-1)\tau}. \quad (1)$$

The above expression is valid for $n > 0$ and for $c_0 = 0$. The sampling interval, τ, is defined as $\tau = (2\Delta H)^{-1}$. The term in-brackets represents the discrete cosine Fourier transform of the signal $\{y_k\}$; the quotient on the right takes into account the normalization of the inverse transformation and the quotient on the left comes from the evaluation of the first derivative of the absorption signal. It is an instructive analogy to link the signal $\{c_n\}$ with the free induction decay (FID) signal, frequently observed in pulsed magnetic resonance experiments. In the absence of a better terminology, we will refer to the signal $\{c_n\}$ as the "FID signal" and to the reciprocal of the magnetic field variable, $n\tau$, as "time".

Following the Lorentzian line shape hypothesis, the HIP is then defined by a fitting model constructed as a sum of exponentially damped sinusoids in an equidistant time grid:

$$c_n = \sum_{k=0}^{K-1} |d_k| e^{i\theta_k} e^{i2\pi n f_k \tau} e^{-n\,\gamma_k \tau} = \sum_{k=0}^{K-1} d_k e^{in\Omega_k \tau}. \quad (2)$$

The complex amplitudes are represented by $\{d_k\}$ and $\{\Omega_k\}$ represents the complex frequencies, with $k = 0,\ldots,K-1$. Therefore, the complete characterization of the FID signal requires the determination of $4K$ real unknowns.

Once the "line list", defined by the set of real parameters $\{|d_k|, \theta_k, f_k, \gamma_k\}$, is available, the corresponding spectral representation in the Nyquist range, $-\Delta H \leqslant \varphi \leqslant \Delta H$, can be easily constructed from the analytic Fourier integral of Eq. 2:

$$S(\varphi) = 2\sum_{k=1}^{K} \frac{|d_k| e^{i\theta_k}}{\gamma_k + 2\pi i(\varphi - f_k)}. \quad (3)$$

This representation is complex and its odd real part corresponds to the absorption spectrum. The parametric representation of the EPR signal originated from a given line list (meaning, the first derivative of the absorption spectrum) can be calculated by means of the numerical differentiation of $\mathrm{Re}[S(\varphi)]$ in the range $0 \leqslant \varphi \leqslant \Delta H$. It should be noted that the experimental magnetic field variable can be recovered by a simple translation, $H = H_1 + \varphi$ for $\varphi \geqslant 0$. Also note that the factor 2 multiplying Eq. (3) was introduced to compensate the loss of signal by taking only the positive φ side of the spectrum.

The next step concerns the calculation of the line list for a given FID signal. This can be accomplished by simple linear algebra and the details are well described in Ref. [20]. To avoid repetitions, we will only outline the method in the following few paragraphs.

First, a matrix U_p of dimension $M = L/2$ (with $p = 0, 1$) is defined such that its elements are directly given by the signal $\{c_n\}$:

$$[U_p]_{nm} = c_{n+m+p}. \quad (4)$$

Then, a generalized eigenvalue problem, GEP, is formed for the eigenvalues $\{\mu_k\}$ and eigenvectors $\{B_k\}$:

$$U_1 B_k = \mu_k U_0 B_k. \quad (5)$$

The eigenvectors must be orthonormalized with respect to the overlap matriz U_0:

$$B_i^T U_0 B_j = \delta_{ij}. \quad (6)$$

Finally, the line list is calculated by the expressions:

$$\mu_k = e^{i\tau\Omega_k} \quad (7a)$$

$$\sqrt{d_k} = B_k^T C. \quad (7b)$$