

A SIMULATION METHOD OF NMR SPECTRA OF POLYCRYSTALS

S. Galindo and L. González-Tovany

Instituto Nacional de Investigaciones Nucleares

Benjamín Franklin 161

Col. Escandón. Código Postal 06140

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ABSTRACT

We present a very simple Monte Carlo-simulation-method of NMR (Nuclear Magnetic Resonance) spectra of polycrystals. We also give one example of its applications.

RESUMEN

Presentamos un método Monte Carlo muy simple de simulación de espectros de RMN (Resonancia Magnética Nuclear) de policristales. Damos también un ejemplo de sus aplicaciones.

The theoretical simulation of NMR spectra of polycrystalline samples is a useful tool in extracting information about anisotropic interactions in solids. Therefore it is desirable to possess a simple and reliable method for calculating simulated spectra.

It is the purpose of this note to present a very simple simulation technique, together with one example illustrating its applications.

The method is based on our previously reported⁽¹⁾ Monte Carlo technique for simulating ESR spectra of randomly oriented paramagnets, and can be described as follows: Given a general nuclear spin Hamiltonian, it is in principle possible to diagonalize this Hamiltonian or to use perturbation theory to obtain the values of ν , the frequency at which resonance occurs, i.e.,

$$\nu = \nu(\theta, \phi),$$

where θ and ϕ are the spherical polar angles made by the applied magnetic field with respect to the principal axis coordinate system of a crystallite.

If we generate N random directions (θ', ϕ') with the aid of a computer by means of the formulas⁽¹⁾ $\cos\theta' = 1 - 2\gamma'$ and $\phi' = 2\pi\gamma''$ where γ' and γ'' are two independent random numbers uniformly distributed in the interval $0 \leq \gamma \leq 1$, we can then calculate the resonance frequency $\nu(\theta', \phi')$ for each random direction and compare each ν with the values defined by M subintervals into which the frequency range has been divided.

Every time the calculated frequency $\nu(\theta', \phi')$ falls within the limits of a subinterval, the computer is instructed to add a "count" in the register corresponding to that subinterval.

The polycrystalline NMR absorption function $I(\nu)$ is then the summation of the absorption intensities of all the individual crystallites. The contribution from each crystallite can be taken as:

$$f(\nu - \nu_n^0),$$

where $f(\nu - \nu_n^0)$ is the equation for a normalized line function centred at the frequency ν_n^0 . This frequency corresponds to the center of the subinterval, $\nu_n^0 = \frac{1}{2} (\nu_{n+1} - \nu_n) + \nu_n$. Hence the overall $I(\nu)$ absorption

function is

$$\sum_n T_n f(\nu - \nu_n^0),$$

where T_n is a weighting factor for each frequency subinterval, and is taken to be equal to the number of Monte Carlo-generated counts on each subinterval as previously described.

To illustrate the effectiveness of this computer-simulation method, we have chosen as an example the NMR spectrum of the central transition of ^{51}V in KVO_3 at 16 MHz, as published by Baugher et al.⁽²⁾.

This spectrum can be described by means of the nuclear-Hamiltonian⁽²⁾

$$H_N = H_Z + H_Q + H_{CQ},$$

where H_Z , H_Q and H_{CS} are respectively the Zeeman, quadrupole and chemical shift terms.

Second order perturbation theory yields⁽²⁾ an expression $\nu^{(0, \phi)}$ for a general orientation of the applied magnetic field. Using this and the values of the nuclear spin-Hamiltonian parameters⁽²⁾, the NMR spectrum can be then calculated by the technique presented in this note. The result is shown in Fig. 1, together with the experimental and theoretical spectra obtained by Baugher et al.⁽²⁾. In obtaining our simulated spectrum of Fig. 1, 1×10^5 random orientations were Monte Carlo-generated. The number of frequency subintervals was 10^3 each with a width of 45 Hz. The line shape function $f(\nu - \nu_n^0)$ was assumed to be the derivative of a gaussian function having a width of 1.1 KHz.

As can be readily seen in Fig. 1, Baugher et al.⁽²⁾ simulation and ours agree well with the experimental spectrum. This indicates that our technique is quite accurate and compares well with the other method, besides having the advantage of being very simple indeed.

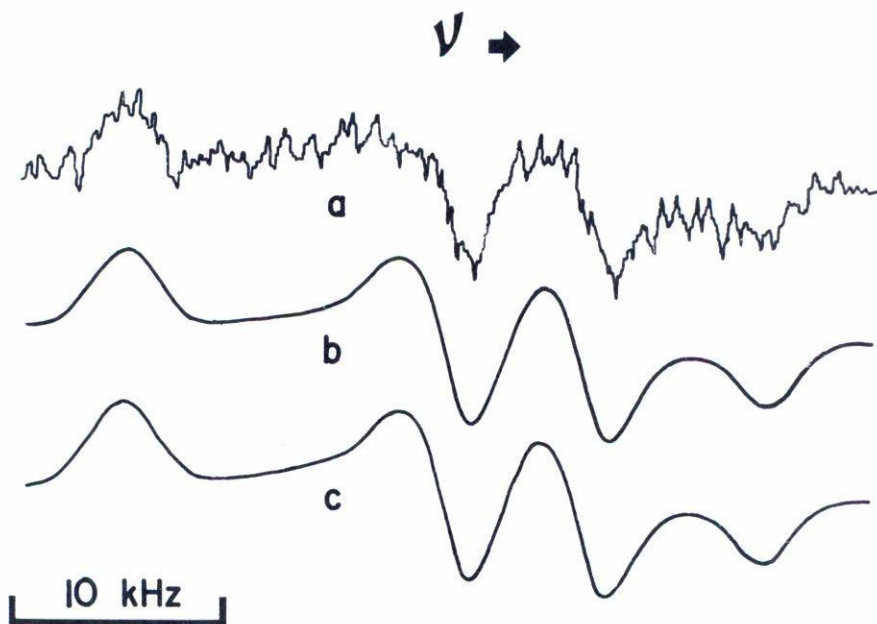


Fig. 1. The 16 MHz NMR spectrum of ^{51}V in KVO_3 . Comparison of the experimental (a) and computer-simulated derivative spectra; (b) Baugher *et al.* method (2) and (c) the present method.

REFERENCES

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