NMR powder spectra in case of strong quadrupole interaction

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Abstract

We suggest the algorithm of straightforward numerical simulation of a powder NMR spectra in compounds with a strong quadrupole splittings. Results of our simulation exhibit a good fit of the experimental data even in case of moderate computing resources. It is shown that asymmetry parameter of the nuclear quadrupole interaction, quadrupole frequency and isotropic part of Knight shift can be evaluated from the powder NMR spectrum. The behavior of magnetic and quadrupole relaxation rates (the latter - at some assumption) over the spectra can be also simulated and allows one to determine the mechanism of nuclear spin lattice relaxation.

Key words: NMR; NQR; powder; $YBa_2Cu_3O_7$; $AsCu_3$

1. Introduction

Many new materials are available only in form of powders and ceramics. If quadrupole or Zeeman interaction is much stronger than another, perturbation theory appeared to be useful for the powder nuclear magnetic resonance (NMR) spectra analysis [1]. In case when these interactions are in speaking terms, perturbation theory is not valid any more and numerical methods should be used. An accurate simulation of the spectra supposes taking into account not only splittings of the energy levels but also probabilities of transitions caused by radio frequency (RF) excitation. From computational point of view it means that we need eigenvectors as well as eigenvalues of Hamiltonian. In this sense numerical methods are preferable even in case of spin I=3/2, when analytical solution of secular equation is known [2]. We found that simulation efficiency can be improved due to the fact that averaging of transition probabilities could be done using only two directions of RF magnetic field relative to the crystal axes.

2. Simulation

The model system is ensemble of non-interacting spins I in powder crystallites. The mutual orientation of applied magnetic field, RF field and crystallographic frame is defined by three Euler angles - α,β, and γ. The main Hamiltonian H including Zeeman and quadrupole interaction can be written as a function of two angles - α and β. In order to find the transition frequencies it is necessary to find unitary transformation T, obeying the following equation $T^{-1}HT = D$, where D is diagonal real matrix containing energy values. The algorithms for solving this problem are well described in literature. Hereby we have the frequencies of all possible $I(2I+1)$ transitions.

NMR signal intensities are defined by the matrix elements of RF excitation Hamiltonian H_1 depending on all three Euler angles: $w_{ij} = \left|\left(T^{-1}H_1T\right)_{ij}\right|^2, i > j;$ $i,j = 1\ldots(2I+1)$. It appeared that averaging of probabilities over γ can be provided using only two γ -values shifted by $\pi/2$:

$$\frac{1}{2\pi}\int_0^{2\pi} w_{ij}d\gamma = \frac{1}{2}\left[w_{ij}(\gamma) + w_{ij}(\gamma+\pi/2)\right].$$

This fact is valid for any main Hamiltonian and gives

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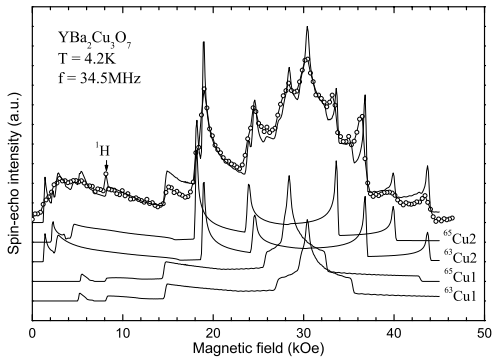

Fig. 1. The copper NMR powder spectrum in $YBa_2Cu_3O_7$ high-T_c superconductor.

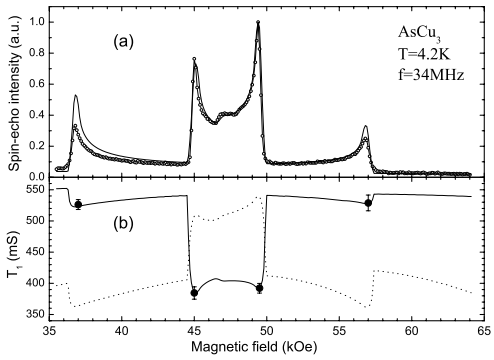

Fig. 2. ^{75}As NMR powder spectrum (a) and nuclear spin-lattice relaxation time (b) in $AsCu_3$ compound. Solid line in (b) is simulation of magnetic relaxation, dotted line - quadrupole relaxation, solid circles represent experimental data.

substantial advantage for numerical calculations.The lineform function used in simulation was rectangular line form with a width equal to the bandwidth of spectrometer.

Another information, that can be deduced from NMR studies of powder spectra, is relaxation mechanism [3]. Knowing unitary transformation matrix T for any particle of the powder it is possible to find the relative relaxation rates over the spectrum in case of magnetic and quadrupole relaxation. The probabilities of all the transitions caused by magnetic relaxation are proportional to $\left|\left(T^{-1}I_\mu T\right)_{ij}\right|^2, \mu = x, y, z$. Solving the system of differential equations for the populations of the energy levels with initial conditions corresponding to the saturation of the transition under the study one can get the relaxation rate. Simulation of quadrupole relaxation is somewhat uncertain. The relative contributions of the different terms of quadrupole Hamiltonian to the relaxation process are not well defined. We can only argue that the wave functions are strongly mixed and possibly it is not of principal importance. It was assumed that transition probabilities caused by quadrupole relaxation are proportional to $\left|\left(T^{-1}I_\mu I_\nu T\right)_{ij}\right|^2; \mu, \nu = x, y, z$.

3. Experimental and Discussion

We present two experimental data sets with a fits as an example of application of our simulation procedure. Copper NMR spectrum of powder sample of high-T_c superconductor $YBa_2Cu_3O_7$ at 4.2K is presented in Fig. 1. The well known parameters of quadrupole Hamiltonian and Knight shift values for this compound [4] were used. There are two non-equivalent positions of copper in the crystal structure of $YBa_2Cu_3O_7$ compound - Cu1 and Cu2, the ratio of the number of these positions being 1:2. There are two naturally abundant copper isotopes - ^{63}Cu and ^{65}Cu (both with a spin $I = 3/2$). Results of computer simulation for all four components are shown at the bottom of Fig. 1 by solid lines. The total spectrum which is weighted sum of four simulated ones fits experimental data fairly well - all the peaks can be identified.

Another example is ^{75}As NMR in $AsCu_3$. Experimental and simulated powder spectra are plotted in Fig. 2(a). The quadrupole frequency value of ν_Q=15.063MHz was used for the simulation [5]. The quality of fit proves that η=0 and K=0.23(1)% for ^{75}As in $AsCu_3$ at T=4.2K. The Fig. 2(b) shows experimental values of relaxation times T_1 and two calculated dependencies for magnetic (solid line) and quadrupole (dotted line) relaxation. Obviously, ^{75}As relaxation in this compound has magnetic origin.

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