Genetic Algorithm in the EPR Study of Powder Spectra of Charge-Transfer tm-p-PD:Chloranil Complex

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Received 5 May 2007; revised 3 September 2007
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Abstract. The temperature dependence of the electron paramagnetic resonance (EPR) powder spectra of tm-p-PD:Chloranil has been studied. A qualitative analysis of the spectra suggests that the line width of an unpaired spin center varies with temperature, $g$ parameters may vary, too, but generally there is no simple way to assign parameters to the spectra unless the EPR data are confronted with an appropriate synthetic model. As a model for the detailed simulation and analysis, an orthorhombic spin Hamiltonian is adopted and an anisotropic line width of the paramagnetic charge-transfer center is assumed. The results are the best-fit values $g_{xx}$, $g_{yy}$, $g_{zz}$ and the three line width parameters, respectively. A genetic algorithm was designed for the EPR spectra best-fit search in the six-parameter space and the results were obtained automatically without operator intervention. The numerical procedure was accelerated with a computing cluster.

1 Introduction

The continuous-wave X-band electron paramagnetic resonance (EPR) powder spectra of tm-p-PD:Chloranil charge-transfer (CT) complex are recorded at various temperatures in the range of 119–298 K in the form of a first derivative of EPR absorption as shown in Fig. 1. The spectra can be represented by a single magnetic center of rhombic symmetry with a spin Hamiltonian of the form $\mathcal{H} = \mu_B BSg$. Both $g$ and the individual line width anisotropies contribute to the apparent asymmetry of the powder profile.

Motivated by Spalek et al. [1, 2] and Filipic and Stancar [3] we use the genetic algorithm (GA) routines to extract the $g$ main elements and individual line width components from the powder data and plot the temperature dependence of the quantities. Matlab was used as an implementation environment with high-level specialized toolboxes facilitating the GA data analysis. Here, the task of simulating the powder spectra for a given set of parameters is accomplished with the Easyspin simulation tool [4], which is plugged into the GA pack [5, 6] maintained by GEATbx (genetic and evolutionary algorithm toolbox) for use with Matlab by Pohlheim [7]. While the simulation of the powder EPR spectra requires
massive computations, to lower the time cost of the calculations a set of personal computers was organized into a small computer cluster with a local area multicomputer (LAM)/message passing interface (MPI) [8] environment.

2 Genetic Algorithm

One can roughly define the optimization procedure as a minimization of some function (or functional) dependent on problem parameters. Usually, the minimum is sought in the search space in a regular deterministic manner, i.e., using local optimization algorithms such as gradient methods or by trial-and-error manual operation. Results of trial-and-error search of the best-fit EPR parameters of tm-p-PD:Chloranil powders have already been published [9]. What we have learned is that for compromise between efficiency and accuracy, the search should be performed in the following sequence: $g$ variations first, isotropic width parameter adjustment next, and finally the anisotropy of the line width. The local optimization procedures are not free from the operator’s intervention: one has to provide promising starting points to the algorithm stages to obtain satisfactory results. On the other hand, the GAs [5, 6] perform well in wide search spaces and their usefulness in the EPR data analysis has been already proven [1–3].

To start with the GA, it is necessary to specify the coding method to define the genetic operators and the objective function and to make a decision