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Temperature Dependence of \hat{g} Tensor Anisotropy in (tm-*p*-PD):Chloranil, Charge Transfer Complex Powders

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The powders of 2,3,5,6-tetramethyl-*p*-phenylenediamine:chloranil charge transfer complex were studied by EPR. Numerical pack EPR–NMR was used to simulate and fit the X-band experimental data in the temperature range of 119–298 K. Very good agreement between the experiment and simulations permits to obtain the main values of \hat{g} matrix and plot their temperature dependence. At 150 K the main g values are $g_{xx} = g_{yy} = 2.0041$ and $g_{zz} = 2.0015$. g splitting factor varies significantly with temperature and shows an anomaly near 200 K. The signal narrows with the temperature increase, which agrees with the earlier observation. Individual component linewidth, used in the simulation is anisotropic and amounts to 0.1–0.8 mT; which is reasonable when compared with those measured earlier for the single crystals of *p*-phenylenediamine:chloranil, where the narrowest lines are quoted to be 18 μ T.

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1. Introduction

Donor–acceptor complexes of *p*-phenylenediamine-chloranil (PDC) had been a subject of EPR study in the past. Hughes and Soos [1] attributed the observed single crystal spectra to PD cation and chloranil anion radicals ($S = 1/2$) characterized with $g_{\parallel} = 2.0024$ and $g_{\perp} = 2.0054$, almost axially symmetric. Very narrow

lines were reported and attributed to three magnetically inequivalent ion-radical chains. There is very few reports on magnetic resonance in this group of charge transfer complexes and it appears interesting to investigate the possibility of getting some insight into the properties of *chloranil*, *bromanil*, and *iodanil* complexes with other adducts using numerical methods of analysis of EPR powder spectra since the crystals are difficult to obtain.

2. Synthesis of the charge transfer complex

2,3,5,6-Tetramethyl-*p*-phenylenediamine (tm-*p*-PD) (Aldrich) was recrystallized from absolute ethanol. Chloranil (Fluka) was recrystallized from benzene. Both were dried in vacuum. The CT-complex (Fig. 1) was precipitated by mixing a hot saturated benzene solution of chloranil with an equimolar solution of tm-*p*-PD in benzene. The greenish-black powder was dried after filtration in vac-

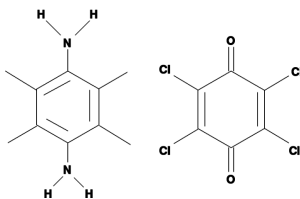


Fig. 1. tm-*p*-PD:chloranil structure.

uum for at least four hours. The CT-complex was sealed under vacuum in glass tubes to avoid contact with air. For comparison: Hughes and Soos obtained tiny single crystals of PDC in the vacuum sublimator from the phenylenediamine and chloranil powder using a cold finger technique.

3. Experimental

EPR powders spectra of tm-*p*-PD:chloranil were measured in the temperature range from 119 K to 298 K. A home-made (Radiopan) homodyne EPR X-band spectrometer was used, sample powder was sealed in the ampoule and its temperature controlled with nitrogen flow system. First derivative analog signal was recorded and field-calibrated with an NMR probe. The spectra were digitized using WinDIG EPR [2] application; later the dataset of typically about 8000 points was compared with the powder data simulation program [3]. Klystron frequency locked to the TE₁₀₂ resonator varied but slightly with temperature (9.059–9.071 GHz). For the full set of data corresponding to 119–298 K range of temperatures there is an apparent shift and line broadening of the powder signal profile on varying the temperature. Weil's NMR–EPR numerical pack [3] allows for the linewidth of individual spin packet anisotropy, which was also accounted for. The best fit (Fig. 2) was attempted assuming the spin Hamiltonian

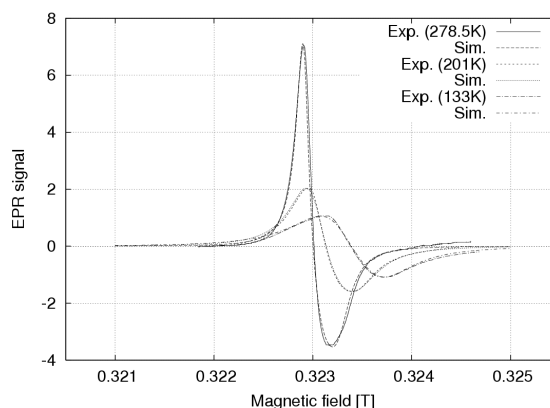


Fig. 2. An example of the experimental and simulated data for three temperatures: $T = 278.5$ K, 201 K, and 133 K, respectively. Experimental (Exp.) and simulated (Sim.) data are superimposed. Quality of the fit is apparently the same for all 22 data sets.

with $S = 1/2$, low symmetry Zeeman splitting matrix, and neglecting hyperfine interactions. The simulation was carried out starting with the best g -fit followed by individual linewidth δB , its anisotropy and final readjustment of all the spin-Hamiltonian parameters, i.e. g_{ii} , δB_{ii} where $i = x, y, z$. The amplitude of the simulated powder spectra was adjusted manually for the best fit to the experiment and the resulting temperature dependence of the amplitude follows a smooth monotonic function.

4. Results and discussion

The powder spectra simulation model requires that the line shape is predefined: we adopted a Lorentzian function and used the option that individual spin packet width is anisotropic. Its anisotropy follows the angular dependence of \hat{g} tensor according to the algorithm [3]: $\delta B = LineWidth \times (B^T \cdot W \cdot B) / B^2$, where W is a linewidth anisotropy diagonal matrix and $(LineWidth \times W)$ yields three main δB_{ii} values. B is the vector defining magnetical field in the crystal coordinates. The results of the best fit lead to the two sets of the individual linewidths $\delta B_{xx} = \delta B_{yy}$ and δB_{zz} (Fig. 3). The chloranil spectra intensity seems to follow a Curie $1/T$ dependence. The corresponding graph is plotted below (Fig. 4). The most dramatic and intriguing is the behavior of \hat{g} tensor. As observed in Fig. 5, there is an abrupt change in g -factor splitting at temperatures around 200 K, from axially symmetric to rhombic. It may reflect a rearrangement occurring in the charge-transfer complex. Reported earlier, for tm- p -PD:chloranil at room temperature there were the following parameters: $g = 2.0023$, overall linewidth 1.1 mT [4]. Those data were obtained in 1958 with an early ESR measuring setup with the resonance magnetically swept at 50 Hz and the absorption displayed on the oscilloscope. Possibly, the accuracy of the measurement was inadequate to read

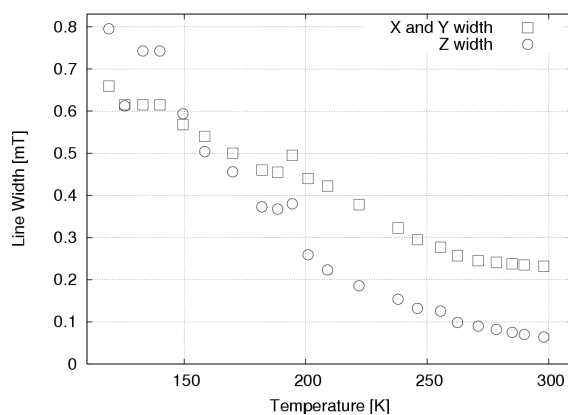


Fig. 3. Individual linewidth assumed for the microcrystals for the best fit varied from 0.1 mT to 0.8 mT, and the width anisotropy was taken for account. $\delta B_{xx} = \delta B_{yy}$, δB_{zz} .

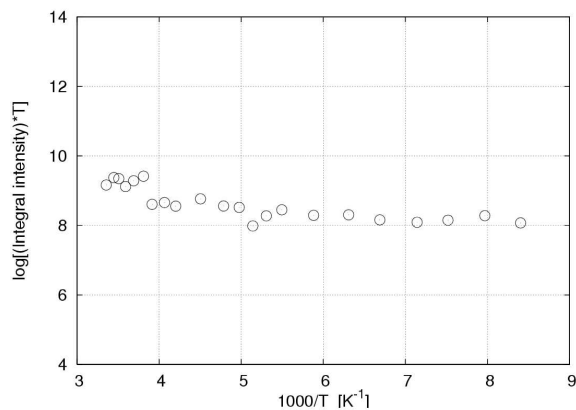


Fig. 4. Logarithm of the product of integral intensity and temperature as a function of reciprocal temperature.

the g_{\parallel} splitting value. The linewidth, quoted for the tm-*p*-PD:chloranil powder [4] agrees well with B_{pp} “line spread” (Fig. 6) and $(g_{xx} + g_{yy} + g_{zz})/3 = 2.003$ in our case. No indication was given of g dependence on temperature or rhombicity of the centers. We maintain that the powder spectra may not only be a source of the set of numbers related to spin Hamiltonian and the linewidth but give an indication on an abrupt change occurring in the structure of paramagnetic centers. The structural data of the crystal is still unavailable; single crystal studies would certainly give an unambiguous answer, and the attempt would be made to grow the crystals to corroborate the described findings.

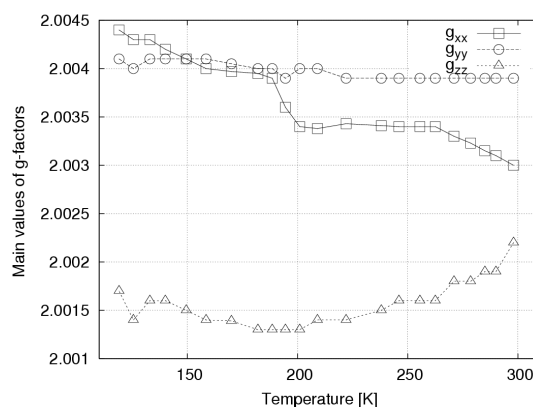


Fig. 5. g_{xx} , g_{yy} , and g_{zz} splitting factors as a function of temperature.

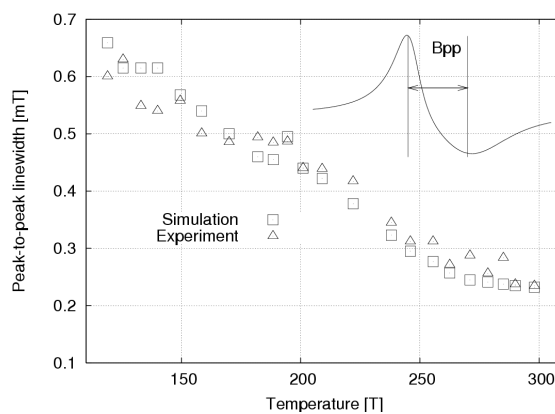


Fig. 6. Simulated and experimental B_{pp} line-spread parameter. Reasonably good fit proves that the model and its parameters are correct. Triangles and squares denote experimental and simulated data, correspondingly. The inset explains the line-spread B_{pp} definition.

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