Influence of magnetic agglomerates on EPR spectra of free radicals embedded in organic matrix

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Abstract

Two samples containing an extended free radical network derived from the condensation of cyanuric chloride with p-phenylenediamine have been prepared. Both samples (designated as sample 1 and 2) contained free radicals. Additionally, sample 2 contained a very small amount of magnetic centres, part of it in form of agglomerates. The magnetic resonance spectra (EPR/FMR) of these samples were measured in the 4–290 K temperature range. At room temperature the EPR spectrum of sample 2 is the sum of two lines attributed to two different magnetic centres: a narrow line at H_r=3373.46(3) Gs (g_{eff}=2.0031(1)) with linewidth ΔH_{pp}=8.63(2) Gs (due to free radicals) and a broad line centred at H_r=3053(5) Gs (g_{eff}=2.240(1)) with linewidth ΔH_{pp}=1010(5) Gs (arising from magnetic iron oxide agglomerates). The spectrum of sample 1 constituted a single resonance line centred at H_r=3371.64(3) Gs (g_{eff}=2.0043(1)) with linewidth ΔH_{pp}=7.02(2) Gs. The integrated intensities decreased with decreasing temperature in both spectra in the high temperature range. This type of behaviour is similar to what is observed for magnetic nanoparticles in nonmagnetic matrixes. The resonance field of the broad line shifts to low magnetic fields upon lowering temperature with the gradient $\Delta H_r/\Delta T$=2.3(1) Gs/K, while the narrow line shifts towards high magnetic fields with $\Delta H_r/\Delta T$ =2.7(1)x10^{-3} Gs/K for sample 1 and $\Delta H_r/\Delta T$ =3.6(1)x10^{-3} Gs/K for sample 2. The linewidth of the broader line increases with decreasing temperature while for the narrow line this change was only minor (especially at higher temperatures) in both samples. The magnetic iron oxide clusters produce an internal magnetic field which could act on free radicals and its strength depends essentially on relative concentration of clusters. The resonance field at different temperatures is essentially dependent on the existence of magnetic clusters with a stronger process observed for sample 2. This could suggest that the reorientation processes are more intense for sample without magnetic clusters.

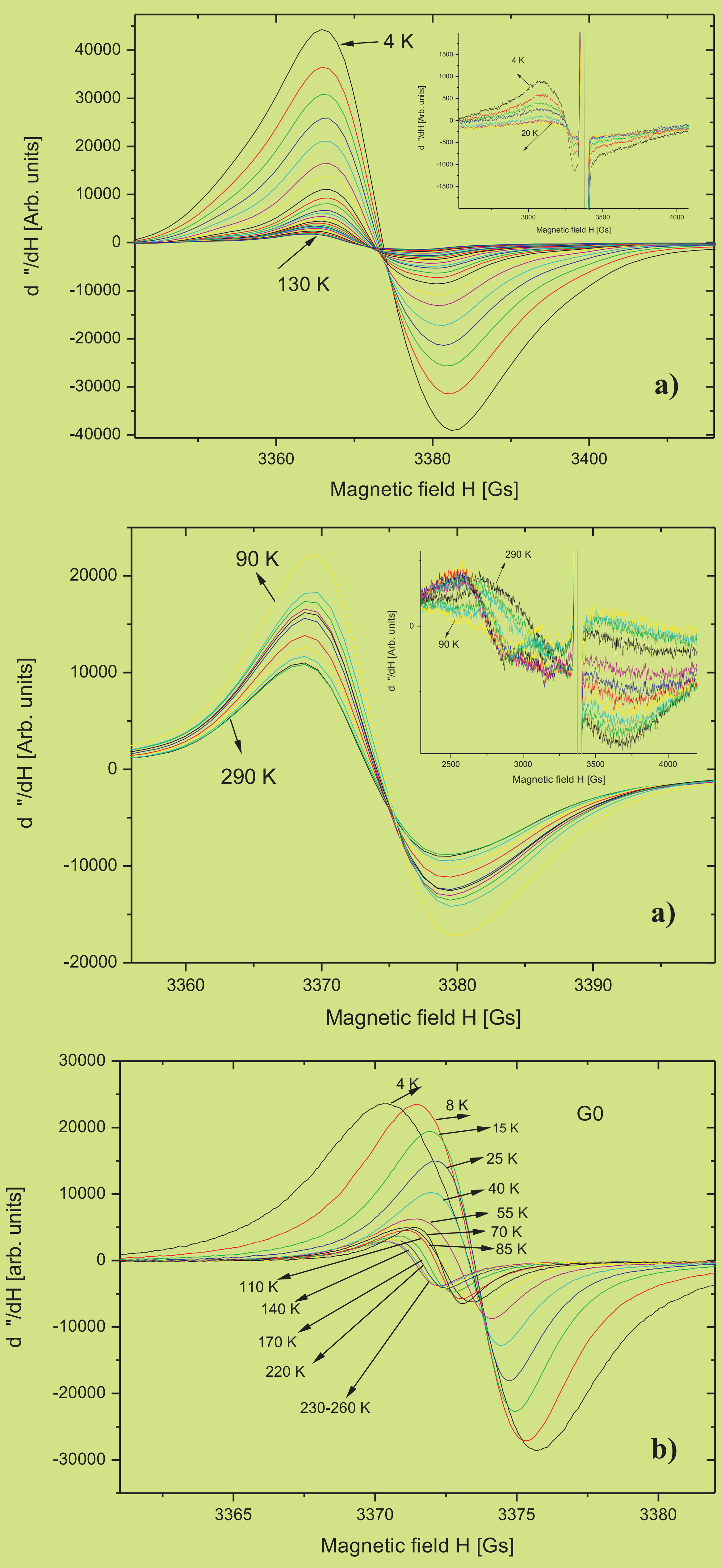
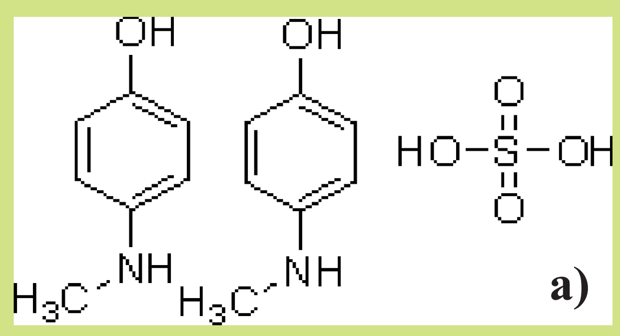


Figure 2 Temperature dependence of the EPR spectra of (a) extended free radical network derived from condensation of cyanuric chloride with p-phenylenediamine, and (b) 8-Hydroxy-1,3,6-pyrenetrisulfonic acid, trisodium salt. The insets show the spectra in extended magnetic field range.

Sample designation	I_{4K}/I_{RT}	ΔH_{4K} [Gs]	ΔH_{RT} [Gs]	Θ_{CW} [K]	$\Delta H_r/\Delta T$ [Gs/K]	Source
1	16	2.30(2)	5.34(2)	0.40(3)	0.027(3)	This work
2	34	10.51(3)	13.83(3)	0.74(3)	0.037(3)	This work
3	45	7.42(2)	13.30(3)	1.06(3)	0.035(3)	[10]
4	80	8.23(2)	14.07(3)	1.23(3)	0.075(3)	[9]

Table 1. Values of different parameters calculated from EPR spectra: I_{4K}/I_{RT} – ratio of the integrated intensities at 4 K and RT; ΔH_{4K}, ΔH_{RT} - linewidths at 4 K and room RT; Θ_{CW} – Curie-Weiss temperature; $\Delta H_r/\Delta T$ – temperature gradient of resonance field at low temperature. Sample 1 is without additional magnetic centres, samples 2 to 4 contain an increasing amount of additional magnetic centres.



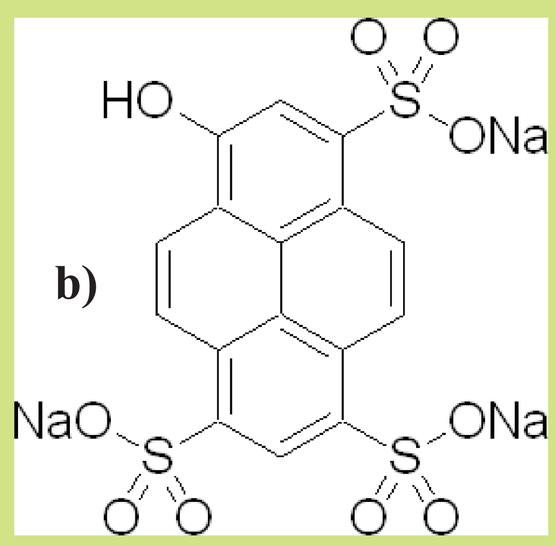


Figure 1 The p.- methylaminophenol sulfate (a) and the 8-Hydroxy-1,3,6-pyrenetrisulfonic acid,trisodium salt (b).

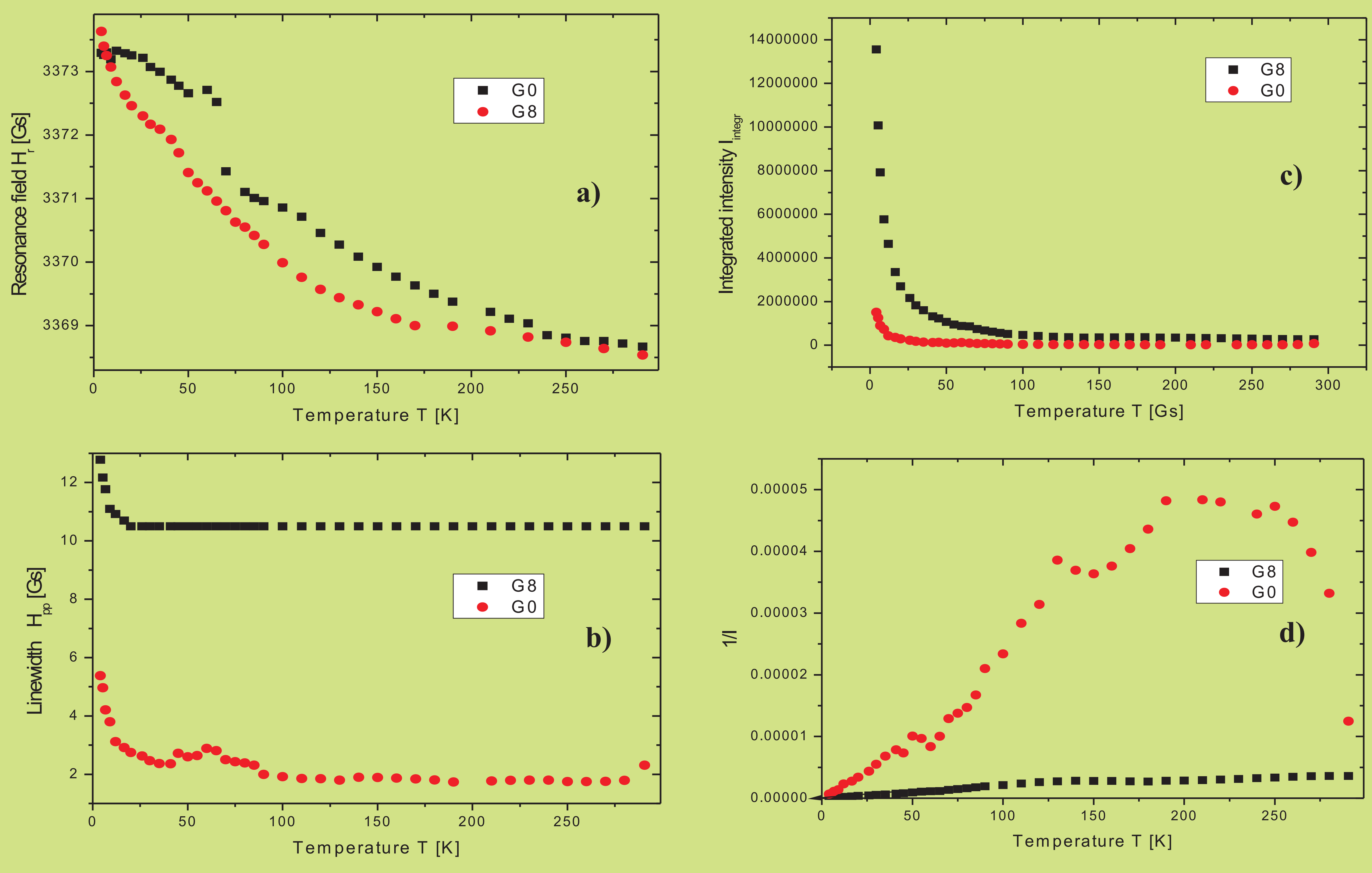


Figure 3 Temperature dependence of the parameters of EPR spectra for both samples, a) resonance field (H_r), b) peak-to-peak linewidth (ΔH_{pp}), c) integrated intensity (I_{integr}) and d) reverse of integrated intensity.

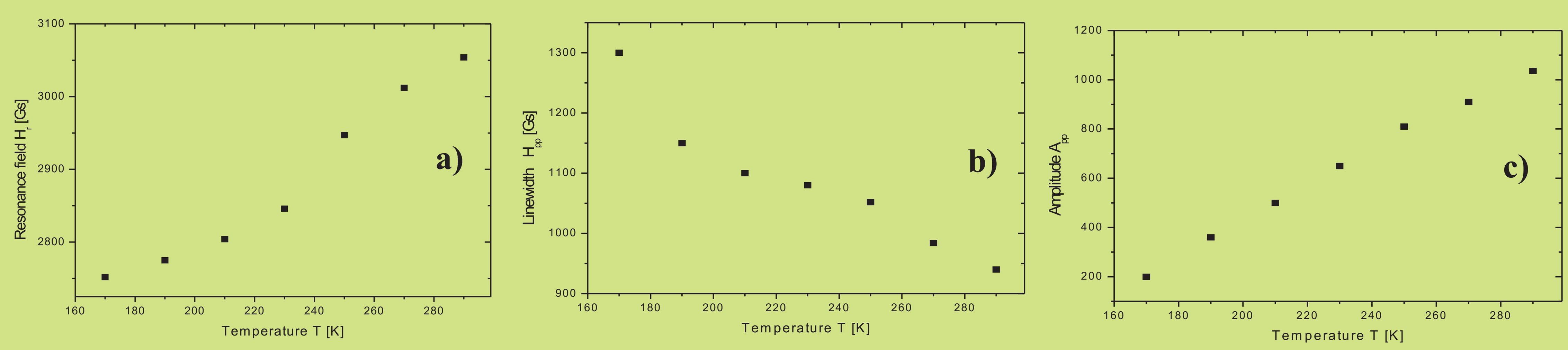


Figure 4 Temperature dependence of the parameters of FMR spectra for sample 2: a) resonance field (H_r), b) peak-to-peak linewidth (ΔH_{pp}), c) signal amplitude (A_{pp})