HIGH FIELD ESR INVESTIGATION OF IRON Fe^{III} CENTER IN MALARIAL PIGMENT AND ITS SYNTHETIC SUBSTITUTE BETA-HEMATIN

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A parasite, *Plasmodium falciparum* (PF), causes malaria that annually claims at least 1 million of lives. In the trophozoite phase, PF invades red cells of the human blood and catabolizes hemoglobin, using the amino acids for *de novo* protein synthesis and aggregating heme into an inert crystal called hemozoin [1, 2]. Multiple lines of evidence suggest that traditional drugs against malaria, quinolines, might act by inhibiting crystallization of hemozoin [2]. In our previous work, we applied the EMR facility at the NHMFL to study the local symmetry of iron centers in β-hematin, a synthetic substitute of hemozoin. The HFESR spectra acquired at cryogenic temperatures and in the broad frequency range of 92 to 369 GHz revealed the presence of a single high-spin S=5/2 Fe^{III} of axial symmetry in the bulk phase of β-hematin [4]. In this work, we extend our spectroscopic studies to the natural malarial pigment, hemozoin.

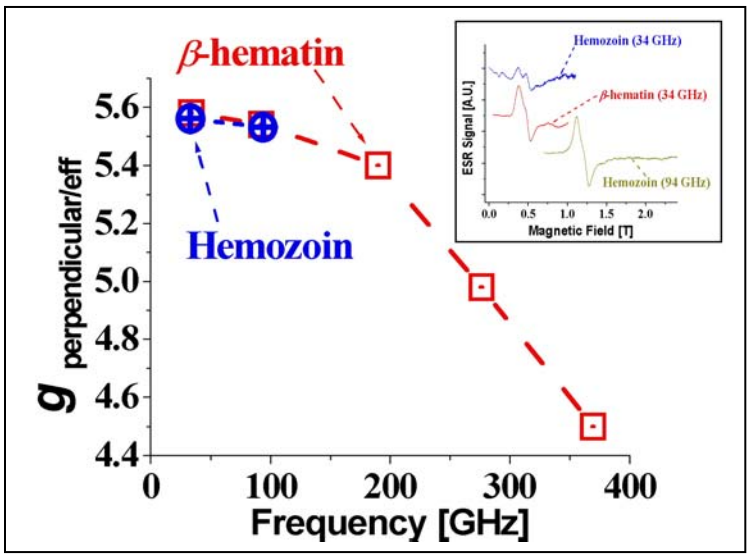

Fig. 1. The values of $g_{perpendicular/eff}$ for hemozoin (blue circles) and β-hematin (red squares) as a function of microwave frequency. Inset: Low-field portions of ESR spectra acquired at 35 GHz for hemozoin and β-hematin and at 94 GHz for hemozoin.

The ESR spectra were acquired at cryogenic temperatures from the minute amounts of hemozoin inserted into the single-mode TE_{011} cylindrical cavities of the 34 GHz Bruker EleXsys (EPFL, Lausanne) and 94 GHz Bruker EleXsys (NHMFL, Tallahassee), respectively. Similarly to our observations for β-hematin, the complex low-field ESR spectra previously observed for hemozoin [5] have been significantly clarified. The distinctive spectroscopic features comprising the perpendicular and parallel spectral components of the high spin Fe^{III} (S=5/2) of axial symmetry have been observed. The derived values for the spectroscopic factor, $g_{perpendicular/eff}$, as a function of microwave frequency for hemozoin and β-hematin are shown in Fig.1. Two values of $g_{perpendicular/eff}$ obtained for hemozoin at 34 and 94 GHz are in good agreement with the set of $g_{perpendicular/eff}$ values measured for β-hematin.

Thus, our findings strongly point to the existence of the high-spin S=5/2 Fe^{III} of axial symmetry also in the bulk phase of hemozoin.

Acknowledgements

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References

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