

Electron paramagnetic resonance of nanocrystalline manganese-incorporated bronze titanium dioxide

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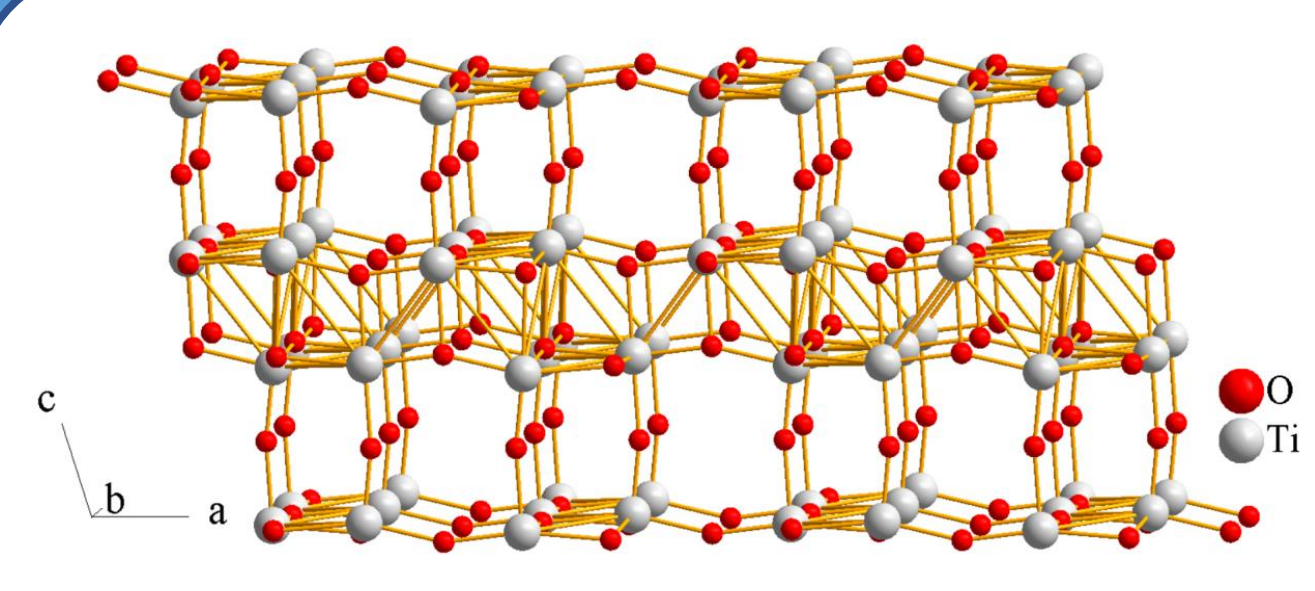
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Relevance

The needs of modern technology for more advanced electrochemical energy storage devices are steadily growing, so the search for both new materials for them and to improve the characteristics of existing materials are very relevant. Currently, titanium dioxide (TiO_2) is considered as one of the possible materials for electrodes of electrochemical energy storage devices. However, this material has one significant drawback - low electrical conductivity. Last research have shown [see for example : W. Zhang *et al. Power Sources*. 2015. V. 276. P. 39], that some electrochemical characteristics of titanium dioxide are noticeably improved when certain ions of the iron group are introduced into it.

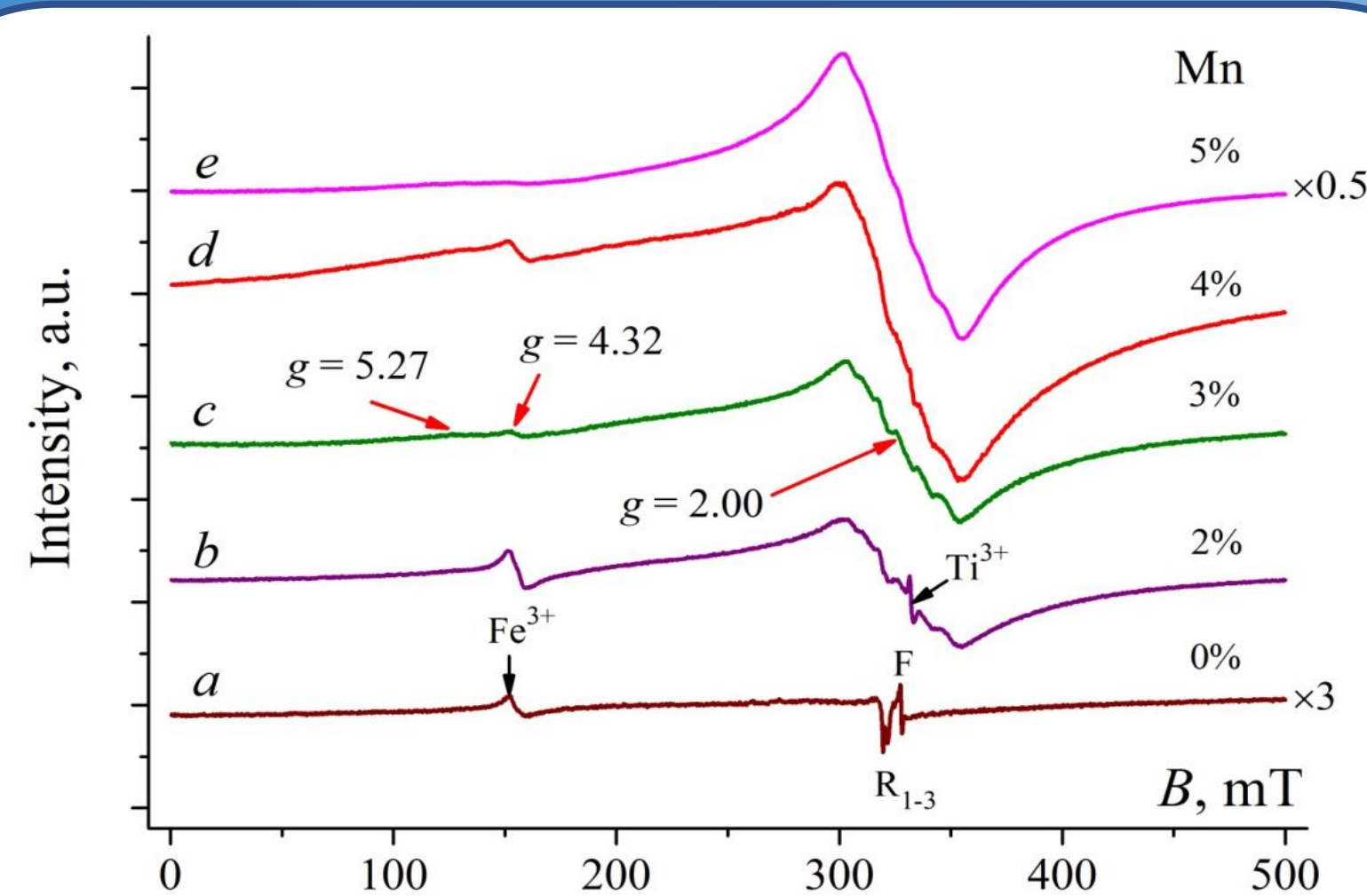
Objects

Titanium dioxide nanoparticles with the structure of bronze $\text{TiO}_2(\text{B})$ co-doped with manganese and fluorine/nitrogen ions. The samples were synthesized in the Laboratory of Functional and Electrochemically Active Materials of the Institute of Chemistry, Far East Branch, Russian Academy of Sciences.



Crystal structure of $\text{TiO}_2(\text{B})$

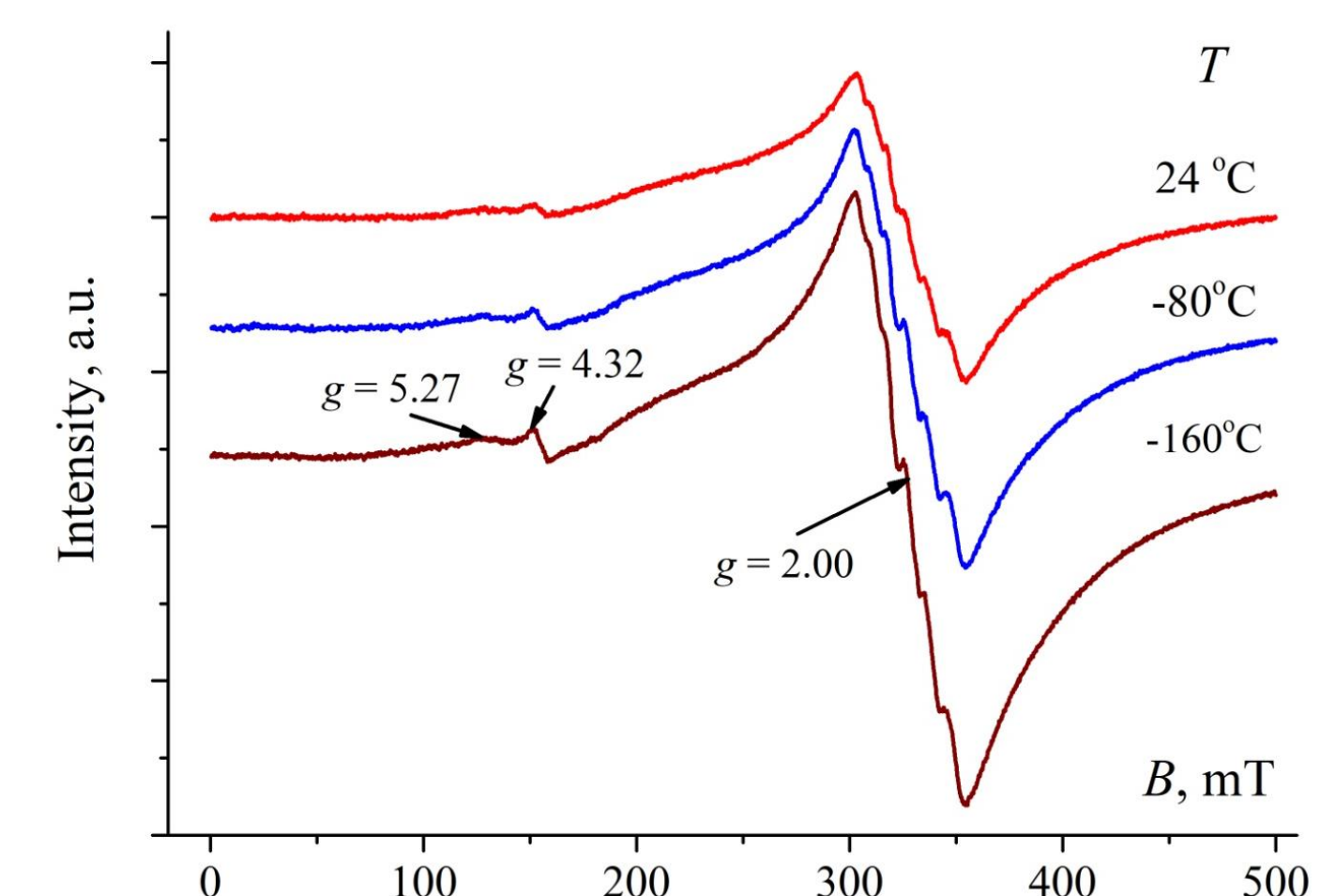
EPR spectrum in the X-band



EPR spectra of undoped (a) and doped with different amounts of manganese (b-e) $\text{TiO}_2(\text{B})$ powders in the X-band at 22°C

EPR spectra of $\text{TiO}_2(\text{B})\text{:Mn}$ powders in the X-band

- 1) The initial $\text{TiO}_2(\text{B})$ powder contains several weak lines (R_{1-3}) whose g -factors (2.064, 2.056, 2.044) are close to the g -factors of the $\dot{\text{O}}^-$ and $\dot{\text{O}}\text{H}^-$ radicals in titanium dioxide [Yang G *et al. Mater. Chem.* 2010. V. 20. P. 5301].
- 2) The EPR spectra of all manganese-doped samples are dominated by a broad intense component with a weakly expressed sextet structure characterized by the spectroscopic splitting factor $g \sim 2.00$.
- 3) The EPR spectra of doped samples also contain a broad low-intensity component with $g \sim 5.27$ and a line with $g \sim 4.32$.



EPR spectra of $\text{TiO}_2(\text{B})$ powder doped with ~3% manganese at various temperatures

Manganese in $\text{TiO}_2(\text{B})$

Mn^{2+} , $3d^5$
 $S=5/2$, $I=5/2$

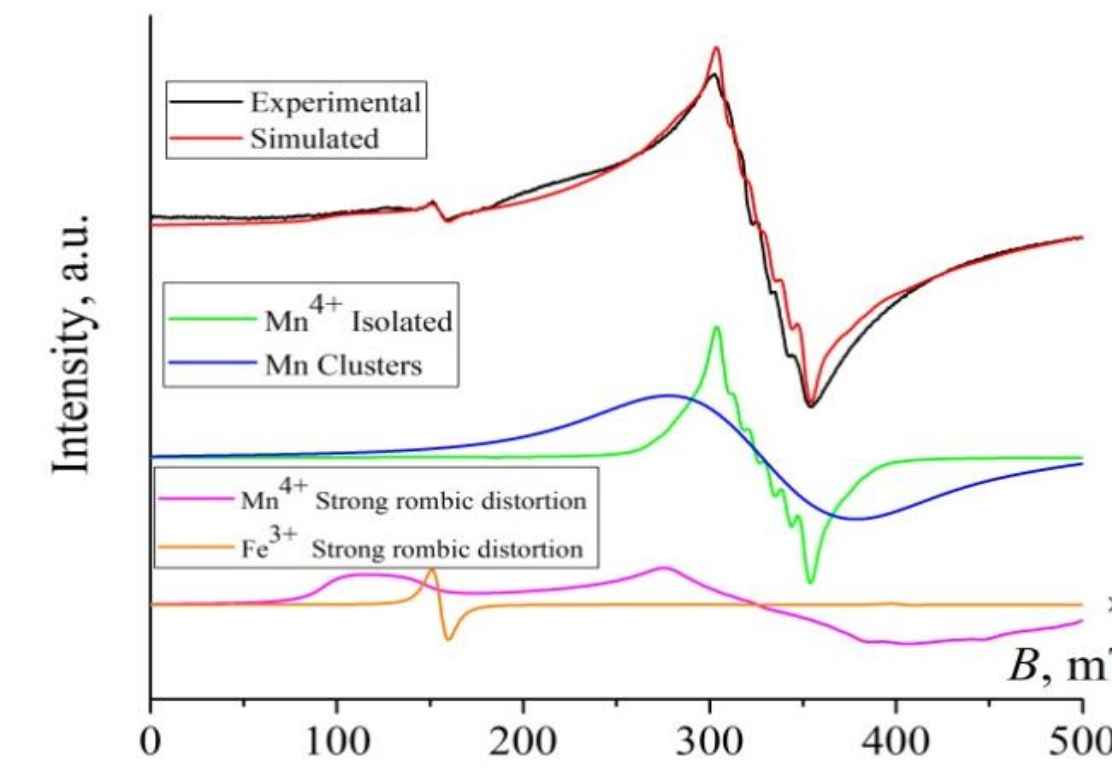
Mn^{3+} , $3d^4$
 $S=2$, $I=5/2$

Mn^{4+} , $3d^3$
 $S=3/2$, $I=5/2$

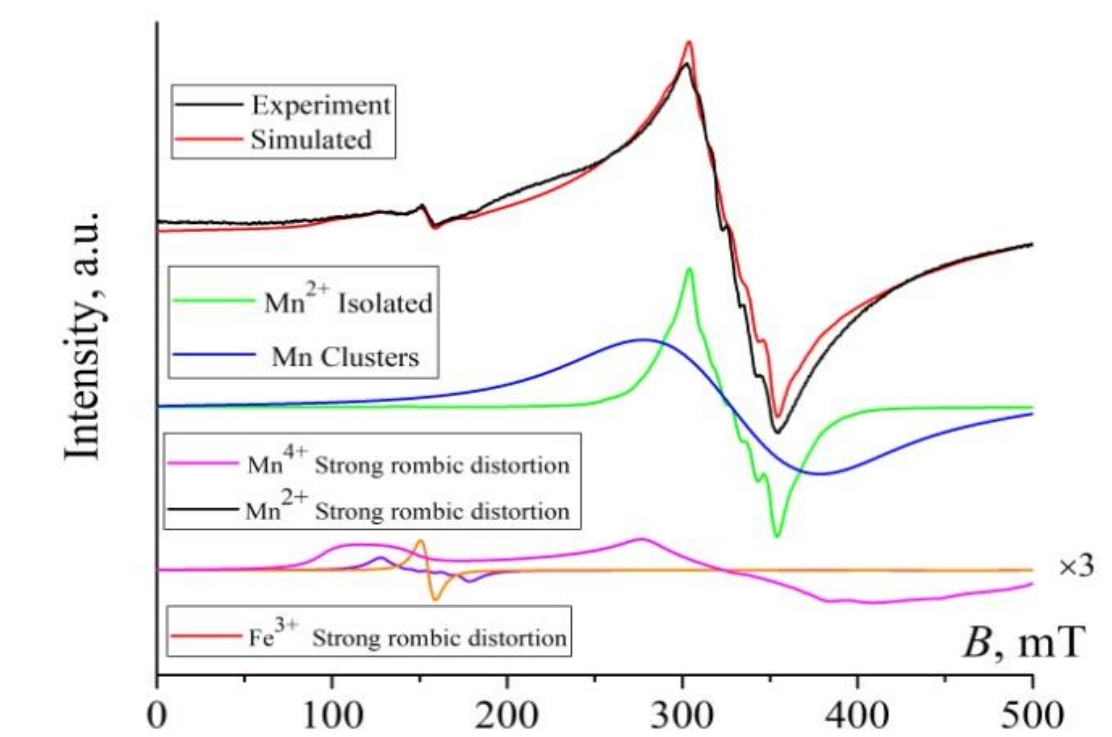
Not observed at room temperature

The main line of the EPR spectrum of the $\text{TiO}_2(\text{B})\text{:Mn}$ powder can belong to a) Mn^{2+} , b) Mn^{4+} , or c) be a combination of resonances on these ions.

Variants of Approximation of the Main Component of the EPR Spectrum of $\text{TiO}_2(\text{B})\text{:Mn}$ Powders in the X-band



Approximation of the main component of the spectrum by Mn^{2+} lines

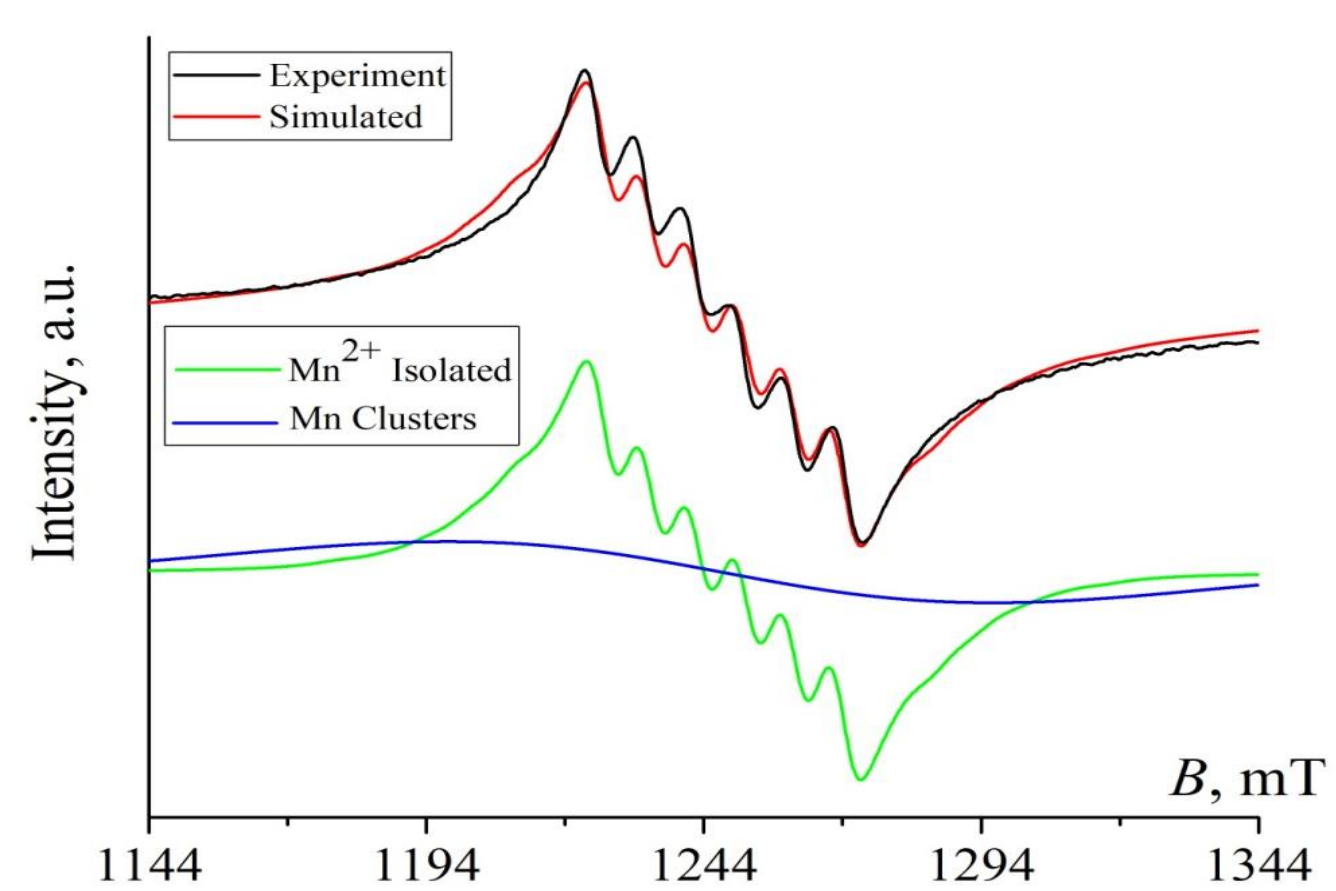


Approximation of the main component of the spectrum by Mn^{4+} lines

EPR spectrum in the Q-band

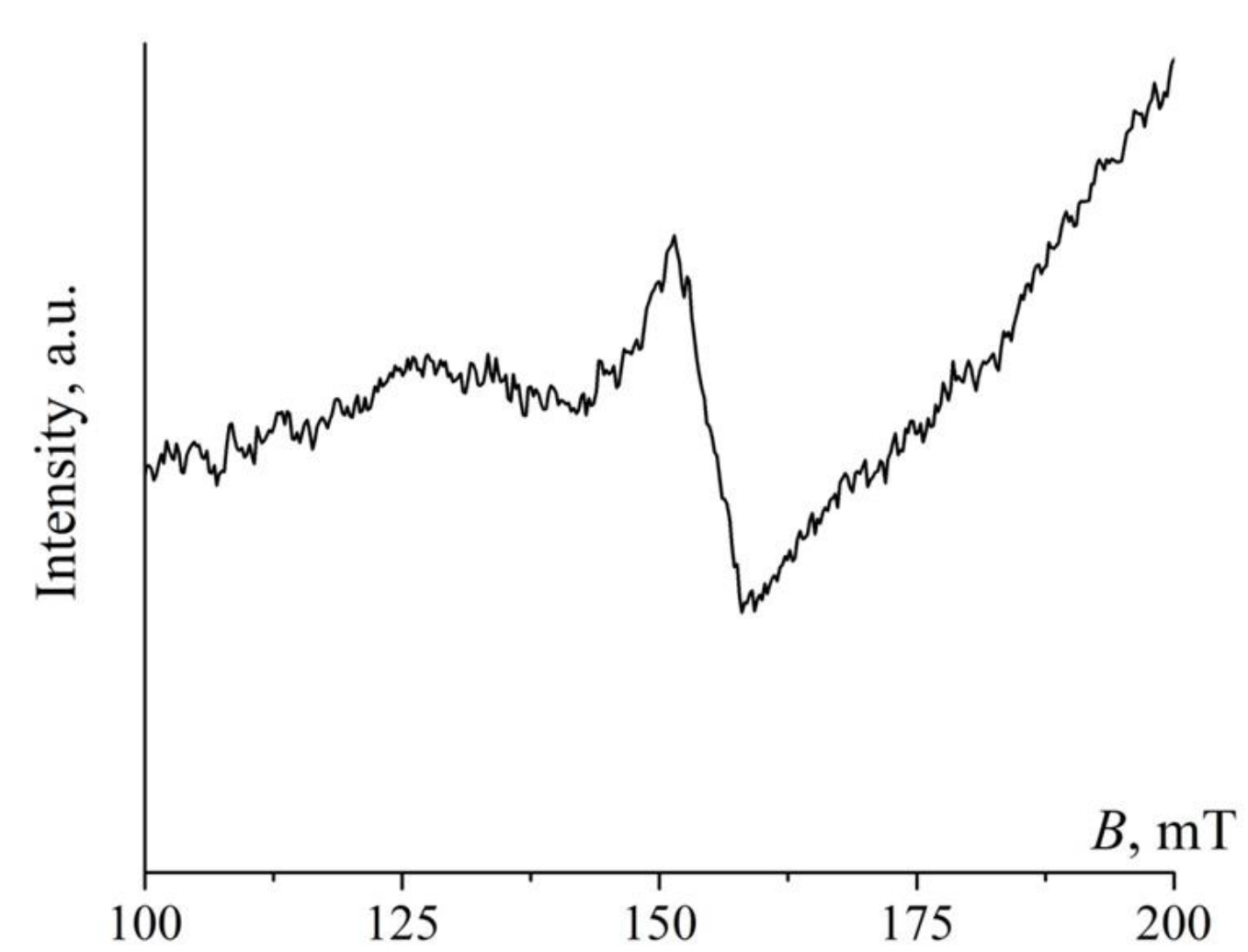
EPR spectra of $\text{TiO}_2(\text{B})\text{:Mn}$ powders in the Q-band

- 1) The sextet structure of the main signal with $g=2.00$ in the Q-band is better resolved than in the X-band. This frequency dependence of the spectrum can be explained by the decrease in the transition to the Q-range of the contributions to the EPR spectrum of the so-called forbidden transitions.
- 2) The experimental value of the hyperfine structure constant of the main signal of the EPR spectrum $A=8.76$ mT. According to the literature [see, for example: Saponjic Z.V. *et al. J. Phys. Chem.* 2006. V. 110. P. 25441] such a value of A is characteristic of the EPR spectra of Mn^{2+} ions (the typical value of A for Mn^{4+} ions is less than 8.1 mT). Consequently, the sextet component of the main resonance belongs to the Mn^{2+} ions.
- 3) The broad structureless component of the main resonance indicates the presence of manganese clusters in the sample, whose 3d electron spins are involved in exchange interactions.



EPR spectra of the $\text{TiO}_2(\text{B})$ powder doped with ~3% manganese at room temperature in the Q-band

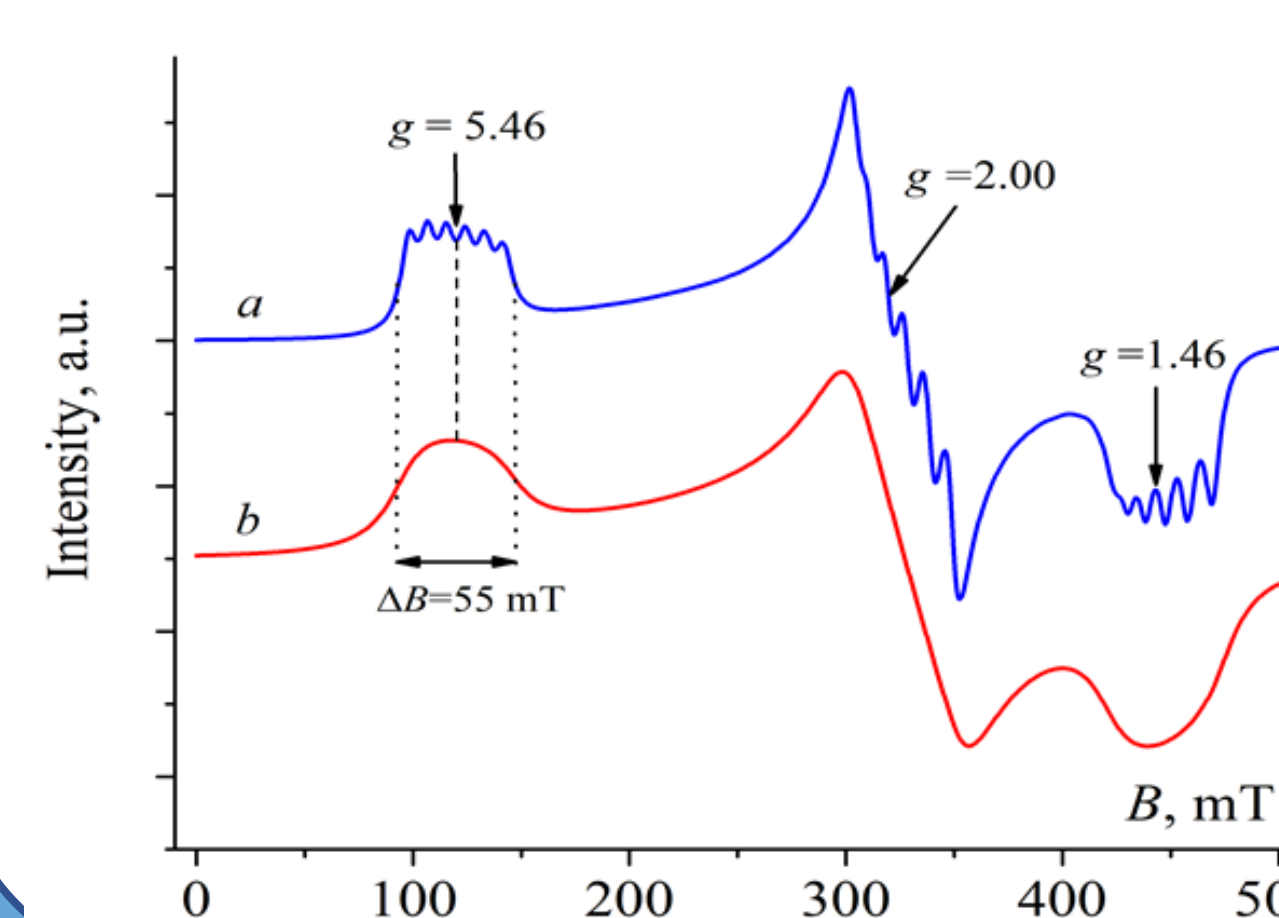
Low-field part of the EPR Spectra in X-band



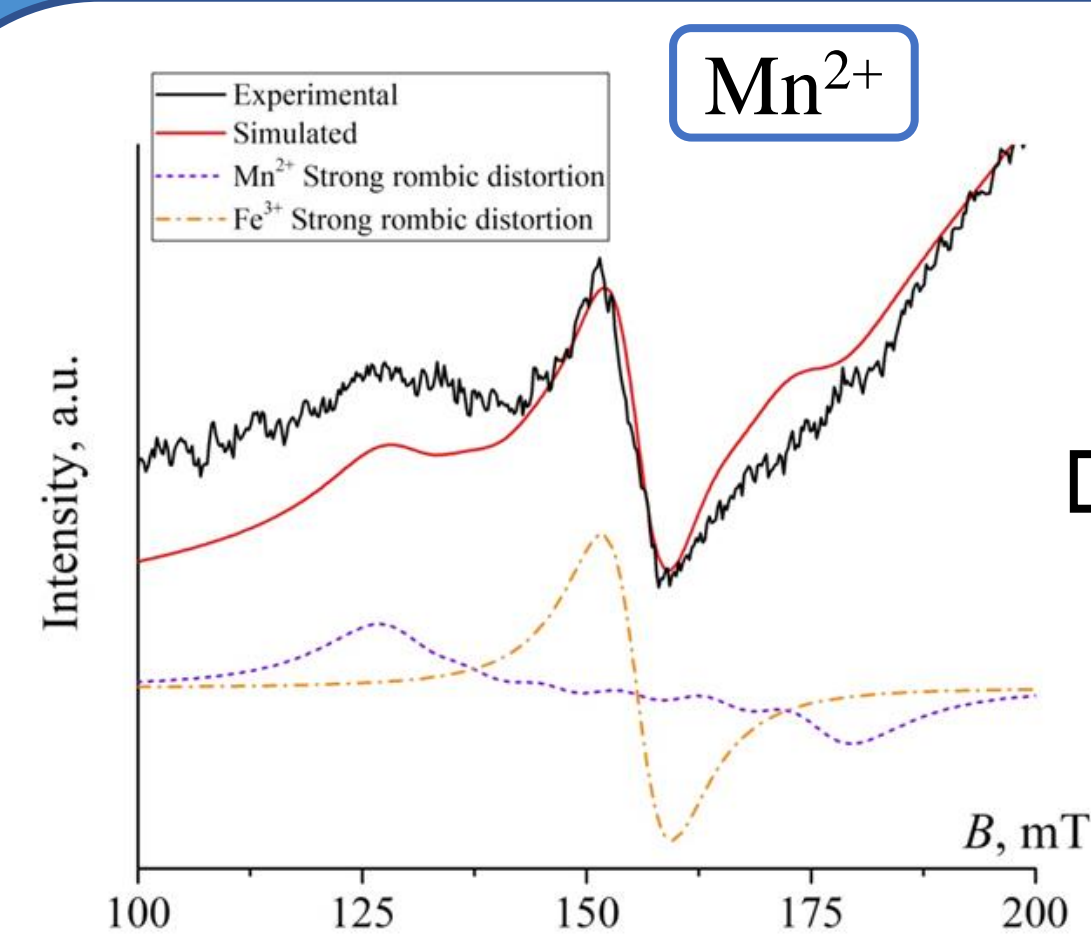
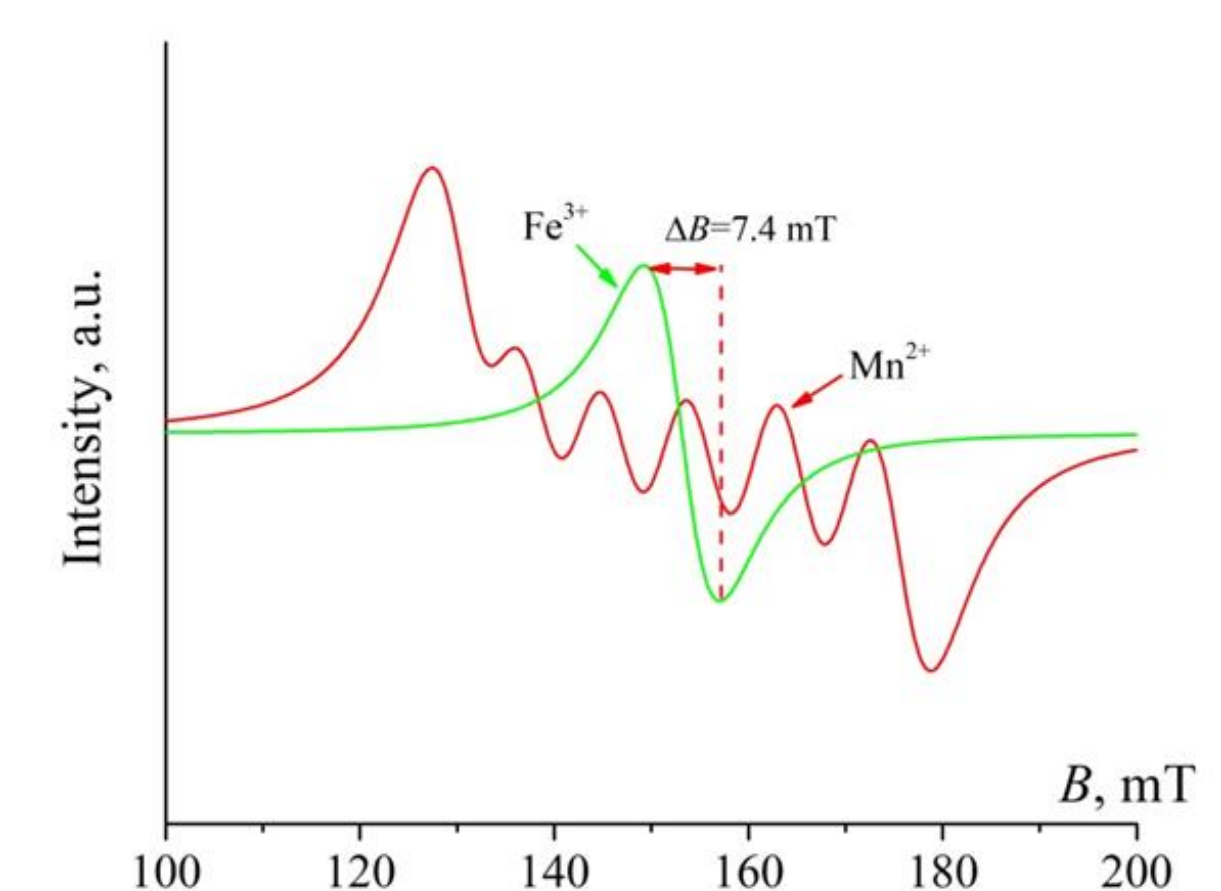
EPR spectra of $\text{TiO}_2(\text{B})$ powder doped with ~3% manganese at room temperature in the X-band

The line with $g \sim 4.32$ is typical for ions with $3d^5$ configuration (Mn^{2+} , Fe^{3+}), which are under the influence of crystal fields with strong rhombic distortion [Castner T. *et al. J. Chem. Phys.* 1960. V. 32. P. 668]. This information suggests the possibility of explaining the entire low-field EPR spectrum of $\text{TiO}_2(\text{B})\text{:Mn}$ in terms of similar concepts of the crystal fields acting on impurity ions.

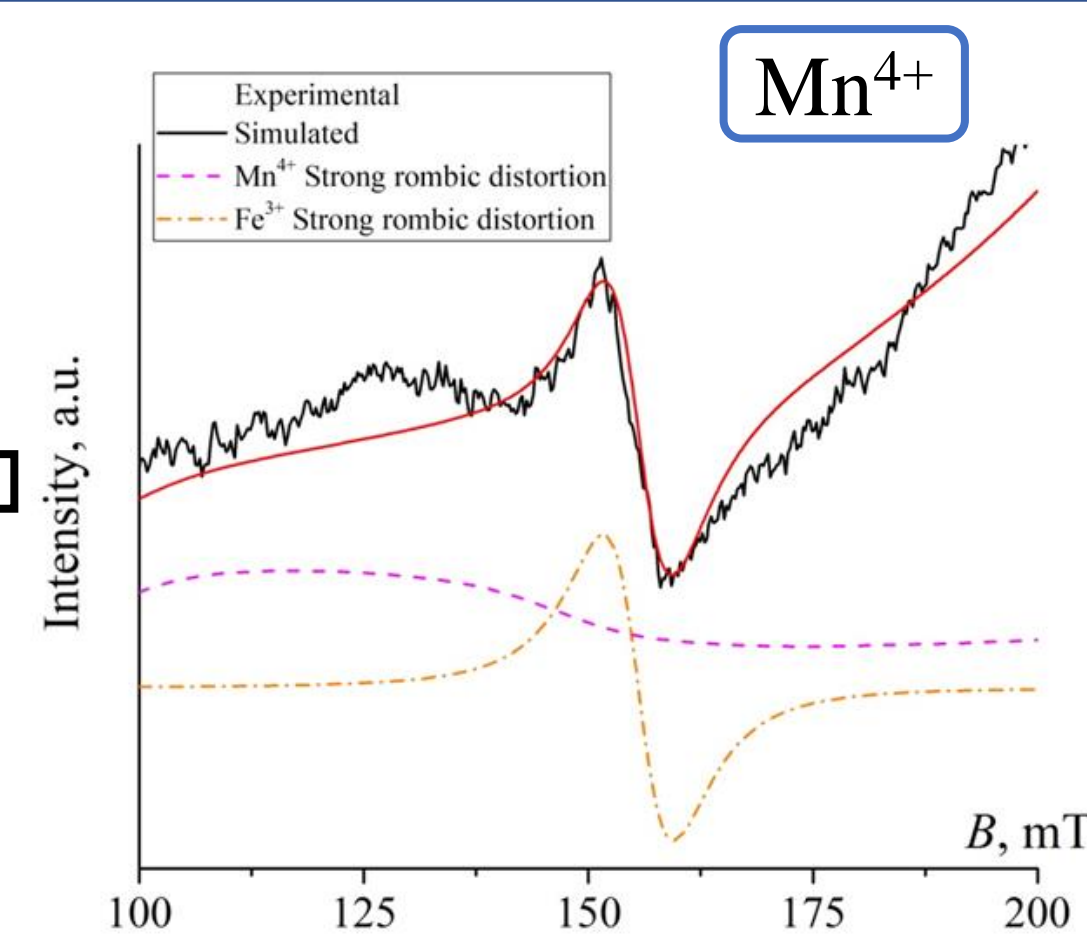
Theoretical EPR spectra of a powder, whose particles contain Mn^{4+} ($3d^3$, $S=3/2$) ions in crystalline fields with strong rhombic distortion



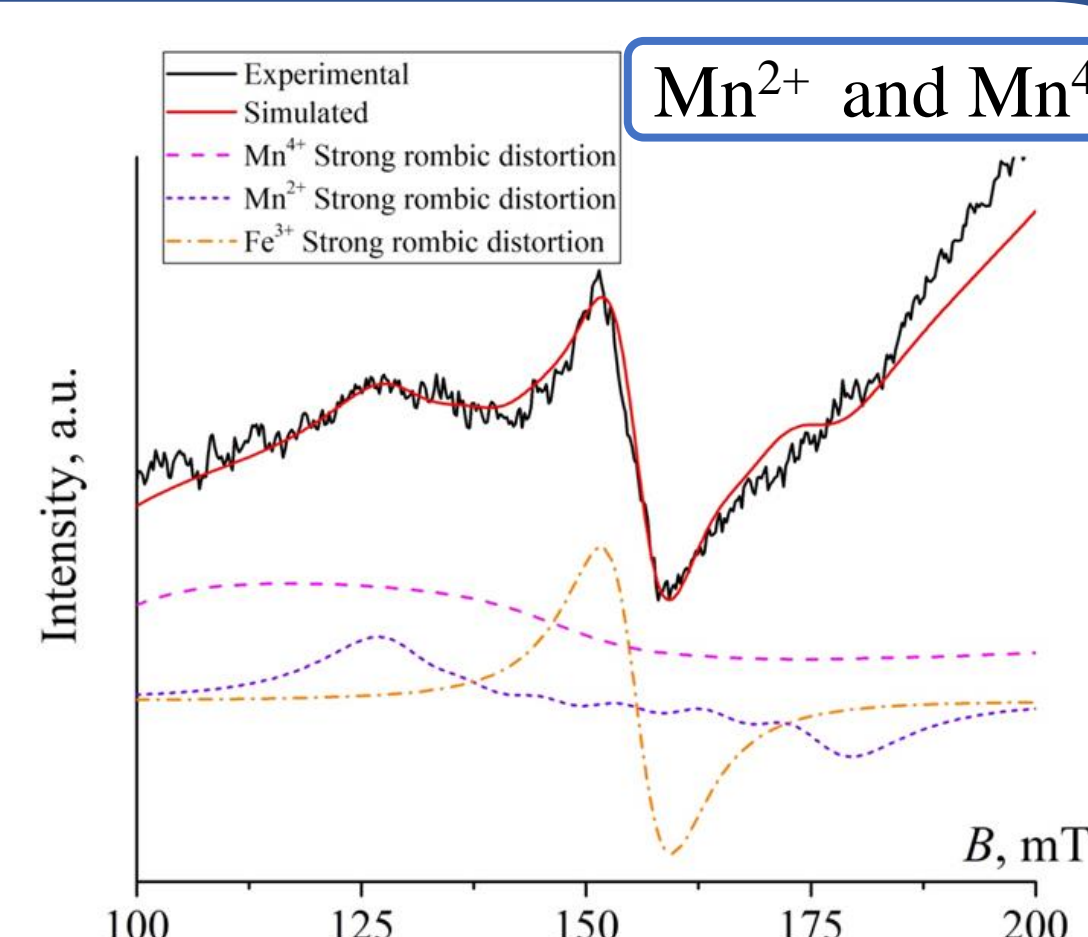
Theoretical EPR spectra of a powder, whose particles contain Mn^{2+} and Fe^{3+} ($3d^5$, $S=5/2$) ions in crystal fields with strong rhombic distortion



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The best approximation of the experimental spectrum in weak fields is achieved at assuming the simultaneous presence of Mn^{2+} and Mn^{4+} ions in the sample

Conclusions

- 1) The data of the analysis of the EPR spectra of $\text{TiO}_2(\text{B})\text{:Mn}$ powders in the Q-band allow us to conclude that the main part of impurity manganese ions is in the Mn^{2+} oxidation state. A small part of them is in crystalline fields with strong rhombic distortion.
- 2) The samples contain clusters of manganese ions, whose 3d electron spins participate in exchange interactions that average the spectra of individual ions.
- 3) In small amounts, the samples also contain Mn^{4+} ions, which are under the influence of crystal fields with strong rhombic distortion.
- 4) Crystalline fields with strong rhombic distortion can exist near the surface and in the interstices of $\text{TiO}_2(\text{B})$ particles.