

Temperature Independent Isotropic EPR Spectra of $[(\text{CH}_3)_4\text{N}]_2\text{MnCl}_4$ and $[(\text{CH}_3)_4\text{N}]_2\text{FeCl}_4$ Single Crystals

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Electron paramagnetic resonance of $[(\text{CH}_3)_4\text{N}]_2\text{MnCl}_4$ and $[(\text{CH}_3)_4\text{N}]_2\text{FeCl}_4$ single crystals was studied between 20 and 400 K. The peak-to-peak derivative linewidths of these crystals seem not to change in this temperature interval and approximately 100 mT for $[(\text{CH}_3)_4\text{N}]_2\text{MnCl}_4$ and ~20 mT for $[(\text{CH}_3)_4\text{N}]_2\text{FeCl}_4$. The spectra were found to be isotropic, with $g = 2.0039$ for $[(\text{CH}_3)_4\text{N}]_2\text{MnCl}_4$ and $g = 2.0042$ for $[(\text{CH}_3)_4\text{N}]_2\text{FeCl}_4$. This temperature independence is attributed to isotropic strong exchange interactions of Mn^{2+} and Fe^{2+} nuclei, and it seems that hindered rotation of the MnCl_4^{2-} and FeCl_4^{2-} tetrahedra does not occur in this temperature interval.

Key words: EPR, Exchange, Peak-to-peak linewidth, Temperature dependence, $[\text{MnCl}_4]^{2-}$, $[\text{FeCl}_4]^{2-}$.

Introduction

Electron paramagnetic resonance on paramagnetic systems yields information on structures, phase transitions and the interaction among the paramagnetic species themselves and surroundings. $[(\text{CH}_3)_4\text{N}]_2\text{MnCl}_4$ (hereafter TMATC-Mn) and $[(\text{CH}_3)_4\text{N}]_2\text{FeCl}_4$ (hereafter TMATC-Fe) exhibit four phases between 292.1 and 173.0 K [1–3] and 286 and 241 K [4, 5], respectively.

In this work we expected that the peak-to-peak derivative linewidth variations of single crystals of these substances with temperature would indicate the above mentioned properties, interactions of the Mn^{2+} and Fe^{2+} ions among themselves and environments, and any kind of mobilities of the $[\text{MnCl}_4]^{2-}$ and $[\text{FeCl}_4]^{2-}$ tetrahedra. Therefore we have undertaken this study on TMATC-Mn and -Fe.

Experimental

The TMATC-Mn and -Fe single crystals were grown by slow evaporation of the saturated aqueous solutions containing in the stoichiometric ratio 2 : 1 $[(\text{CH}_3)_4\text{N}]\text{Cl}$ and

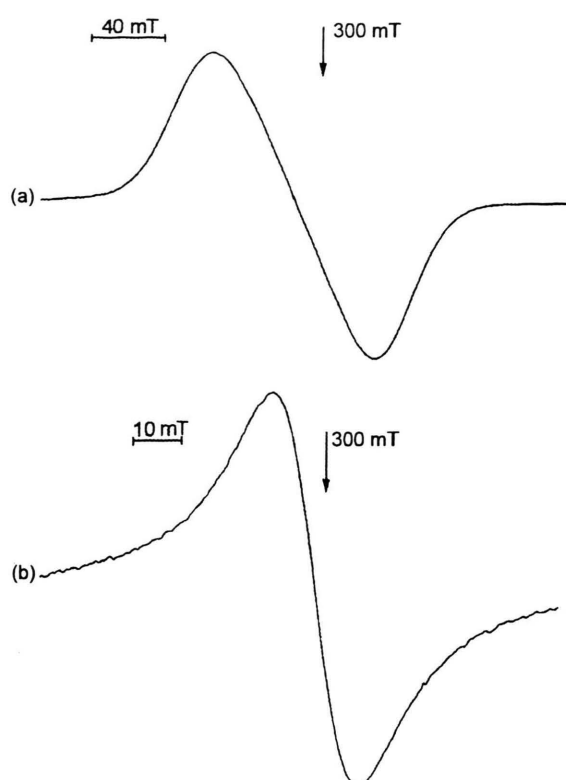


Fig. 1. EPR spectra of a) $[(\text{CH}_3)_4\text{N}]_2\text{MnCl}_4$ and b) $[(\text{CH}_3)_4\text{N}]_2\text{FeCl}_4$ at room temperature.

$\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ for TMATC-Mn and FeCl_2 for TMATC-Fe. The single crystals belong to the A_2BX_4 family. TMATC-Mn exhibits orthorhombic symmetry and TMATC-Fe is monoclinic [1, 5].

The EPR spectra were recorded with a Varian E-109C model X-band spectrometer equipped with a Varian temperature controller, using 100 kHz field modulation and 2 mW microwave power. The values were determined by comparison with a DPPH sample of $g = 2.0036$.

Results and Discussions

The EPR spectra of TMATC-Mn and -Fe are shown in Figure 1. The spectra consist of one line from 400 down to 20 K. The peak-to-peak derivative linewidth is ~100 mT for TMATC-Mn and ~20 mT for TMATC-Fe, and they do not change with temperature between 400 and 20 K within the limits of experimental errors. The

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spectra were also found to be isotropic, and the g values are 2.0039 for TMAFC-Mn, and $g = 2.0042$ for TMAFC-Fe. This temperature independence of the peak-to-peak derivative linewidths and the isotropic behaviour of the

g factors are indications of strong exchange interactions of Mn^{2+} and Fe^{2+} ions among themselves in these respective compounds, and fast mobility of the $[\text{MnCl}_4]^{2-}$ and the $[\text{FeCl}_4]^{2-}$ tetrahedra from 400 down to 20 K [6–9].

- [1] I. Bolesta, Yu Furgala and I. Kityk, *Phase Trans.* **56**, 1 (1996).
- [2] H. Shimizu, N. Abe, N. Yasuda, S. Fujimoto, S. Sawada, and Y. Shiroishi, *Japan Appl. Phys.* **18**, 867 (1979).
- [3] O. G. Vlokh, B. V. Kaminskii, I. I. Polovinko, and S. A. Sveleba, *Izvestiya RAN Ser. Fiz.* **56**, 79 (1992).
- [4] S. Swada, *Phys. Soc. Japan* **2**, 72 (1979).
- [5] H. Shimizu, N. Abe, N. Kokubo, N. Yasuda, and S. Fujimoto, T. Yamaguchi, and S. Swada, *Solid State Commun.* **34**, 363 (1980).
- [6] M. Sharnoff and C. W. Reimann, *J. Chem. Phys.* **43**, 2993 (1965).
- [7] P. W. Anderson and P. R. Weiss, *Rev. Mod. Phys.* **25**, 269 (1953).
- [8] T. G. Castner and M. S. Seehra, *Phys. Rev.* **413**, 38 (1971).
- [9] P. W. Anderson, *J. Phys. Soc. Japan* **9**, 316 (1954).