Temperature Independent Isotropic EPR Spectra of $[(CH_3)_4N]_2MnCl_4$ and $[(CH_3)_4N]_2FeCl_4$ Single Crystals

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Electron paramagnetic resonance of $[(CH_3)_4N]_2MnCl_4$ and $[(CH_3)_4N]_2FeCl_4$ 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 $[(CH_3)_4N]_2MnCl_4$ and ~20 mT for $[(CH_3)_4N]_2FeCl_4$. The spectra were found to be isotropic, with $g = 2.0039$ for $[(CH_3)_4N]_2MnCl_4$ and $g = 2.0042$ for $[(CH_3)_4N]_2FeCl_4$. 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, $[MnCl_4]^{2-}$, $[FeCl_4]^{2-}$.

Introduction

Electron paramagnetic resonance on paramagnetic systems yields information on structures, phase transitions and the interaction among the paramagnetic species themselves and surroundings. $[(CH_3)_4N]_2MnCl_4$ (hereafter TMATC-Mn) and $[(CH_3)_4N]_2FeCl_4$ (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 $[MnCl_4]^{2-}$ and $[FeCl_4]^{2-}$ tedrahedra. 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 $[CH_3]_4NCl$ and $MnCl_2 \cdot 2H_2O$ 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 $g = 2.0036$.

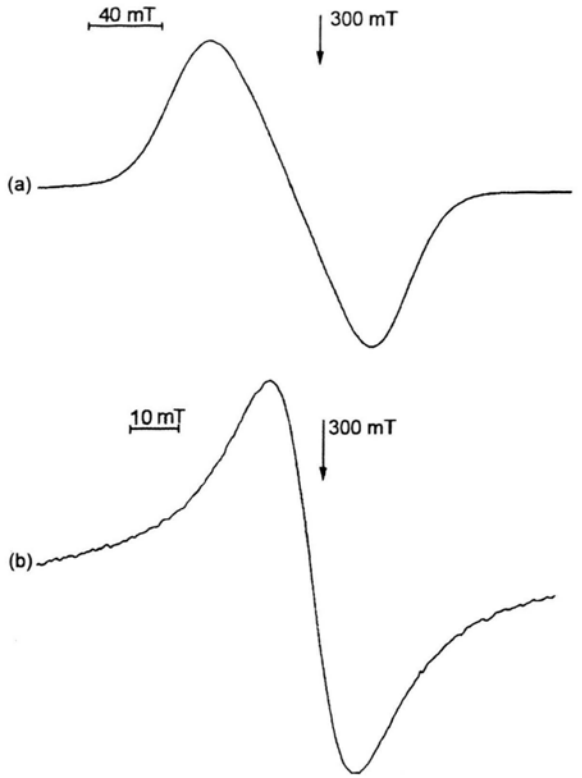

Fig. 1. EPR spectra of a) $[(CH_3)_4N]_2MnCl_4$ and b) $[(CH_3)_4N]_2FeCl_4$ at room temperature.

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 TMATC-Mn, and $g = 2.0042$ for TMATC-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 $[MnCl_4]^{2-}$ and the $[FeCl_4]^{2-}$ tedrahedra 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. Shimuzu, 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).

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