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ESR : EXCHANGE NARROWING IN $TlMnCl_3$

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Mn^{2+} esr linewidth measurements have been carried out in exchange narrowing systems $KMnF_3$, $RbMnF_3$ and MnF_2 and a systematic discrepancy between the experimental and the predictions of the theory in its simplest form has been reported.[2] In this paper, we report a similar discrepancy for the exchange narrowed system $TlMnCl_3$, if the assumed line profile for the line shape function $I(\omega)$ is a truncated Lorentzian. However, better agreement with the experimental linewidth is obtained, if $I(\omega)$ is a truncated double Lorentzian.

$TlMnCl_3$ was prepared by heating ($\simeq$ at $600^\circ C$) a stoichometric mixture of TlCl and $MnCl_2.4H_2O$.[3] ESR experiments for a powder sample of $TlMnCl_3$ were carried out on a conventional esr spectrometer operating in X band with 100 KC modulation.[4] An exchange narrowed signal of linewidth (half width at half maximum) = 20 $\pm$ 1 gauss is observed (Figure 1) over a temperature range from $30^\circ C$ to $-150^\circ C$, suggesting that the transverse relaxation time T_2(= longitudinal relaxation time T_1) is independent of temperature. This exchange narrowed line broadens out and disappears at $-158^\circ C$, suggesting that the system undergoes an antiferromagnetic transition.[3]

The esr linewidth for an exchange narrowed system is calculated using the moment method developed by Van Vleck[5,6] and the linear response theory by Anderson and Weiss.[7] Due to the computational difficulties involved in calculating the moments beyond M_4, one assumes a line profile for $I(\omega)$, for the experimentally observed lineshape whose linewidth is characterised by the available moments. We find that if $I(\omega)$ is a truncated Lorentzian (TL), the linewidth calculated is much less than the experimental value.[2] However, the linewidth can be calculated assuming different line profiles[1] for $I(\omega)$. For the gaussian Lorentzian (GL), the Truncated Double Lorentzian (TDL) and the Gaussian Double Lorentzian (GDL) line shapes, the linewidths (δ) are given as follows:

$$\delta^{GL} = \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \frac{M_2^{3/2}}{M_4^{\frac{1}{2}}} \qquad (1)$$

$$\delta^{TDL} = \frac{2\sqrt{3}}{\pi} \frac{M_6^{\frac{1}{2}} M_2^{2}}{M_4^{3/2}} \frac{B(\eta)^{3/2}}{C(\eta)^{\frac{1}{2}} A(\eta)^2} \qquad (2)$$

$$\delta^{GDL} = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{M_6^{\frac{1}{2}} M_2^{2}}{M_4^{3/2}} \frac{b(\eta)^{3/2}}{c(\eta)^{\frac{1}{2}} a(\eta)^2} \qquad (3)$$

where the symbols have been defined by equations (3.1) to (3.10) of reference 1.

The moments M_2 and M_4 were calculated with an untruncated dipolar Hamiltonian and the isotropic exchange interaction, for the powder case. An approximate expression for M_6 was used from reference 1. $M_2 = 1.6967 \times 10^{21}$ sec^{-2}; $M_4 = 9.8825 \times 10^{48}$ sec^{-4}; $M_6 = 1.1096 \times 10^{76}$ sec^{-6}, with $a = 5.02$ Å; $\omega_{ex} = 5.09 \times 10^{12}$ sec^{-1}; $T_N = 115^{\circ}$K where the symbols have their usual meaning. The calculated linewidths for different line profiles and the deviation from the experimental value are given in the table below:

Line Shape	Calculated linewidth δ_{cal} (gauss)	Ratio $\frac{\delta_{expt}}{\delta_{cal}}$
TL	3.63	5.52
GL	5.01	3.99
GDL	13.20	1.52
TDL	18.76	1.07

The fourier transform of the lineshape function $I(\omega)$, is the relaxation function $\phi(t)$ and this is related to the correlation function of the full local field $\psi(t)$[1]. In the large exchange limit, $\psi(t)$ decays in a time of the order of $\hbar/J$. It can be shown that for $t \gg \hbar/J$,

$$\phi(t) \simeq \exp\left[-\langle\omega(0)^2\rangle t \int_0^\infty \psi(\tau)\,d\tau\right] \qquad (4)$$

where J is the exchange constant. Since $\phi(t)$ is exponential except near $t = 0$, the central portion of $I(\omega)$ is Lorentzian with a width $\delta = \langle\omega(0)^2\rangle \int \psi(t)dt$ and so δ is proportional to the area under the curve $\psi(t)$ vs t. $\psi(t)$ can be evaluated for different line profiles, by taking the fourier transform of $I(\omega)$ and using the expression (4). It can be shown that for different line profiles $I(\omega)$, the curve $\psi(t)$ vs t follows the gaussian shape for small values of t, whereas it deviates from gaussian form differently for large values of t. So, for the TDL line shape which predicts a linewidth closer to the experimental value and has the largest area under the curve $\psi(t)$ vs t, $\psi(t)$ falls off less rapidly than

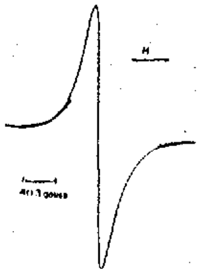

Fig. 1 Exchange narrowed ESR line of Mn^{2+} in $TlMnCl_3$ at room temperature (24°C). The kink at the centre of the line is due to DPPH.

the gaussian form especially for large values of t. Since $\psi(t)$ is the sum of both auto correlation functions and pair correlation functions of the full local field[1], we feel that this deviation of $\psi(t)$, for large values of t arises due to an additional contribution coming from pair correlation functions in the presence of exchange interactions.

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