

ANOMALOUS FREQUENCY-DEPENDENCE OF THE EPR LINEWIDTH IN THE  
ONE-DIMENSIONAL PARAMAGNET TETRA-METHYL-AMMONIUM-MANGANESE-CHLORIDE (TMMC)

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(Received 21 June 1979 by B. Mühlischlegel)

Frequency-dependent EPR experiments have been performed on TMMC with the magnetic field perpendicular to the chain axis. The frequency dependence of the linewidth differs considerably from the normal behaviour found in three-dimensional (3D) paramagnets. The frequency dependence of the linewidth can be explained with a mode-coupling theory. The dynamic shifts have been inferred from the experimental data.

## 1. INTRODUCTION

IT IS WELL KNOWN by now that the dimensionality of the magnetic interactions is extremely important for the dynamical properties of paramagnets [1]. At high temperatures this becomes very apparent for the long-wavelength modes. The expected hydrodynamic behaviour of these correlations depends heavily on the dimensionality. The long-wavelength correlations dominate the spectral functions which are observed in an EPR or NMR experiment in these low-dimensional materials [1, 2]. Magnetic resonance in paramagnets is an excellent example of motional narrowing and is referred to as exchange narrowing. In 3D systems one deals with a weak-coupling case. The main features of such a situation are a Lorentzian lineshape and very effective narrowing. An important aspect of the weak coupling approximation is that the correlation function describing the narrowing (the "local correlation function") is being propagated in time by the bath Hamiltonian (in this case: the Heisenberg interaction) only and not also by the interaction Hamiltonian (in this case: the dipole-dipole interaction between the electronic spins). The local correlation function is a pure Heisenberg correlation function within the weak-coupling approach. For 1D paramagnets the simple weak-coupling approach cannot be used any longer to explain the magnetic resonance. The Kubo and Tomita theory [3] can be classified as a sophisticated weak-coupling approach. This theory can be used to describe the normal EPR resonance in paramagnets of any dimensionality.

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Recently it has been demonstrated that in 1D systems the exchange narrowing is so ineffective that a remnant of the dipolar spectrum can be found and the first observation of such a satellite was reported in the same study [4]. An interesting aspect of these additional resonance is that the theory of Kubo and Tomita fails completely in describing these new resonances. An extensive mode-coupling calculation has shown that the mode-coupling can be used to describe all magnetic-resonance phenomena of low-dimensional paramagnets including the satellites [2]. It is the purpose of this paper to show that the mode-coupling is also superior to the Kubo and Tomita theory in the description of the normal EPR resonance.

An important experimental tool for the study of the long-wavelength dynamics of 1D paramagnets is the study of the frequency dependence of the EPR linewidths and linepositions. Using this technique the present authors have found very clear evidence for spin diffusion of some four-spin correlation functions [5]. This experiment was performed with the external magnetic field making an angle of  $54.7^\circ$  ("magic angle") with the chain axis of the 1D paramagnet. Only at this orientation a Lorentzian lineshape is observed and an interpretation with the help of a weak-coupling approach is possible. The frequency dependence of the linewidth at other orientations is also interesting but less simple to interpret. It has been pointed out however that the mode-coupling theory and the Kubo and Tomita theory predicts very different results for the frequency dependence of the EPR linewidth with the magnetic field making an angle of  $90^\circ$  with the chain axis ( $\theta = 90^\circ$ ) [2]. The orientation  $\theta = 0^\circ$  is less

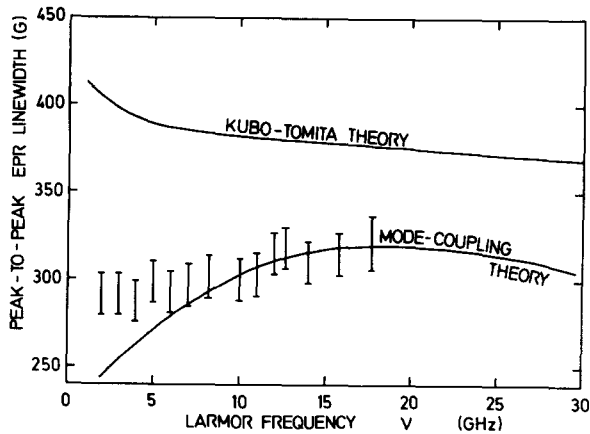


Fig. 1. EPR linewidth of TMMC as a function of microwave frequency with the magnetic field perpendicular to the chain axis. The drawn curves refer to calculated linewidths.

interesting from our standpoint because no frequency dependence is expected in this case. The difference between the mode coupling and the Kubo and Tomita theory for the  $\theta = 90^\circ$  orientation can be understood readily. The broadening interaction, for instance the dipolar coupling between the spins, can be partitioned in secular and non-secular contributions. The local correlation function determining the spectrum will also have secular and non-secular contributions. If the evolution operator of this local correlation function does not contain the broadening mechanism, the introduction of the non-secular terms will always give rise to an extra broadening. These non-secular contributions are dependent on the Larmor frequency  $\omega_L$ , and the experimentalist can reduce the influence of the non-secular terms by increasing  $\omega_L$ . When  $\omega_L$  is very large the non-secular terms can be neglected. In cubic paramagnets this effect is known as the "10/3 effect". In the Kubo and Tomita theory the evolution operator of the local correlation function does not contain the broadening mechanism and for that reason the non-secular terms will always give rise to a "normal" dependence on the Larmor frequency. In the mode-coupling theory the local correlation function (the "memory function") is propagated by a much more complicated evolution operator. The mode-coupling theory takes the dipole-dipole interaction into account to infinite order due to a summation of an infinite subset of diagrams. The evolution operator of the local correlation function does contain the dipolar interaction in the mode-coupling theory. In such a theory the influence of the introduction of the non-secular terms is much more difficult to predict because in addition to the normal extension of the local correlation function on introducing the non-secular terms there is the change of evolution operators. A more effective decay of the local correlation function is

caused since an extra decay channel has been introduced. This effect opposes the normal extension of the local correlation function and no a priori prediction is possible concerning the influence of the non-secular terms. A change in  $\omega_L$  effects the non-secular contribution to the local correlation function but also influences the evolution operators of the secular and non-secular contribution to the local correlation function. This indicates that in 1D paramagnets an anomalous frequency dependence of the linewidth is expected for orientations of the magnetic field where both secular and non-secular terms contribute substantially to the linewidth. For this reason the  $\theta = 90^\circ$  orientation is very suitable for the search for an anomalous frequency dependence. The predicted anomalous frequency dependence was referred to as the "inverse 10/3 effect" [2].

## 2. EXPERIMENTAL RESULTS

We have performed EPR experiments on TMMC (tetra-methyl-ammonium-manganese-chloride) in the frequency range  $\nu = 2-18$  GHz at room-temperature with  $\theta = 90^\circ$ . For the experimental details on the helix-type spectrometer we refer to [6]. In Fig. 1 we present the results of the linewidths. It is clear that indeed an anomalous frequency dependence is observed. The frequency dependence deviates substantially from a monotonous decrease of linewidth as a function of increasing Larmor frequency. To amplify this anomalous dependence we have calculated the frequency dependence with the help of the Kubo and Tomita theory [3] and with the help of the mode-coupling as developed by one of us [2]. In principle both theories do not contain any adjustable parameter, so the linewidths can be calculated in an absolute way. However, these absolute linewidths are about 80% too large compared to experiment. This discrepancy has been discussed in several places and several possible explanations have been put forward. To circumvent this problem one usually introduces one adjustable parameter. One should realize that only one adjustable parameter is used to explain a wealth of experimental data. The parameter we will use is the one-dimensionality parameter  $\eta$ .

$$\eta^{3/2} = S(S+1) \left( \frac{D}{c^2} \right)^{-1/2} \omega_D^2 \left\{ \sum_{j=1}^{\infty} j^{-3} \right\}^2, \quad (1)$$

in which  $c$  is the lattice parameter and  $\omega_D = g_0^2 \mu_B^2 / c^3 \hbar$ .  $D$  is the spin diffusion coefficient. We have used  $\eta = 3.4$  GHz for the Kubo and Tomita calculation and  $\eta = 3.0$  GHz for the mode-coupling calculation. These values are chosen because for these values the experimental linewidth at  $\theta = 0^\circ$  agrees with experiment for both theories. The calculated frequency-dependent EPR linewidths are shown in Fig. 1, too.

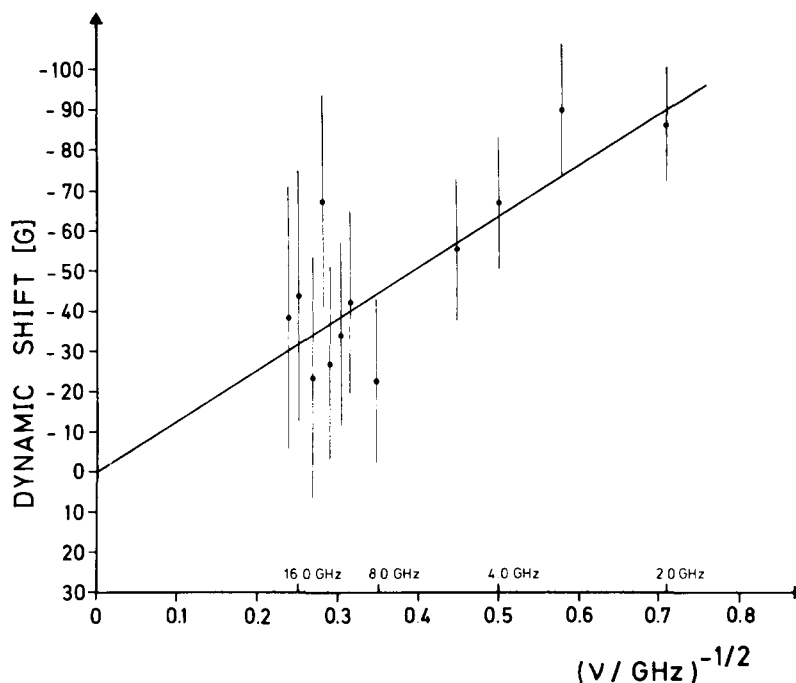


Fig. 2. The dynamic shift of the EPR lineposition of TMMC as a function of microwave frequency with the magnetic field perpendicular to the chain axis. The drawn line refers to a least square fit of the data to equation (2).

In addition we have measured the linepositions of the EPR lines as a function of the Larmor frequency. The dynamic shift is only due to the non-secular terms, and these can be treated with the help of a weak-coupling approach. For this reason both theories give rise to the same frequency dependence of the dynamic shift. The experimental lineposition  $H_{\text{res}}(\nu)$  was fitted to the following relation,

$$H_{\text{res}}(\nu) = \gamma\nu + \delta\nu^{-1/2} \quad (2)$$

A least square fit to the experimental data gives

$$\gamma = 358(1) \times 10^{-9} \text{ Gsec}$$

and

$$\delta = (-0.4 \pm 0.1) \times 10^7 \text{ Gsec}^{-1/2}.$$

The dynamic shift, defined as  $H_{\text{res}}(\nu) - \gamma\nu$ , has been presented in Fig. 2, together with the fit of equation (2). If we would have calculated the linepositions with the help of the mode-coupling the parameter  $\delta$  would have been

$$\delta = -0.2 \times 10^7 \text{ Gsec}^{-1/2}.$$

### 3. DISCUSSION

We have observed an anomalous frequency dependence of the  $\theta = 90^\circ$  EPR linewidth in TMMC for experimental frequencies lying between 2 and 18 GHz. From Fig. 1 it is clear that a conventional weak-coupling-type

approach like the Kubo and Tomita theory would predict a completely different frequency dependence. The result of the mode-coupling theory is much closer to the experimental points, although a somewhat lesser performance is observed in the low-frequency region. The trend of the experimental results is completely in agreement with the mode-coupling result and in disagreement with the Kubo and Tomita result.

The dynamic shift does not differ much in the two theories. The experimental dynamic shift is somewhat larger than the calculated one in the mode-coupling theory. We have no explanation for this, although one must be careful in calculating the lineposition, because there are many static contributions to the linepositions.

One might refer to the observed frequency dependence of the linewidth as to a "reverse 10/3 effect" to indicate a reverse frequency dependence compared to 3D materials. Recently a reverse 10/3 effect has also been found in the linewidths of the dipolar induced satellites in the EPR spectrum of TMMC [8].

*Acknowledgement* -- This work was partly supported by the Deutsche Forschungsgemeinschaft.

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