THE SHAPE OF THE EPR LINE FOR $NiSiF_6 \cdot 6H_2O$*

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(Received April 2, 1979)

The Tanaka and Kondo method of calculating the absorptive part of the magnetic susceptibility was applied for $NiSiF_6 \cdot 6H_2O$. It was shown that the absorption signal comes from the superposition of two signals from domains of the grain with different values of the JD^{-1} ratio.

The problem of fitting the shape of the EPR line for $NiSiF_6 \cdot 6H_2O$ $JD^{-1} < 1$ based on Kubo's linear theory [2] has been the subject of recent investigations [1, 3, 4]. The molecular field approximation was used and the temperature dependence of the spectrum was taken into account [3, 4]. Both methods lead to results different from the actual behaviour of χ'' (see Fig. 1 in [3]). The appearance of the third maximum in the absorptive part of the magnetic susceptibility still has not been explained. It could be possible [3] that in the powder sample the absorption signal comes from the superposition of two signals from domains of grains with different values of the JD^{-1} ratio. We have checked this possibility for some groups of mixing parameters and the result can be formulated as below.

It was shown in [4] that under the asumptions of $JD^{-1} \ll 1$ and $T > T_c$ the absorptive part of the magnetic susceptibility can be described by

$$\chi''(\omega) = \mathrm{th}\,\frac{\beta\omega}{2}\,[I_0(\omega)+I_S(\omega)],$$

where $I_0(\omega)$ describes the line shape:

$$I_0(\omega) = \sum_{\alpha=-S}^{S-1} \tilde{I}_\alpha \sqrt{\frac{\pi}{2\sigma_{\alpha,0}^2}}\, \exp\,[-(\omega_\alpha+\Delta\omega_\alpha+\omega)^2/2\sigma_{\alpha,0}^2],$$

* This work was supported by the Polish Academy of Sciences.

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and

$$I_S(\omega) = \sum_{\alpha=-S}^{S-1} \sum_{\substack{\varrho=-2S+1,\\ \varrho\neq 0}}^{2S-1} I_\alpha \frac{\sigma^2_{\alpha,\varrho}}{4D^2\varrho^2}\,\delta(\omega-\varepsilon_\alpha+2D\varrho)$$

represents the satellite part (see [4]). $\sigma^2_{\alpha,\varrho}$ and $\sigma^1_{\alpha,\varrho}$ denote the parameters of the line shape and these are connected with the first and second momentum of the correlation function $\langle S^+S^-\rangle$. If we assume that there are zones in the grain with different JD^{-1} ratio ($JD^{-1} = p$) e.g., ionic groups in the boundary and in the interior of the grain, we can consider the signal as being the sum of signals from these zones. Let us further assume that the number of ions contributing to the signal is N. The number of boundary-type ions is N_1 and $JD^{-1} = p_1$. The number of interior-type ions is N_2 and $JD^{-1} = p_2$. Certainly $N_1+N_2 = N$. We consider constant $p = 0.078$ determines experimentally as a mean value

$$cp_1+(1-c)p_2 = p,$$

due to c equal $\frac{N_1}{N}$. The fact that the position of the main maximum of χ'' depends strongly on p (Fig. 1) as well as its shape and width (Fig. 2) can justify this hypothesis.

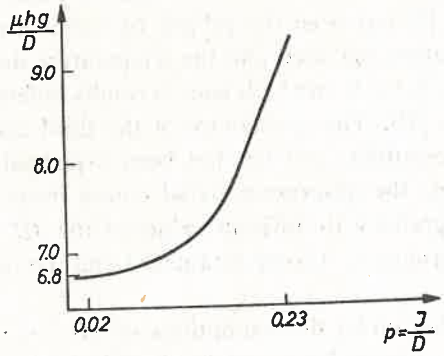

Fig. 1. The position of the main maximum of χ'' as a function of $p = JD^{-1}$ for $t = 25.8$

For the numerical calculations we used the expression:

$$\chi''(p) = \chi''(p_2)+\alpha\chi''(p_1),$$

where α stands for the parameter of mixing and depends linearly on the ratio of the number of ions of both types. Some number of pairs (p_2, p_1) were tested for different α's. Fig. 3 shows the results for (0.05, 0.19) and $\alpha = 0.1, 0.2, 0.333, 0.5$. For $\alpha = 0.5$, the absorption curve becomes wider and the appearance of the third maximum is slightly signalized. For (0.06, 0.2) we also observed a more pronounced change in the shape for $\alpha = 0.5$ (Fig. 4). The most satisfactory results were observed for (0.09, 0.23) with $\alpha = 0.5$ (Fig. 5). The shape of the EPR line is very similar to the data of Svare and Seidel [5] (Fig. 6). The line is wide

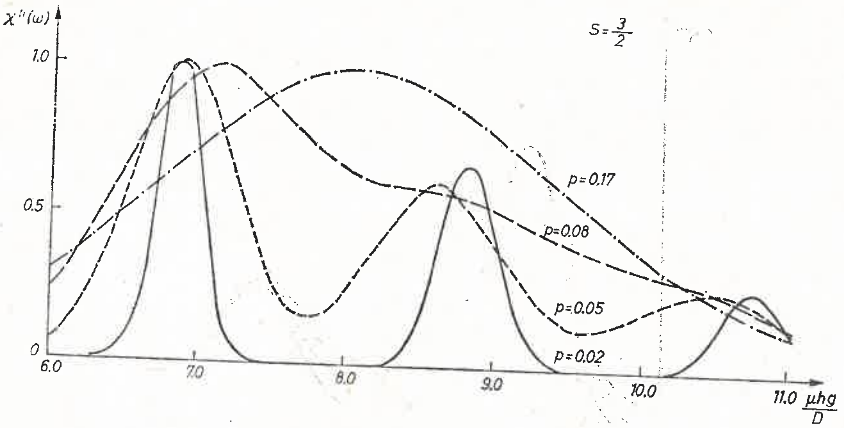

Fig. 2. The line shape as a function of $p = JD^{-1}$ for $S = 3/2$ and $t = 25.8$

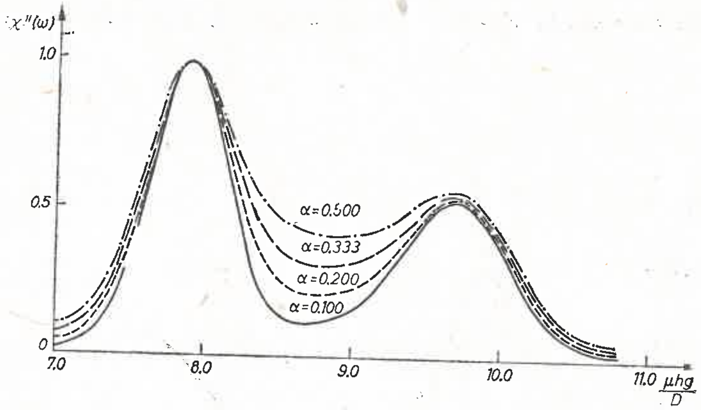

Fig. 3. The line shape for $S = 1$ for different α's and $(p_2, p_1) = (0.05, 0.19)$, $t = 25.8$

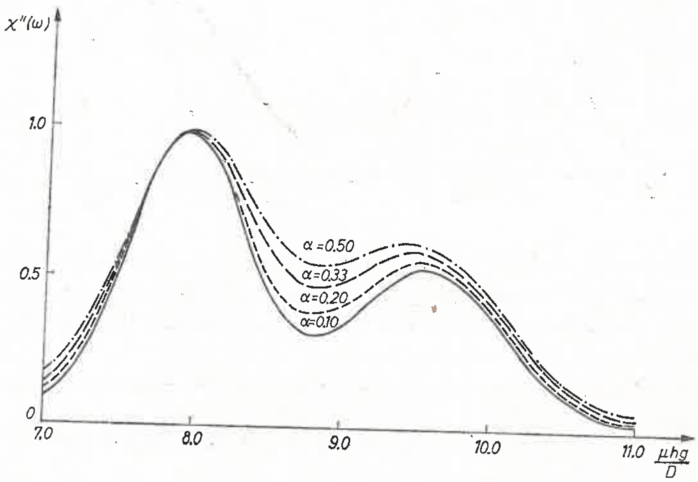

Fig. 4. The line shape for $S = 1$ for different α's and $(p_2, p_1) = (0.06, 0.2)$, $t = 25.8$

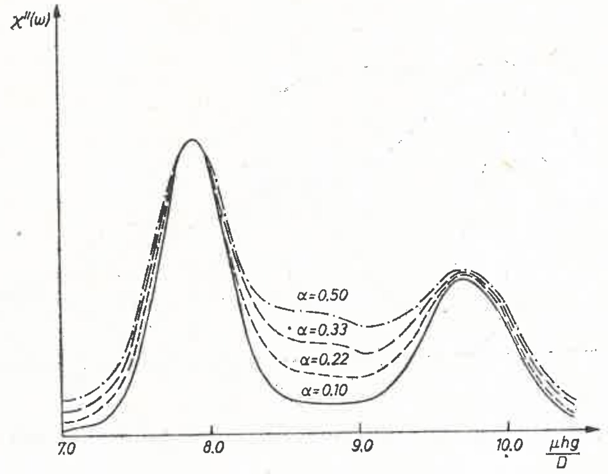

Fig. 5. The line shape for $S = 1$ for different α's and $(p_2, p_1) = (0.09, 0.23)$, $t = 25.8$

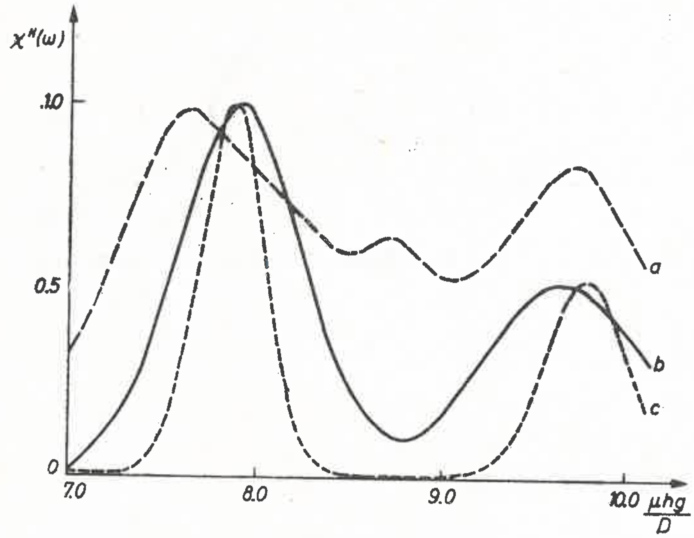

Fig. 6. χ'' as a function of external magnetic field. Curves a, b, c represent the experimental data for $NiSiF_6 \cdot 6H_2O$ obtained by Svare and Seidel [5], the results of Kubo's linear theory within MFA [3, 4] and the results of Tanaka and Kondo approximation [1] respectively

and the small bend appears between the main maxima. All these results refer to a temperature of $t = \frac{kT}{D} = 25.8$ which corresponds to 4.2 K i.e., they concern the double value of the phase transition temperature.

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