STUDY OF COLLOIDAL SUSPENSION OF β-FeOOH PARTICLES

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In the present work it is shown that the Mössbauer spectra of β-FeOOH[1] can be fitted with theoretical spectra computed using the model of ionic spin relaxation of Van der Woude and Dekker[2]. In this model the electronic spins are assumed to flip stochastically between discrete Zeeman levels due to the interaction with local fluctuating field. In order to simplify the calculation we considered the spin of iron to be S = 1/2 though the actual one is 5/2. Since only $S_z = 1/2 \rightarrow S_z = -1/2$ transitions are possible in this case the intensity distribution of Mössbauer peaks depends upon spin flip frequency Ω in the following manner:

$$I(x) = -\frac{1}{\delta}\,\frac{A(1-\eta^2) + G(1+x^2-2\eta x+A^2)}{(1-x^2) + A^2(x-\eta)^2 + AG(x^2+2\eta x+1)} \qquad (1)$$

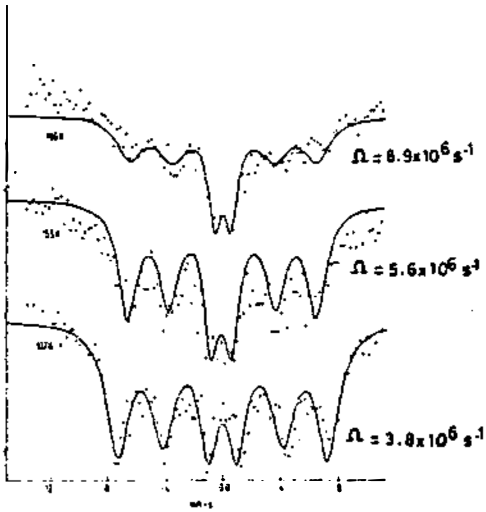
where $A = (\frac{2\Omega}{1-\eta})/\delta$ is the effective spin flip frequency, η magnetic order parameter, $G = 1/\tau\delta$ the relative natural line width, 2δ the energy difference between the two states and $x = v/\delta$. Supposing that $\eta \ll 1$ and $G = 0$ the positions of the peaks are given with

$$x = \pm\left(1 - \frac{A^2}{2}\right)^{1/2} - \frac{A^2\eta}{2(2-A^2)} \quad \text{if} \quad A < 1,4 \quad \text{, and} \qquad (2)$$

$$x = \frac{A^2\eta}{2-A^2} \quad \text{if} \quad A > 1,4 \qquad (3)$$

In the region of slow relaxation rate $A \ll 1$, each nuclear transition corresponds to two lines at $x = \pm 1$ with the intensity $I(\pm 1) = \frac{1}{\Omega}\frac{1-\eta^2}{(1\pm\eta)^2}$ and the width: $2\Gamma = A(1-8\eta)$. Thus, the experimental spectra would have the peaks of equal intensity not taking into account the relative intensity ratio of 4:3:2. The width of peaks is approximately inversely proportional to δ. When A and η are small the two peaks corresponding to $+\delta$ and $-\delta$ are separated by $A\eta/1-A^2$.

For the case that spin flip frequency becomes comparable to δ, more complex spectra are obtained. Two peaks for each nuclear transition are obtained if $\eta < 0,3$ and only one if $\eta > 0,3$. For $\eta = 0$ and $A = 1$ the two peaks appear at $x = \pm 0,7$ and have an intensity of $4/3\delta$ and a width of $\delta\sqrt{2}$. Therefore the inner peaks in spectra are higher and narrower than the outer ones. Increasing Ω, the peaks move



towards $x = -\eta$ and their intensity becomes $I(-\eta) = - \frac{1}{\delta} A/(1-\eta^2)$. The shape of the spectra depends mainly upon Ω, δ, and η. Using the above derivation for the shape of the spectra of ^{57}Fe in β-FeOOH measured in temperature region 77 to 250 K, it is observed that correlation frequencies are comparable with the Larmor frequency. In order to obtain quantitative parameters of Ω, δ, η, a least square computer fit was made. For this purpose we took into account the following parameters: the width of peaks 0.4 mm/s, relative line intensity 4:3:2, separation of the peaks δ_1 = 6.59 mm/s and $\delta_1:\delta_2:\delta_3$ = 1:0'579:0'157 taken from the spectra at 77 K where fluctuation effect can be neglected. By treating the parameters of Ω, η, and scaling factor as free in least square fitting of experimental Mössbauer data to equation (1), the electron spin flip frequencies Ω were obtained as given for some typical spectra in the figure.

The strong temperature dependence of the relaxation frequency can also be interpreted in terms of a fluctuation of the magnetization vector between two easy directions of the superparamagnetic particle: $\nu = \nu_0 \exp -(KV/kT) = \Omega$. The spectra in the region 107-200K can correspond to the condition $\nu \approx \delta$ with the supposition that distribution of frequencies is caused by the distribution of volumes.

Therefore we can conclude that both above relaxation theories lead to a good understanding of the spectra of β-FeOOH. Van der Woude treatment fits well the behaviour of superparamagnetic particles if the atomic spin flipping frequency is identified with τ^{-1}, where τ is the relaxation time of the magnetization vector of the particle.

References

1. D.Hanžel and F.Sevšek, J. de Physique 37 (1976) C6-247
2. F.Van der Woude and A.J.Dekker, Phys. Stat. Sol. 13 (1966) 181