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SPIN RELAXATION EFFECTS IN Fe(NO₃)₃ AND Fe(ClO₄)₃
FROZEN SOLUTIONS AND IN Fe(ClO₄)₃ CRYSTAL HYDRATES

F. SONTHEIMER, D. L. NAGY (*), I. DÉZSI (*), T. LOHNER (*), G. RITTER
D. SEYBOTH and H. WEGENER

Physikalisches Institut der Universität Erlangen-Nürnberg, 8520 Erlangen, BRD

Résumé. — Les spectres Mössbauer de solutions gelées de Fe(NO₃)₃ et de Fe(ClO₄)₃ ainsi que ceux des hydrates cristallisés de Fe(ClO₄)₃, ont été étudiés en l'absence de champ et pour différents champs magnétiques externes allant jusqu'à 80 kG. Toutes ces substances montrent d'importants effets de relaxation. Le temps de relaxation dans les solutions gelées (1) dépend du champ appliqué et est assez long pour des champs forts (∼ 10⁻⁷ s). Dans les hydrates cristallisés (2) le temps de relaxation est indépendant du champ et beaucoup plus courts (∼ 10⁻⁹ s). En l'absence de champ externe, les spectres des hydrates cristallisés montrent que la relaxation n'est pas nettement isotrope ni longitudinale, quoique ce dernier modèle semble un peu meilleur.

Abstract. — Mössbauer spectra of Fe(NO₃)₃ and Fe(ClO₄)₃ frozen solutions and Fe(ClO₄)₃ crystal hydrates have been studied in zero external field and in various magnetic fields up to 80 kG. All these substances show pronounced relaxation effects. The relaxation time in the frozen solutions (1) is found to be field dependent and rather long in high fields (∼ 10⁻⁷ s). In crystal hydrates (2) the relaxation times turn out to be field independent and much shorter (∼ 10⁻⁹ s). The zero field spectra of the crystal hydrates show neither a pronounced isotropic nor longitudinal relaxation, though the latter model seems somewhat better.

Introduction. — Relaxation properties of high-spin Fe³⁺ compounds have been extensively studied by Mössbauer effect in the past few years. Because of the strength of the spin-spin relaxation, the Fe³⁺ ions have to be apart at least about 5 Å to cause an observable effect in the spectrum. This can be attained using crystal hydrates rather than water-free compounds. Further dilution is easily established in frozen solutions. Thus a wide range of relaxation times can be covered.

In the absence of external magnetic fields a general description of Mössbauer spectra exists for the limit of fast relaxation [1].

This is not the case for slow relaxation. The above general model involves too many parameters when an external field is applied. Other models, however, as those of Wegener [2] and van der Woude [3] describe the high-field spectra for fast and slow relaxation respectively.

1. Frozen solutions. — 1.1 Experiment. — Two ferric nitrate solutions were prepared by dissolving Fe(NO₃)₃·9 H₂O (23.3 mg/cm³ natural iron) in distilled water for one absorber and in a mixture of 60 % glycerol and 40 % distilled water for the other. HNO₃ was added to reach a pH value of zero. The ferric perchlorate water solution contained 3.5 mg/cm³ iron enriched to 80 % and had a pH value of zero. This pH value nearly all of the ions exist in the form Fe³⁺·6 H₂O [4]. The solutions were frozen by immersion in liquid N₂. A longitudinal magnetic field was applied.

1.2 Experimental results. — The absorber containing 23.3 mg/cm³ natural iron without glycerol was measured at 78 K and 4.2 K in zero external magnetic field. The result was a broad single line (not Lorentzian) of 2.5 mm/s half width for both temperatures. The Fe(ClO₄)₃ absorber was measured at 4.2 K. It yielded a single line of about the same line width and form. The spectrum of the Fe(NO₃)₃ absorber with 60 % glycerol at 4.2 K and 0 K shows a magnetic field splitting of 580 kG.

The spectra of the absorbers without glycerol with varying magnetic field applied are shown in figures 1 and 2. They show six lines with field dependent broadenings, intensities and positions, indicating relaxation effects.

Spectra of the Fe(NO₃)₃ absorber with glycerol are shown in figure 3. No relaxation effect can be detected. The intensities of the lines change with growing external field according to a Boltzmann population of the six Zeeman levels of the Fe³⁺ high-spin ion which has spin ½.

For all spectra (Fig. 1-3) the extracted quadrupole splitting is zero.

For fields smaller than 15 kG the spectra have also

(*) Central Research Institute for Physics, 1525 Budapest, Hungary.

(*) On leave of absence from the Central Research Institute for Physics, Budapest, Hungary.
FIG. 1. — Mössbauer spectra of Fe(NO₃)₃ frozen solution at 4.2 K. The pH value is 0. Ordinate: relative intensities.

FIG. 3. — Mössbauer spectra of Fe(NO₃)₃ frozen solution with 60 % glycerol at 4.2 K. pH value is 0. Ordinate: relative intensities.

been measured but not plotted here. Down to about 5 kG a magnetic splitting of 580 kG can be recognized.

1.3 DISCUSSION. — The relaxation model of van der Woude [3] implies a frequency $\Omega$ which is a measure for the number of spin flips occurring per unit time. This model allows calculations of Mössbauer spectra for all values of $\Omega$. In this work the model was treated numerically in a computer program. To fit the measured spectra just one parameter, namely $\Omega$, was varied with varying magnetic field. The transmission scales of the theoretical and experimental spectra were adjusted by multiplying the theory with a scale factor computed in least squares fits. For the line width $\Gamma_0$ the line width of the Mössbauer source was inserted.

The fact that the single line spectra measured at 78 K and 4.2 K have the same line width indicates that the main source of atomic spin relaxation is not spin-lattice interaction but rather spin-spin interaction. Spin-spin interaction should be reduced when the spin density is lowered. This is reached when glycerol is added to the solutions at constant iron concentration because it is known that glycerol acts as a glass former [5] which prevents clustering of the magnetic ions. So the well-resolved hyperfine spectra we got for the Fe(NO₃)₃ absorber with 60 % glycerol at 0 K and 4.2 K confirms the assumption of dominating spin-spin interaction. Thus the application of the model by van der Woude seems reasonable. Below 15 kG,
however, the theory gets continuously worse with lowered field. There the interaction energy of the electron shell of Fe$^{3+}$ in the crystal field seems to become comparable with the Zeeman energy of the atomic spin.

Figure 3 shows the fits of the spectra of the Fe(NO$_3$)$_3$ absorber with 60 % glycerol (solid line). For all magnetic fields the best fits are obtained with $\Omega = 0$. Five of the six spectra generated by the six Zeeman levels of the ferric ion can easily be detected in the 20 kG spectrum for example, because for a negative spin the external field is antiparallel to the field at the nucleus while for a positive spin it is parallel to it.

The spectra of figures 1 and 2 were also fitted with the model of van der Woude with only one free parameter $\Omega$ (solid lines). Not surprisingly, they are very similar because in both cases the dominating ionic species is Fe$^{3+} \cdot 6$ H$_2$O.

In every spectrum the outer lines of the spin $-\frac{3}{2}$ and spin $-\frac{1}{2}$ spectra can be found (line 1 and 6 and 2 and 5). The magnetic splitting is 580 kG and 348 kG as expected from the spectra of figure 3. Then the Larmor frequencies of the Mössbauer nucleus in the field of the atomic spin $-\frac{3}{2}$ and $-\frac{1}{2}$ respectively differ by a factor of 348/580. These frequencies have to be related to the relaxation frequency. Thus the spin $-\frac{3}{2}$ spectrum should be stronger affected by relaxation than the spin $-\frac{1}{2}$ spectrum. This is actually the case in the measured spectra. The lines number 2 and 5 are much broader than the lines number 1 and 6.

In the Fe(ClO$_4$)$_3$ frozen solution relaxation times should be longer than in the Fe(NO$_3$)$_3$ frozen solution by a factor of about ten. This is expected from the different iron concentrations assuming a $R^{-3}$ law of spin-spin interaction ($R =$ average distance between two neighboring iron atoms). In figure 4 the relaxation frequencies $\Omega$ extracted from the theoretical fits are plotted against the external magnetic field. The values for the two solutions are of the same order. We conclude that in both solutions clustering of the magnetic iron atoms occurs.

Fig. 5 shows a fit of the 80 kG spectrum of Fe(ClO$_4$)$_3$ with the relaxation time extracted from the 10 kG spectrum. It leads to vanishing lines 2 and 5 and to reduced lines 1 and 6.

The magnetic field dependence of the relaxation time may be explained by an effect discovered by Marup [6]. In Fe(NO$_3$)$_3$, 9 H$_2$O hydrate and frozen solutions be found that the ionic levels of the spins $S_1$ and $S_2$ of two Mössbauer atoms have a different energy splitting when a magnetic field is applied because of different directions of the electric field gradient at spin 1 and spin 2. Simultaneous transitions of two neighboring spins conserving energy in the spin system then become less probable. Consequently the spin-spin relaxation time is increased.

2. Fe(ClO$_4$)$_3$, 6 H$_2$O and Fe(ClO$_4$)$_3$, 9 H$_2$O. — 2.1 The zero-field-spectra. — Mössbauer spectra of most Fe$^{3+}$ crystal hydrates with fast relaxation and zero quadrupole splitting are Y-shaped, they consist of a rather sharp peak at the centre and two considerably wider peaks at the same position.

There exist, however, spectra of different shape. The above description holds only for a longitudinal relaxation [1]. In the case of isotropic relaxation the line shape remains Lorentzian, though the width may increase considerably [1]. Iron ammonium alum NH$_4$Fe(SO$_4$)$_2$·12 H$_2$O is a good example of isotropic relaxation [1].

Fe(ClO$_4$)$_3$, 6 H$_2$O and Fe(ClO$_4$)$_3$, 9 H$_2$O have rather broad absorption lines which seem to be nearly Lorentzians. To check this point, Mössbauer spectra of both compounds have been recorded at various temperatures between 4.2 and 295 K. The absorber thickness was 10 mg Fe/cm$^2$. The spectra were fit both with a longitudinal and an isotropic relaxation model.
The three Lorentzians of the longitudinal model have relaxation broadenings of $(y/2) (3 A_x - A_y)^2$, $(y/2) (A_x - A_y)^2$ and $(y/2) (A_x + A_y)^2$ and intensities of $\frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}$, respectively [1]. Here, $A_x$ and $A_y$ are the hyperfine coupling constants of the excited and ground state respectively and $\gamma$ is a phenomenological relaxation constant having a well-defined physical meaning [1].

In the isotropic model the relaxation broadening of the single Lorentzian is

$$(y/2) (15 A_x^2 - 10 A_x A_y + 3 A_y^2)$$

The results of these fits are collected in the following table:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temp. (K)</th>
<th>Longitudinal model residual linewidth (mm/s)</th>
<th>Isotropic model linewidth (mm/s)</th>
<th>$\gamma$ (s/mm)</th>
<th>$\Delta$Misfit %</th>
<th>Isomer shift (*) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CIO$_4$)$_3$, 6 H$_2$O</td>
<td>4.2</td>
<td>0.65(2)</td>
<td>1.16(1)</td>
<td>0.039(2)</td>
<td>0.09</td>
<td>0.47(1)</td>
</tr>
<tr>
<td></td>
<td>87</td>
<td>0.65(3)</td>
<td>1.26(1)</td>
<td>0.048(3)</td>
<td>0.13</td>
<td>0.41(1)</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>0.69(4)</td>
<td>1.46(3)</td>
<td>0.063(6)</td>
<td>0.21</td>
<td>0.33(1)</td>
</tr>
<tr>
<td></td>
<td>276</td>
<td>0.69(6)</td>
<td>1.51(4)</td>
<td>0.071(9)</td>
<td>0.25</td>
<td>0.31(1)</td>
</tr>
<tr>
<td>Fe(CIO$_4$)$_3$, 9 H$_2$O</td>
<td>4.2</td>
<td>0.77(4)</td>
<td>1.30(1)</td>
<td>0.040(4)</td>
<td>0.07</td>
<td>0.45(1)</td>
</tr>
<tr>
<td></td>
<td>87</td>
<td>0.64(1)</td>
<td>1.17(1)</td>
<td>0.041(2)</td>
<td>0.12</td>
<td>0.40(1)</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>0.47(2)</td>
<td>1.30(2)</td>
<td>0.083(4)</td>
<td>0.76</td>
<td>0.30(1)</td>
</tr>
</tbody>
</table>

(*) With respect to metallic iron at room temperature.

Here, $\Delta$Misfit is the difference of the Misfits introduced by Ruby [7] for the fits with the isotropic and longitudinal model, respectively.

As an example, figure 6 shows the two fits of the 220 K spectrum of the hexahydrate.

Now, the following conclusions can be drawn:

- the spectra show neither a pronounced isotropic nor a pronounced longitudinal relaxation, though especially at higher temperatures — the latter model seems to fit somewhat better. Probably, the relaxation is some intermediate one.
- Both the isomer shifts and the relaxation parameters of the two hydrates coincide within the experimental errors. One may therefore conclude that the environment of the Fe$^{3+}$ ion is nearly the same in both compounds.

2.2 SPECTRA IN AN APPLIED FIELD. — A model describing Mössbauer spectra in the case of fast relaxation in a high applied field was developed by Wegener in 1965 [2]. The only compounds however, on which this model has been checked, were, to our knowledge NH$_4$Fe(SO$_4$)$_2$, 12 H$_2$O [8] and some related systems [9]. Since the zero-field-spectra can be more or less understood using a fast relaxation model, one might expect that this holds for the spectra in an applied field too.

The spectra were measured at 4.2 K in applied longitudinal fields up to 50 kG. Some typical spectra are shown on figures 7 and 8. These are very similar indeed to those of NH$_4$Fe(SO$_4$)$_2$, 12 H$_2$O [8]. Just as in this case the distance $\Delta V^*\nu$ of the inner lines of the hexahydrate (corrected for the applied field) is proportional within the experimental error to the relative magnetization $M/M_{max}$ which is supposed to follow an $S = \frac{1}{2}$ Brillouin function with a saturation field of 585 kG. The corrected distance $\Delta V^*\nu$ of the outer lines, however, deviates markedly from the straight line, in
accordance with the theory [2]. The same behaviour holds for the nonahydrate, too.

In Wegener's model the spectra are described by two relaxation times \( \tau_1 \) and \( \tau_2 \), the first being responsible for the line broadenings, the second for the line shifts [2]. Figure 9 shows the observed line widths of the inner and outer lines \( \Gamma_1 \) and \( \Gamma_2 \) resp. for the hexahydrate. Above about 15 kG, the data can be well fitted to Wegener's model, with the assumption that the residual line widths for the inner and outer lines are unequal \((\Gamma^\text{res}_1 = 0.37 \text{ mm/s}, \Gamma^\text{res}_2 = 0.47 \text{ mm/s})\). This fact might be due to the finite absorber thickness (about 10 mg Fe/cm\(^2\)) and to some inhomogeneities of the sample. The best fit in this region yields \( \tau_2 = 2.43 \times 10^{-9} \text{ s} \). Analogous evaluation for the nonahydrate yields \( \Gamma^\text{res}_1 = 0.41 \text{ mm/s}, \Gamma^\text{res}_2 = 0.54 \text{ mm/s}, \tau_2 = 2.48 \times 10^{-9} \text{ s} \). Below about 15 kG the assumptions of the model are not fulfilled: in this region the zero field Kramers splitting may already play an important role, since the applied field direction is no longer the quantization axis.

**FIG. 7.** — Spectra of Fe(Clo\(_4\),6 H\(_2\)O at 4.2 K in various longitudinal fields. The solid lines are computer fits with the longitudinal model (the \( H = 0 \) spectrum) and with Wegener's model (the \( H > 0 \) spectra) resp.

**FIG. 8.** — Spectra of Fe(Clo\(_4\),9 H\(_2\)O at 4.2 K in various longitudinal fields. The solid lines are computer fits with the longitudinal model (the \( H = 0 \) spectrum) and with Wegener's model (the \( H > 0 \) spectra) resp.

**FIG. 9.** — Linewidths of the outer (upper points) and inner (lower points) lines of the hexahydrate vs. relative magnetization \( M/M_{\text{max}} \). The solid lines are the best fits (see text).
The relaxation shift of the outer lines $\Delta \delta$ is shown in figure 10 for the hexahydrate. The theoretical curve belongs to the relaxation time $\tau'' = 1.34 \times 10^{-9}$ s. For the nonahydrate $\tau'' = 1.04 \times 10^{-9}$ s was found.

We may conclude that the applied theory [2] works for substances other than ferric ammonium alum if the relaxation is fast and the applied field is high enough.

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