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INFLUENCE OF Fe²⁺ CONCENTRATION ON THE MÖSBAUER SPECTRA OF Ni₃Fe₂₋O₄ SYSTEM

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Résumé. — On a étudié les spectres Mössbauer du système Ni₃Fe₂₋O₄ à la température ambiante. Le champ magnétique hyperfin et le déplacement isomérique pour Fe⁵⁷ en position octaédrique montrent une dépendance en fonction de la teneur en Fe²⁺ qui est compatible avec un comportement plutôt collectif des électrons 3 d ions de fer pour les compositions x < 0,7 et un comportement d’électrons plus localisés pour x > 0,7.

Abstract. — The room temperature spectra of the Ni₃Fe₂₋O₄ system were investigated. The dependence on the Fe²⁺ concentration of the B site magnetic hyperfine field and of the isomer shift is a good evidence for a mostly non-localized behavior of the iron 3 d electrons in the compositional range x < 0,7 and for a more localized one in the range x > 0,7.

1. Introduction. — The Mössbauer spectra of Fe₂O₄, NiFe₂O₄ and some nickel-iron ferrites were investigated by several authors [1-11]. In order to get more information about the magnetic hyperfine field, isomer shift and line broadening of the A site and B site sextets in the presence of a variable amount of Fe²⁺ ions we have investigated the Mössbauer spectra of the Ni₃Fe₂₋O₄ system. A rather great difference between the Mössbauer spectra of the compositions with x < 0,7 and x > 0,7 was observed and interpreted in terms of a change in the behaviour of the 3 d electrons, from a non-localized to a more localized one.

2. Experimental. — The Mossbauer absorbers were prepared from 9 compositions (Table I) in the Ni₃Fe₂₋O₄ system and Co⁵⁷ diffused into copper was used as a source. The source-detector geometry and the thickness of the absorbers were optimized for the case of Fe⁵⁷ enriched absorbers [12, 13] and a computer program [14] adapted for two six line patterns was used.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Composition</th>
<th>Ni₃Fe₂₋O₄</th>
<th>(H_{\text{eff}}(B)/\mu_0) (kOe)</th>
<th>(I.S.(B)/\mu_3) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.08 1.92 4</td>
<td>105.5</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.04 1.96 3.98</td>
<td>105.3</td>
<td>0.024</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.89 2.11 3.99</td>
<td>110.1</td>
<td>0.021</td>
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</tr>
<tr>
<td>4</td>
<td>0.64 2.36 3.99</td>
<td>104.8</td>
<td>0.014</td>
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<tr>
<td>5</td>
<td>0.47 2.53 3.98</td>
<td>104.2</td>
<td>0.076</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.23 2.77 4</td>
<td>103.2</td>
<td>0.072</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.07 2.93 4</td>
<td>102.4</td>
<td>0.077</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.05 2.95 4</td>
<td>102.4</td>
<td>0.083</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0  3  4</td>
<td>102.2</td>
<td>0.075</td>
<td></td>
</tr>
</tbody>
</table>

3. Results and discussion. — The room temperature values of the magnetic hyperfine fields \(H_{\text{eff}}(A)\), \(H_{\text{eff}}(B)\), isomer shifts \(I.S.(A)\), \(I.S.(B)\), and supplementary line widths \(W_2(A)\) and \(W_2(B)\) versus the nickel concentration x are plotted on figure 1, 2 and 3.

For Fe₂O₄ the values of 491.6 ± 0.9 and 460.2 ± 0.7 kOe for \(H_{\text{eff}}(A)\) and \(H_{\text{eff}}(B)\) respectively, are in very good agreement with the more recent measurements of Evans and Hafner [5] and Kündig and Hargrove [7]. The values \(H_{\text{eff}}(A) = 492.2 ± 1.0\) and \(H_{\text{eff}}(B) = 525.7 ± 1.1\) kOe for the composition with x = 1.04 are very close to those obtained by Morel [9] for NiFe₂O₄. A striking feature is the almost constant value of \(H_{\text{eff}}(A)\) for all compositions with an
average of 491.1 ± 0.4 kOe, while $H_{\text{eff}}(B)$ increases continuously with $x$, reaching the value of about 525 kOe, characteristic for the B site Fe$^{3+}$ in NiFe$_2$O$_4$, in the 0.64 < $x$ < 0.89 range. The quadrupole shift is practically zero for both A and B sextets.

The inseparability of the Fe$^{2+}$ and Fe$^{3+}$ contributions to the B site hyperfine field allow us to suppose that, at least for high Fe$^{3+}$ concentrations, the value of $H_{\text{eff}}(B)$ is a simple average given by

$$H_{\text{eff}}(B) = \left\{ \begin{array}{l} H_{\text{eff}}(\text{Fe}^{3+} - B) [\text{Fe}^{3+}] + \\
+ H_{\text{eff}}(\text{Fe}^{2+} - B) [\text{Fe}^{2+}] \end{array} \right\} \left[ [\text{Fe}^{3+}] + [\text{Fe}^{2+}] \right]^{-1} (1)$$

where $H_{\text{eff}}(\text{Fe}^{3+} - B)$ and $H_{\text{eff}}(\text{Fe}^{2+} - B)$ are the B-site hyperfine fields for non-interacting Fe$^{2+}$ and Fe$^{3+}$ ions, [Fe$^{3+}$] and [Fe$^{2+}$] being the corresponding concentrations per unit formula for a given composition.

As Fe$_3$O$_4$ and NiFe$_2$O$_4$ have practically the same Curie point and both are inverse spinels,

$$H_{\text{eff}}(\text{Fe}^{3+} - B)$$

can be taken as equal to the room temperature value of 525 kOe for $H_{\text{eff}}(B)$ in NiFe$_2$O$_4$. Applying formula (1) to Fe$_2$O$_4$, one gets a reasonable value of 395 kOe for $H_{\text{eff}}(\text{Fe}^{2+} - B)$.

The calculated from (1) dependence on $x$ of $H_{\text{eff}}(B)$ is plotted in figure 1. The agreement with the experimental data is quite satisfactory for $x < 0.7$.

The values of the ratio $H_{\text{eff}}(B)/n_0$ where $n_0$ is the average number of unpaired spins per B site iron ion, are given in Table 1. Its almost constant value suggests a fairly good proportionality between $H_{\text{eff}}(\text{Fe}^{3+} - B)$ and $H_{\text{eff}}(\text{Fe}^{2+} - B)$ and the total spins $S_{\text{Fe}^{3+}}$ and $S_{\text{Fe}^{2+}}$, i.e. $H_{\text{eff}}(\text{Fe}^{3+} - B) = A.S_{\text{Fe}^{3+}}$, where $A$ is independent on $n$. This result is in good agreement with the theory of the hyperfine field of transition metal ions [15].

In the composition range in which $H_{\text{eff}}(B)$ appears as averaged, the supplementary line width $W_s$ is an increasing function of $x$. Supposing the averaging is due to some relaxation process and using the formula given by Van der Woude and Dekker [16] for the half-width of the Mössbauer line, one gets for the correlation time which describes the fluctuations of $H_{\text{eff}}(B)$, a value of about $3 \times 10^{-7}$ s, which is $10^3 - 10^4$ times the value obtained from electrical conductivity data [6] assuming a fast electronic exchange by hopping.

The supplementary line width would be for such a relaxation mechanism $10^3 - 10^4$ times narrower than the observed one. The necessity of averaging the hyperfine field, pointed out by the Mössbauer spectra, can be due either to a fast electronic exchange between B site Fe$^{2+}$ and Fe$^{3+}$, or to the formation of a 3 d-band, but up to the present it is difficult to propose the proper mechanism. The rather large line broadening actually observed in Fe$_2$O$_4$ can be due to the presence of an unusual amount of short range order, as mentioned by Kündig and Hargrove [7]. The increase of the line width with $x$ in the range of averaged hyperfine fields can be a result of local fluctuations of the nickel concentration.

For $x > 0.7$ the hyperfine field at B sites and the line width are no more affected by the presence of Fe$^{3+}$, despite the fact that for these compositions the electrical data confirm an electron hopping mechanism of conduction with hopping frequencies still greater than $\nu_l$ [17].

The presence of Fe$^{2+}$ has a great influence on the isomer shift in the compositional range $x < 0.7$. The values of $I.S.(B)$ per one averaged 3 d electron per B site iron ion are given in Table 1. In the compositional range for which the averaging of the hyperfine field holds well, this quantity is almost constant, thus showing that the electron charge densities at the iron nucleus in B sites are averaged, too.

In conclusion, the investigation of the room temperature Mössbauer spectra of the NiFe$_3$-$\text{O}_x$ system points out two different behaviours, corresponding to the compositional ranges $0 < x < 0.7$ and $x > 0.7$.

For the first one, the 3 d electrons belonging to the B site Fe$^{3+}$ and Fe$^{2+}$ seem to be non localized to a high extent, while for the second compositional range they behave as localized. These two compositional ranges correspond to different electrical properties. In the range of $x > 0.7$ the carriers are small radius polarons while for $x < 0.7$ they are probably large radius polarons or band carriers. Hence, there is enough evidence for a strong correlation between the degree of localization of the 3 d electrons in the iron-nickel ferrites and the peculiarities of their Mössbauer spectra.

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References