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MÖSSBAUER SPECTROSCOPY OF DIFFERENT INTERSTITIAL COMPOUNDS AND SOLID SOLUTIONS CONTAINING $^{57}$Fe

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Résumé.- Les variations des paramètres hyperfins du fer sont discutées dans les solutions solides interstitielles, les carbures et les nitrures.

Abstract.- The hyperfine parameters of iron are discussed in interstitial solid solutions, carbides and nitrides.

The aim of this paper is to discuss the hyperfine parameters of iron in interstitial solid solutions and compounds. The compact f.c.c. and h.c.p. structures where interstitials $I$ (I = B, C, N) are in octahedral sites are considered and also the compounds where $I$ are at the centres of trigonal prisms. In this last case the structure is classified as a function of the increasing linkage coefficient $I_{ll}$.

The martensites are excluded from the discussion as their Mössbauer spectra create many problems which are not fully resolved.

1. Hyperfine fields and isomer shifts. - As already noted the effect of the metalloid atoms on the iron atoms should be of short range and the variations of the hyperfine fields may be related to the number ($n$) of interstitial neighbours and to the Fe - $I$ distances ($r$):

$$H = H_{\text{Feo}} - K(r) n$$

(1)

According to /2/ $K(r)$ would vary as $r^{-3}$. Experimental results let us re-examine eq. (1) considering that $K$ may be different for B, C, N:

$$H^I = H^0 - \sum_{j} K^I_I (r_{ij}) n_j$$

(2)

As we only want to determine the general behaviour, we consider solely $K^I_I$ the part of $K^I_I (r_{ij})$ which is independent of $r_{ij}$, then if $n_{\text{eff}}$ is the effective number of $I$ neighbours:

$$H^I = H^0 - K^I_{\text{eff}} n_{\text{eff}}$$

Finally as the hyperfine fields are generally unknown at OK, we only consider the compounds with high Curie temperatures whose $H$ are known at 77 K.

In $\gamma'$ and $\varepsilon$ iron nitrides, each iron atom is surrounded by twelve iron neighbours at a distance which varies between 2.66 Å and 2.73 Å as a function of interstitial content while Fe - N distances are about 1.9 Å. From experimental results /3, 4/ we obtain figure 1 which shows the hyperfine field of iron as a function of the number $n$

$$H^I(n) = 374 - 73 n \text{ (kOe)}$$

(correlation coefficient 0.99).

Fig. 1: Hyperfine fields in iron nitrides (α) and iron carbides (●) as functions of the number $n$ of interstitial nearest neighbours.

$H^0$ is greater than $H_{\text{Feo}}$ as assumed in equation 1 /2,5/ and may be ascribed to the hyperfine field of iron atoms in hypothetical ferromagnetic f.c.c. or h.c.p. iron.

In iron carbides the Fe-C distances are about 2 Å. The iron coordination is 12 in simple carbides and 11 or 12 according to the iron site in Fe$_3$C and Fe$_5$C$_2$ where the scatter in Fe-Fe distances is greater than in the former carbides. The $n$ values are 2 for the Fe$_{\text{I}}$ sites in Fe$_3$C and Fe$_5$C$_2$ while for the Fe$_{\text{II}}$ sites there is a third neighbour at 2.37 Å in

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Fe₃C and at 2.22 Å in Fe₅C₂ /6/. The $H_{II}$ fields in Fe₃C and Fe₅C₂ would then correspond to $n_{eff}$ between 2 and 3, but in a first approximation we take $n = 3$.

Taking hyperfine fields of $c$ carbides /7/ of Fe₃C and Fe₅C₂ /6/ and the possible cubic Fe₃C carbide we obtain:

$$H(n) = 376 - 57 \, n \, (kOe)$$

The $H_0$ values are similar for C and N but differ from the value given by Ino et al. /5/ while the values of $K$ may be compared. In iron borides where the Fe-Fe distances vary from 2.4 Å to 2.72 Å and where only four values are available /15/ equation 2 is difficult to check. Adding the constraint $H_0 = 375 \, kOe$ one obtains

$$H_{II}(n) = 375 - 45 \, n \, (kOe)$$

We conclude that the linear relationship $H_{II}$ (n) is quite well followed in nitrides, rather well in carbides and approximatively in borides. This behaviour may be related to the nature of metalloid atom and to a wider range of Fe-Fe distances when the structure which is simple in nitrides becomes more and more complex with carbon and boron. However, an important part of the total hyperfine field is determined by the linear variations $H_{II}(n)$. Comparison of the Mössbauer spectra of $c$ carbides and nitrides shows nevertheless that the effect of nitrogen on $H$ is mainly restricted to the first coordination shell while carbon acts on more distant neighbours. Finally, the $K_I$ value increases from B to N roughly as $d^{-3}$ if $d$ is the shortest Fe-Fe distance. This does not mean that $K_I$ for a given I, varies as $r^{-1}$ but may be related to the bonding properties which, in particular, reflect the influence of the size of the interstitial.

It is more difficult to extract a simple behaviour from the variations of isomer shifts ($\delta$) because the second order Doppler shift has in most cases not been measured. Only comparison of various environments $\delta$ of a given compound seems to be meaningful: in nitrides $\delta$ increases with $n$ while it remains nearly constant or decreases in carbides and borides.

In the simple picture where the metalloid donates electrons to the 3d levels of Fe without altering them, $H$ decreases and $\delta$ increases with $n$ as observed in nitrides but not in carbides and borides. The direct and indirect contribution of 3d and s electrons to $H$ and $\delta$ does not allow to fully describe the bonding. The donor model has been rejected in borides /8/ : the iron d band being altered probably by hybridization with boron 2s and 2p states and no evidence of boron electrons transfer is found. Finally a large positive conduction band polarization is expected to contribute to $H$. The bonding electrons are probably more and more delocalized from $N$ to $B$. In nitrides a negative charge is found on nitrogen by superstructures reflexion intensities and the centre of the charge cloud in the bonding state may move towards the nitrogen site /9, 10, 11/.

2. Quadrupole splittings. -From the rapid variation of the function $r^{-3}$, where $r$ is an electron-nucleus distance, the electrons which participate in the strong Fe-I bonds are expected to give the major contribution to the quadrupole splittings measured at the iron nucleus. Considering the absolute values of the quadrupole splittings of iron atoms having two interstitial nearest neighbours at a distance close to 2 Å in (Fe₁₋ₓXₓ)₃C (M = Cr, Mn), (Fe₁₋ₓMₓ)₃C, (Mn₁₋ₓYₓ)₃C, M₃N₃C (M = Fe, Mn, $M' = Al$, Ga, Ge, Zn, Sn) and in $\gamma$ Fe₃N, $\gamma$Fe-C and $\gamma$Fe-N /3, 6, 12-14/ we obtain the following table where $\delta$ indicate the angle of the two shortest iron-interstitial bonds for each site.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Iron site</th>
<th>Interstitial - Fe distance (Å)</th>
<th>$\delta$ (°)</th>
<th>$\Delta$ mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₅C</td>
<td>Fe₁₁</td>
<td>2.00 - 2.04</td>
<td>99</td>
<td>0.32</td>
</tr>
<tr>
<td>Mn₅SiC</td>
<td>Mn₁₁</td>
<td>2.00 - 2.05</td>
<td>102</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe₅C₂</td>
<td>Fe₁₁</td>
<td>1.96 - 2.01</td>
<td>100</td>
<td>0.37</td>
</tr>
<tr>
<td>Mn₅SiC</td>
<td>Mn₁₁</td>
<td>2.06 - 2.08</td>
<td>105</td>
<td>0.36</td>
</tr>
<tr>
<td>Fe₅C₂</td>
<td>Fe₁₁</td>
<td>1.97 - 1.99</td>
<td>142</td>
<td>0.80</td>
</tr>
<tr>
<td>Fe₅C</td>
<td>Fe₁₁</td>
<td>1.97 - 1.99</td>
<td>144</td>
<td>0.68</td>
</tr>
<tr>
<td>Mn₅SiC</td>
<td>Mn₁₁</td>
<td>2.18 - 2.32</td>
<td>158</td>
<td>0.71</td>
</tr>
<tr>
<td>Mn₅GeC</td>
<td>Mn</td>
<td>2.10 - 1.95</td>
<td>180</td>
<td>1.5</td>
</tr>
<tr>
<td>Mn₅ZnC</td>
<td>Mn</td>
<td>1.96 - 1.96</td>
<td>180</td>
<td>1.5</td>
</tr>
<tr>
<td>$\gamma$F₇N</td>
<td>Fe₁₁</td>
<td>1.90 - 1.90</td>
<td>180</td>
<td>0.30</td>
</tr>
<tr>
<td>$\gamma$Fe-C</td>
<td>Fe₁₁</td>
<td>1.83</td>
<td>180</td>
<td>0.64</td>
</tr>
<tr>
<td>$\gamma$Fe-N</td>
<td>Fe₁₁</td>
<td>1.83</td>
<td>180</td>
<td>0.35</td>
</tr>
<tr>
<td>$\gamma$Fe-N</td>
<td>Fe₁₁</td>
<td>1.83 - 1.83</td>
<td>180</td>
<td>0.45</td>
</tr>
</tbody>
</table>

One may object that the Fe₁₁ sites of Fe₃C and Fe₅C₂ have a third carbon neighbour (e.g. hyperfine fields). These third neighbours are expected to contribute less than the two closest carbon neighbours because of the very strong variation with distance of the operator determining the quadrupole splittings. In the case of Mn₅SiC, the silicon neighbours presumably effect mainly the s electrons.
that is the isomer shift in the paramagnetic state /12/. The quadrupole splittings increase regularly with the angle of the two iron-carbon bonds and are practically insensitive to the metallic neighborhood of the iron atoms under consideration /12/. The comparison of \( \Delta \) in \( \gamma^\prime \)Fe,N and the perovskite type carbides shows that \( \Delta \) is negative in both cases and that \( \Delta_C = 3 \Delta_N \). In \( \text{Mn}_2\text{N} \) and \( \text{Mn}_3\text{ZnC} \), the quadrupole splittings are such that \( \Delta_C = 2.8 \Delta_N \) and in austenite \( \Delta_C = 2.6 \Delta_N \). This is further confirmed by the observation of high negative anisotropic fields \( H_a \) in \( \text{Mn}_3\text{ZnC} \) and \( \text{Mn}_3\text{GaC} \) doped with \( ^{57}\text{Fe} \) and almost zero anisotropic fields in Fe,N. As the 3d electron dipolar fields may be responsible for the main part of \( H_a \), they are closely related to \( \delta \). These results show that the centre of charge of the bonding electrons is closer to the nitrogen site than to the carbon site, in agreement with the results of Nagakura /9, 10/ and with the difference in the electronegativities of C and N.

References

/2/ Fatsea, G., Phys. Status, Solidi (b) 59 (1973) K23.