PHYSICAL REVIEW B VOLUME 46, NUMBER 14 1 OCTOBER 1992-II

Mössbauer isomer shifts in iron borides based on the local structure of the Fe sites

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(Received 27 May 1992)

An expression for the ^{57}Fe Mössbauer isomer shift in iron borides has been developed, which reproduces accurately the experimental values measured in the nine iron sites existing in FeB, Fe_2B, Fe_3B (body-centered tetragonal), Fe_3B (orthorhombic), as well as in metallic α-Fe and γ-Fe, in terms of their local structure. It is shown that the isomer shift can be described using two terms. The first one depends linearly on the number of boron nearest neighbors of the iron site. The second term is needed because of the volume effects which cannot be neglected in the Fe-B interstitial compounds, and it depends strongly on the average iron-iron interatomic distances. This term gives an account of the important deviations observed from the linear correlation with the number of boron neighbors.

The Mössbauer isomer shift (δ_{IS}) is sensitive to the electronic density at the nuclear site and therefore reflects the changes induced by the different atomic environments on the valence electron band. Modifications in the number and class of neighbors, interatomic distances, etc., produce variations in the occupation number of the electronic states as well as in the extension of the respective orbitals. In the case of ^{57}Fe, by far the most used Mössbauer probe, these variations occur in the 4*s* electrons, which contribute directly to δ_{IS}, and in the 3*d* ones, which play their part mostly through the screening of atomic 3*s* electrons.

Several successful approaches have been taken in the past in order to give empirical or semiempirical descriptions of the ^{57}Fe δ_{IS} in metallic systems, as, for example, those developed by Ingalls[1] for metallic iron and by Miedema and Van der Woude[2] and Van der Kraan and Buschow[3] for transition-metal amorphous alloys and intermetallics. However, none of these descriptions is able to give account of the δ_{IS} values measured in the so-called *interstitial* transition-metal–metalloid intermetallics such as the iron borides.

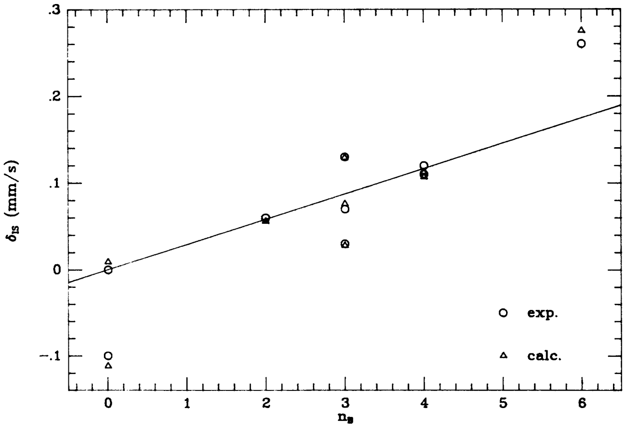

FIG. 1. Comparison of the isomer shift values measured in iron borides, α-Fe and γ-Fe (circles) with those calculated with Eq. (1) (triangles). The straight line represents the first term of Eq. (1), i.e., the linear correlation δ_{IS} vs n_B. Departures from the straight line are due to volume effects [second term of Eq. (1)].

In this work we present a description which successfully reproduces the δ_{IS} values measured in stable and metastable crystalline borides as well as in metallic iron in terms of the local structure of the iron site. Figure 1 shows the experimental δ_{IS} in the nine iron sites present in FeB, Fe_2B, the orthorhombic and body-centered tetragonal allotropic varieties of Fe_3B, α-Fe (bcc), and γ-Fe (fcc). Along with these data, also shown in the figure are the values calculated with the expression

$$\delta_{IS}(\mathrm{mm/s})=0.029\,17 n_B+[\bar{d}_{Fe}(\text{Å})-2.64]n_{Fe}/11 , \quad (1)$$

where n_B and n_{Fe} are the number of boron and iron neighbors within the first coordination shell around the Mössbauer atom (a sphere of about 3 Å radius) and $\bar{d}_{Fe}$ is the mean distance to the considered iron neighbors (see Table I).

TABLE I. Local structure parameters relevant for the calculation of δ_{IS} with Eq. (1). n_B and n_{Fe} are the number of boron and iron neighbors within the first coordination shell to an iron atom, and $\bar{d}_B$ and $\bar{d}_{Fe}$ are the mean distances between the central atom and respective neighbors in this shell.

Boride	Site	n_B	n_{Fe}	$\bar{d}_B$ (Å)	$\bar{d}_{Fe}$ (Å)
FeB	1	6	10	2.15	2.75
Fe_2B	1	4	11	2.18	2.63
t-Fe_3B[a]	1	2	12	2.19	2.638
	2	4	10	2.25	2.635
	3	3	10	2.24	2.575
o-Fe_3B[b]	1	3	12	2.30	2.678
	2	3	11	2.16	2.628
α-Fe	1		14		2.647
γ-Fe	1		12		2.537

[a] Body-centered tetragonal.
[b] Orthorhombic.

The agreement between measured and calculated values is indeed striking and indicates that both contributions to δ_{IS} in Eq. (1) are important. The additive effect of the boron neighbors is similar to that observed by Ingalls, van der Woude, and Sawatzky[4] in diluted iron-based substitutional alloys and the increase rate $\partial\delta_{IS}/\partial n_B \cong 0.029$ mm/(s atom), is almost the same as that produced by aluminum impurities in α-Fe, $\partial\delta_{IS}/\partial n_{Al} \cong 0.030$ mm/(s atom). This term, represented in Fig. 1 by the straight line, sets the general trend of the δ_{IS} behavior. It is somehow surprising that the iron-boron distance does not play an important role in Eq. (1). This may be connected to the rather covalent character of the iron-boron interaction, which would lead to similar boron environments existing in different iron borides. The situation in these compounds could be similar to that found in iron halides and oxides, where the iron-partner distances lie in a range for which the electronic density at the nucleus varies slowly, producing only small changes in δ_{IS}.[5]

The second term gives account of the important deviations of the measured δ_{IS} values from the linear correlation with n_B. It resembles the volume effects observed by Ingalls, van der Woude, and Sawatzky for ^{57}Fe in transition metals. In particular, from the δ_{IS} values obtained from α-Fe under pressure,[1] the volume dependence

$$\Omega\frac{\partial\delta}{\partial\Omega} = 1.330 \pm 0.008 \text{ mm/s} \tag{2}$$

has been obtained at $T = 300$ K. For $\Omega \cong 11.7$ Å^3 (α-Fe at normal pressure and temperature), (2) leads to $\partial\delta/\partial\bar{d}_{Fe} = 1.41$ mm/(s Å), in reasonable agreement with the value $\partial\delta/\partial\bar{d}_{Fe} = 1.27$ mm/(s Å), which follows from Eq. (1).

In the iron borides, the first shell of iron neighbors to an iron site spreads from about 2.40 to about 2.90 Å, and there exists a quite clear separation between this and the next shell centered at about 4.50 Å (see Fig. 2). It is worth noting that only the valence electrons of the iron atoms in the first shell interact directly with those of the central atom, as can be inferred from the extension of the Fe $3d$ and $4s$ radial functions.[6] Therefore only neighbors contained in there should be considered for the description of the δ_{IS} volume effects. Consistent with this statement, in α-Fe we have taken into account the 14 near neighbors and next near neighbors at about 2.48 and 2.87 Å, respectively, but just the 12 near neighbors at 2.54 Å in the case of γ-Fe (Fig. 2). The inclusion of α-Fe and γ-Fe in the correlation (1) can be justified considering that the iron-metalloid compounds have been imagined as generated from metal close-packed arrangements by periodically twinning these structures at the unit-cell level.[7] This process leads to a dense metallic structure which contains prismatic interstitial sites where the metalloid atoms are accommodated. In these compounds the more covalent interaction with the boron neighbors may constitute the driving force for the local structure around an iron atom, conditioning the number and distances to the iron neighbors. The latter, having a direct *metallic* interaction with the central atom, produce on it a volume effect similar to that found in metallic iron. The two apparently independent contributions to δ_{IS} present in Eq. (1) might be a consequence of such situation.

We expect the approach presented here to be helpful for applications of the Mössbauer effect to structural studies of phases containing iron and boron, as may be the case of a recently developed family of supermagnets.[8] In particular, combined with the correlation between the ^{57}Fe hyperfine fields and the number of boron near neighbors proposed by Dubois and Le Caer[9] and by Lines,[10] Eq. (1) would provide more confidence to the structural information obtained with this technique.

It would be interesting to find out whether the present description can be extended to other iron-metalloid systems, especially Fe-C, by an appropriate choice of the constants appearing in Eq. (1). Finally, we hope that the present description will be helpful for those developing theoretical models to the ^{57}Fe δ_{IS}, in the sense of providing guidelines for the study of the Fe-metalloid interstitial systems which are more complex than other ones for which theoretical calculations have already been successfully performed.

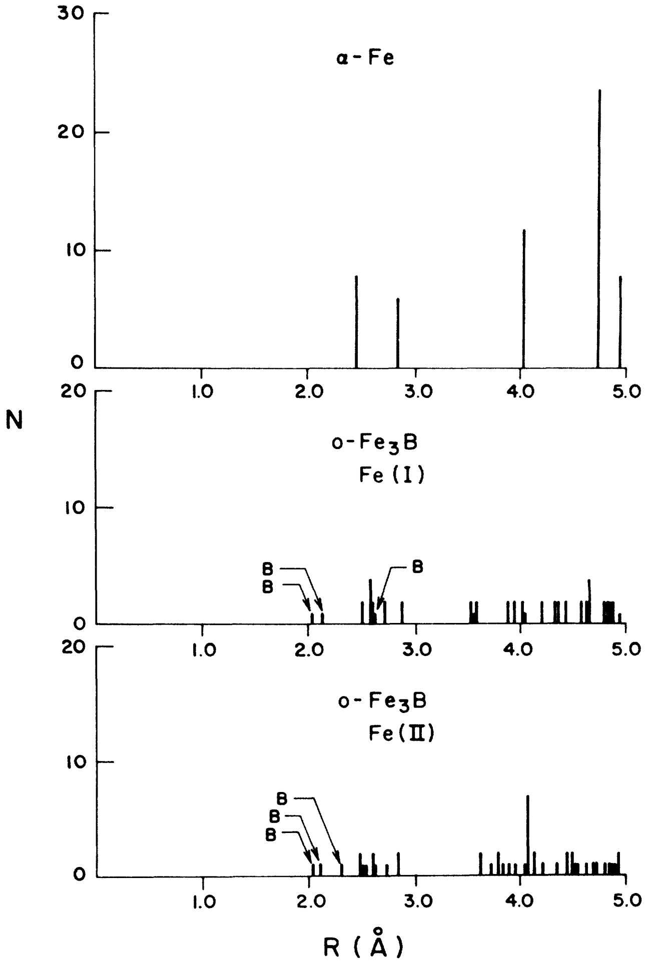

FIG. 2. Radial atomic distributions around an iron site in α-Fe (top) and in sites I and II of orthorhombic Fe_3B (middle and bottom). Boron neighbors are marked with a B.

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