BRIEF COMMUNICATIONS

A Mössbauer Study of the κ Phase in the Fe–W–C System

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It is shown that, taking the absorber thickness properly into account, reliable values of the iron population of the different sites in κ-(Fe–W–C) can be obtained although the resolution in the Mössbauer spectrum is limited. The partial population of one $2a$ crystallographic position was determined to be $40 \pm 2\%$ in good agreement with the value $45 \pm 1\%$ obtained from a recent diffraction study.

Experimental details

The sample used in the present study was prepared by A. Hårsta at the Institute of Chemistry, Uppsala University, and sample preparation and characterization are reported elsewhere (*1*). A powder absorber (3.5 mg/cm²) was investigated at room temperature using a constant acceleration Mössbauer spectrometer. Data from the sample and from a calibration sample was collected using an Apple II+ microcomputer which also controls the motion of the vibrator. Details of the Apple–Mössbauer interface can be found in Ref. (*2*). After each run the resulting data is transferred to a local VAX computer for analysis. The analysis of the experimental spectra is made interactively starting with the calibration spectrum. The programs used are capable of treating combined interactions and can be used for thick absorbers since a thickness correction routine is incorporated also. This routine is based on an approximation to the transmission integral involv-

ing a relation between absorption cross section and the thin absorber line form. The approximation is optimized for single line spectra but has also been shown to work well for more complex spectra (*3*). As is evident from Fig. 1 there are a number of different environments for iron in the carbide under study and in the analysis four different sets of parameters had to be used. The complexity of spectrum also prompted the neutron diffraction study of Ref. (*1*).

Data analysis

The least squares fitting was made in several steps. Since the resolution in the spectrum is poor, different constraints on the parameters were tried. The presence of iron on the $2a$ position (Ref. (*1*)) also affects the hyperfine parameters for the iron atoms in the $6h$ position since there will be variations in their near surrounding. The nearest neighbors to an iron atom in the $6h$ position can be 2 W/0 Fe ($6h_0$), 1 W/1 Fe ($6h_1$), or 0 W/2 Fe ($6h_2$) and we expect to find three
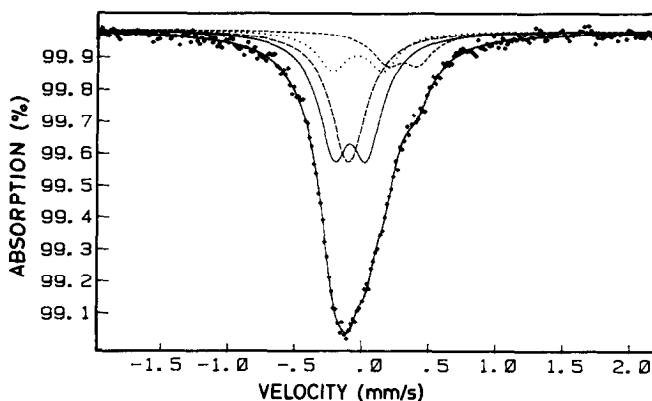
FIG. 1. Room temperature Mössbauer spectrum of κ-Fe–W–C. The different subsets of lines denote the different iron surroundings, the dashed, full, and dotted lines correspond to $6h_0$, $6h_1$, and $6h_2$, respectively, and the finer dashed line to iron on the $2a$ position.

different components in the spectrum that can be attributed to the $6h$ position; they will, in the following, be denoted as indicated in parentheses above. With an iron occupancy of the $2a$ site equal to x and assuming random occupation we would expect intensities of $Nx/3$, $N(1 - x)^2$, $N\,2(1 - x)x$, and Nx^2 for $2a$, $6h$, $6h_1$, and $6h_2$, respectively. The normalization factor is $N = (1 + (x/3))^{-1}$. Several further constraints were used to get good starting values for the final fit which was performed by only restricting the relative amplitudes of the sites to the values corresponding to a random distribution as given above. Since the main aim of this study was the determination of x it was essential to use the thickness correction option in the analysis program. The final values for the fitted parameters are given in Table I. It should be emphasized that from a purely mathematical standpoint further minima in the least squares sum can be obtained. These minima do, however, lead to physically unacceptable solutions.

Discussion

The intensities obtained are further supported by the reasonable values of the hyperfine parameters obtained. The isomer shift for dilute iron in tungsten is 0.15 mm/sec whereas a tungsten impurity in iron gives rise to an isomer shift of -0.03 mm/sec at a near neighbor iron atom (4). Replacement of a tungsten atom by an iron atom should thus lead to a reduction of the electron density at the nucleus and this is what is actually observed since the isomer shift increases when going in the sequence $6h_0 \rightarrow 6h_1 \rightarrow 6h_2$. The electron density at the $2a$ site is rather similar to the one in iron carbides (5).

The quadrupole interaction for $6h_0$ is very weak and the increase for the $6h_1$ and $6h_2$ configurations can be explained in terms of increasing deviations from a nearly spherical charge distribution.

TABLE I

RESULTING MÖSSBAUER PARAMETERS

Site	IS(mm/sec)	Δ(mm/sec)	W(mm/sec)	$I(\%)$
$6h_0$	-0.10 (1)	0.04 (1)	0.13 (2)	31.2 (1.9)
$6h_1$	-0.08 (1)	0.24 (1)	0.13 (2)	46.6 (.5)
$6h_2$	-0.03 (1)	0.38 (1)	0.13 (2)	14.6 (1.3)
$2a$	0.30 (1)	0.22 (1)	0.13 (2)	11.7 (.4)

Notes. The isomer shift (IS) is given with respect to iron metal. Δ is the electric quadrupole splitting. The line width (W) represents the FWHM absorber cross section and was constrained to be equal for all sets. The corrresponding width for the source is 0.14 mm/sec.

The results of the fit can, thus, be treated with some confidence and the value obtained for the population of the $2a$ crystallographic position should be directly comparable to the value obtained in the neutron diffraction study (*1*). The omission of the low intensity iron $6h$ position (*1*) in the fitting procedure should only affect the intensity determination to a lesser degree and the present value of 40(2)% population compares well with the value 45(1)% of Ref. (*1*). It thus seems that the Mössbauer method with proper thickness correction applied gives reliable values even when the resolution in the spectrum is rather limited.

References

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