Atomistic Determination of Diffusion Mechanism on an Ordered Lattice

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By high-temperature ^{57}Fe Mössbauer spectroscopy on single crystals the diffusion mechanism in an ordered structure (stoichiometric Fe_3Si) has been studied on an atomic scale. From the widths and the weights of the quasielastic lines in appropriately chosen crystal directions one can directly infer the elementary diffusion jump mechanism: For the stoichiometric alloy Fe_3Si jumps via the three iron sublattices dominate. At only slightly higher iron concentrations (off stoichiometry), however, jumps via antistructure sites on the silicon sublattice contribute strongly.

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Diffusion in fully and partially ordered structures is not only an academic problem: Because of the increasing interest in ordered intermetallic phases as high-temperature structural materials, understanding the diffusion in such materials at high temperatures is technologically important [1].

Fe_3Si (equivalent to $Fe_{75}Si_{25}$) has DO_3 structure, i.e., a cubic superstructure consisting of four sublattices, in this paper labeled α_1, α_2, β, and γ (Fig. 1). In the fully ordered structure the iron atoms occupy the α_1, α_2, and γ sublattices, whereas the silicon atoms occupy the β sublattice. From the Zeeman splitting of Mössbauer spectra of Fe_3Si taken at room temperature we deduce, following a line well established by Stearns and others [2], that two-thirds of the iron atoms are on sites with four nearest neighbor (NN) iron atoms, i.e., on the α sublattices, and one-third of the iron atoms are on sites with eight NN iron atoms, i.e., on the γ sublattice. This implies that order is practically perfect. For nonstoichiometric alloys a distinct component of iron atoms on α sites with five iron NN's appears, and even a small component attributable to iron atoms with six iron NN's can be distinguished. The fractions of these additional components agree with what is expected from statistics.

Wever and Frohberg [3] and more recently Bakker and Westerveld [4] have proposed that in diffusion on DO_3 lattices the dominant species, i.e., the iron atoms, jump between the three iron sublattices only, i.e., the two α sublattices and the γ sublattice. This model, which we shall call the α-γ model, is primarily a suggestion, and it is not immediately evident why the iron atoms should avoid the fourth sublattice (the β sublattice), i.e., why the creation of antistructure defects on the β sublattice should be forbidden. It appears a challenge to check the α-γ model with an atomistic method.

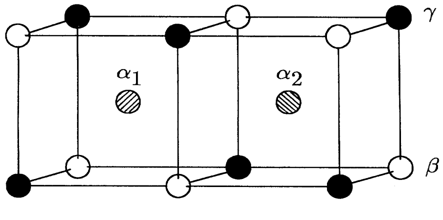

FIG. 1. DO_3 structure of Fe_3Si ($\frac{2}{8}$ of elementary cell). The iron atoms occupy the sublattices α_1, α_2, and γ, the silicon atoms the sublattice β.

Whereas tracer diffusion studies infer atomic diffusion from *macroscopic* properties, as, for instance, the concentration gradient of diffusing atoms, an *atomistic* way to determine the diffusion mechanism is offered by quasielastic Mössbauer spectroscopy (QMS) and by quasielastic incoherent neutron scattering (QNS) [5,6]. These methods measure the self-correlation function, i.e., the movement of an individual nucleus, and therefore study the diffusion phenomena on an atomistic scale. In the present paper we shall show that for the first time Mössbauer spectroscopy has been successfully used to determine atomistic details of the jump mechanism in an *ordered structure.*

With Mössbauer spectroscopy the quasielastic broadening of the Mössbauer resonance absorption line due to motions of the γ-emitting or γ-absorbing atoms can be measured. From the angular dependence of the broadening the elementary diffusion jump is derived, provided the sample is a single crystal. That diffusion can be investigated by Mössbauer spectroscopy was initially proved by Mullen [7], but until now only very few single crystal studies have been performed and all on Bravais lattices, i.e., lattices with only one atom per unit cell [8]. For diffusion on Bravais lattices it was sufficient to use the theory developed by Singwi and Sjölander [5] and by Chudley and Elliot [9]. Rowe *et al.* [10] have extended this theory to diffusion on non-Bravais lattices, i.e., lattices with more than one atom per unit cell. That theory is derived strictly speaking for QNS, but is directly applicable to QMS [11].

According to Ref. [10] NN jumps between three sublattices, as proposed by the α-γ model for the DO_3 structure, are described by a system of three coupled rate equations for the probability $P_i(\mathbf{r},t)$ of finding a diffusing atom at point $\mathbf{r}$ in the ith sublattice ($i=1$ to 3) at a time t,

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$$(\partial/\partial t)P_i(\mathbf{r},t)=\nu\sum_{j,k}(1/n_{ij})[P_j(\mathbf{r}+\mathbf{l}_{ijk'}t)-P_i(\mathbf{r},t)]\,. \qquad (1)$$

Here each site of the ith sublattice is surrounded by n_{ij} sites of the jth sublattice at distances l_{ij}. ν is the jump frequency of the iron atoms from a site on the α_1 or α_2 sublattice into a vacancy on a distinct NN site on the γ sublattice and vice versa. [From detailed balance it follows (see, e.g., Ref. [12]) that in the stoichiometric alloy all these jump frequencies must be equal.]

Fourier transformation ($\mathbf{r}\rightarrow\mathbf{Q}$) leads to the matrix equation $(\partial/\partial t)\mathbf{I}(\mathbf{Q},t)=\nu\mathbf{A}\mathbf{I}(\mathbf{Q},t)$, where $\mathbf{I}(\mathbf{Q},t)$ is the intermediate scattering function and $\mathbf{A}$ is the 3×3 jump matrix made up by the jump vectors;

$$\mathbf{A}=\begin{pmatrix}-2 & E & E^* \\ E^* & -1 & 0 \\ E & 0 & -1\end{pmatrix}. \qquad (2)$$

E is a function of the structure of the "jump lattice." For the present case,

$$E=[\cos(Q_xa)\cos(Q_ya)\cos(Q_za) + i\sin(Q_xa)\sin(Q_ya)\sin(Q_za)] \qquad (3)$$

with Q_x, Q_y, and Q_z the components of the γ wave vector ($Q=72.98\ \mathrm{nm}^{-1}$) relative to the crystal axes and $4a$ the lattice parameter (0.571 nm for $\mathrm{Fe_3Si}$ at 720 °C). The zero values in the matrix indicate that there are no jumps between the α_1 and the α_2 sites, which are further apart than NN.

The incoherent scattering function for QNS (and therefore also the Mössbauer absorption probability which is the equivalent for QMS) are received by a second Fourier transformation ($t\rightarrow\omega$) leading to a function

$$S(\mathbf{Q},\omega)=\sum_p[w_p(\mathbf{Q})\Gamma_p(\mathbf{Q})]/[\Gamma_p(\mathbf{Q})^2+\omega^2]\,. \qquad (4)$$

This function represents a sum of three Lorentzians each with width (HWHM) $\Gamma_p=\hbar\nu M_p$ and weight $w_p=\frac{1}{3}|\sum_i v_i^p|^2$ where M_p ($p=1$ to 3) are the eigenvalues and v_i^p ($p=1$ to 3, $i=1$ to 3) the components of the pth eigenvector of the jump matrix.

Figures 2(a) and 2(b) show the predictions of these calculations which, in the following, will be compared to the experimental results.

Single crystals of the Fe-Si alloy system were grown by the Bridgman technique after melting the constituents in a cold boat. The weighted atomic concentrations were 25, 24, and 20 at.% silicon. An analysis of an $\mathrm{Fe_3Si}$ specimen by wet chemistry and by electron microprobe proved that the composition agreed with the weighted concentration within 0.3 at.% and the room temperature Mössbauer spectra confirmed the analysis. Slices of about 10 mm diameter were cut by a diamond saw with their surfaces parallel to the Laue oriented (111) plane. The thickness was reduced by abrasion followed by chemical etching (final thickness about 30 μm). The quality of the single crystals was checked by rocking curves: Their widths were about 0.5°, the mosaic spread of the crystals was less than 1°, both before and after high-temperature measurements.

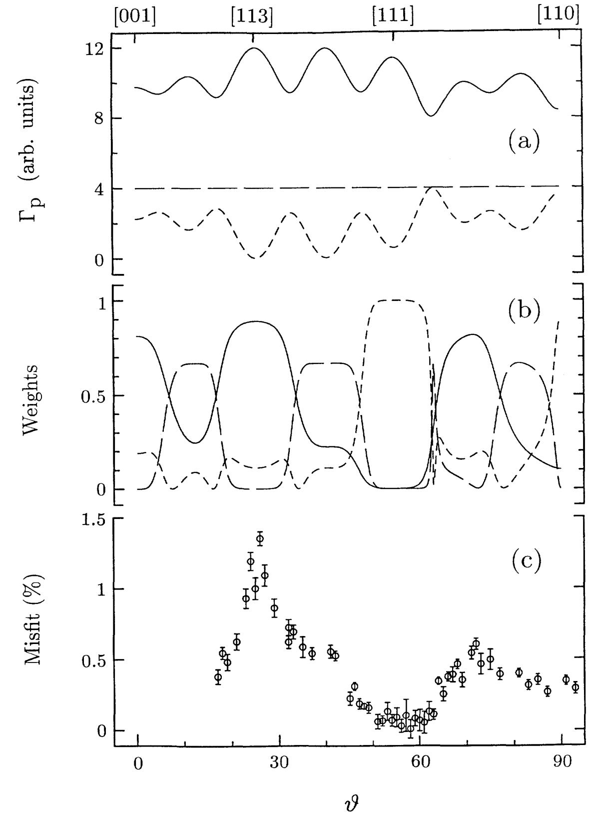

FIG. 2. Model predictions for (a) quasielastic Mössbauer linewidths Γ_p and (b) weights of the Mössbauer lines due to diffusion on the three Fe sublattices α_1, α_2, and γ of $\mathrm{Fe_3Si}$, as a function of crystal orientation. (c) Misfit as a function of crystal orientation if Mössbauer spectrum is fitted with just one Lorentzian line.

Mössbauer measurements were carried out as transmission experiments with a 50 mCi $^{57}\mathrm{Co}$ in Rh matrix as a source. The specimens were encapsulated between two BeO disks fixed by tantalum rings (for details see Ref. [13]) to a rotatory axis. The exact orientation of samples was achieved with an x-ray diffractometer, with the sample encapsulated in the sample holder and in the same geometrical conditions as in the Mössbauer measurement. In the course of the Mössbauer measurements the crystals were rotated around an axis in their surface such that the transmission of Mössbauer γ radiation could be varied from parallel to [110] through [111] to [113].

Figure 3 shows Mössbauer spectra of $\mathrm{Fe_3Si}$ ($\mathrm{Fe_{75}Si_{25}}$) measured at 720 °C in two selected crystal directions, namely, [111] and [113] [14]: In these directions the α-γ model predicts only one and two lines, respectively. To realize that, compare Figs. 2(a) and 2(b) and consider

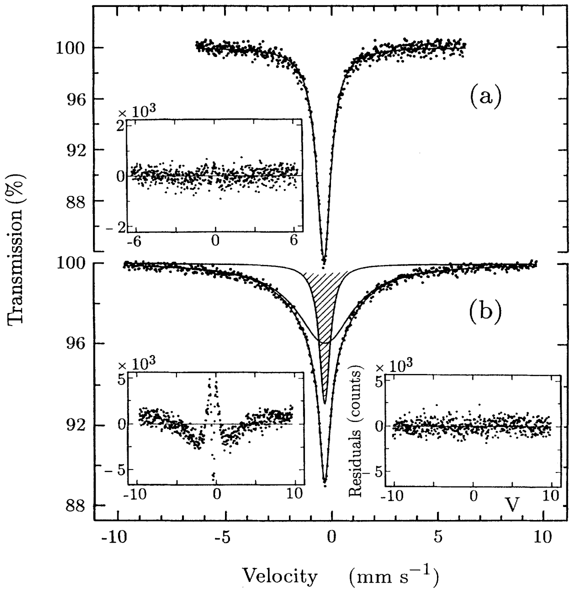

FIG. 3. ^{57}Fe Mössbauer spectra of Fe_3Si single crystal. (a) Transmission in [111] direction, $T=720\,°C$; (b) transmission in [113] direction, $T=720\,°C$. Note that in the [111] direction the spectrum is a single Lorentzian line, whereas in the [113] direction it consists clearly of a narrow and a broad line. This is confirmed by the insets (left) showing the residuals of fits with just *one* line. It is evident that for [113] such a one-line fit is completely insufficient, but that a fit with a narrow and a broad line (inset right) is satisfactory.

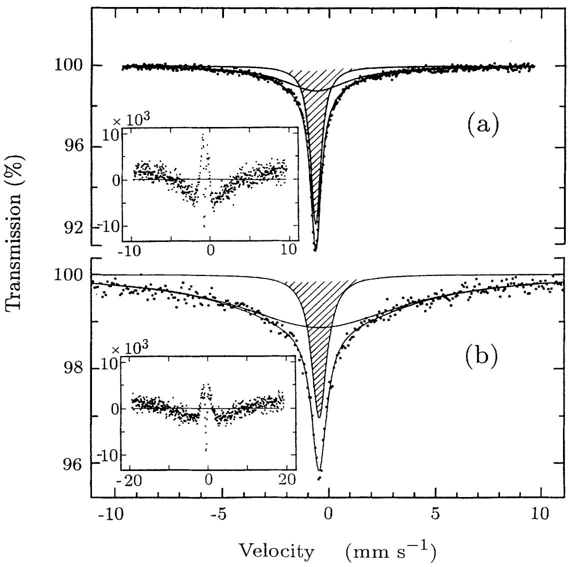

FIG. 4. ^{57}Fe Mössbauer single crystal spectra for transmission in the [113] direction fitted with a narrow and a broad line. (a) $Fe_{80}Si_{20}$, $T=900\,°C$; (b) Fe_3Si, $T=800\,°C$ (here the width of the broader line exceeds the velocity window of ±10 mm s^{-1}). The insets showing the residuals of fits with just *one* line demonstrate that one-line fits are completely insufficient, whereas the present fits with a narrow and a broad line are of the same quality as shown in the right side inset of Fig. 3(b).

that for [111] two of the frequencies and for [113] one of the frequencies have zero weight. Therefore they cannot be detected in the spectrum. The following items are worth noting:

(1) The spectrum in the [111] direction can be well represented by just one Lorentzian line, whereas the spectrum in the [113] direction clearly consists of at least two lines, a narrow one and a broad one. Their fractional intensities (areas of Mössbauer lines) are 20% and 80% in satisfactory agreement with the weights as predicted by the model of 15% and 85%.

(2) If the spectra in other directions (from $\vartheta=15°$ to $\vartheta=90°$ relative to the [001] axis on a great circle via [113], [111] to [110]) are fitted with just *one* Lorentzian line, irrespective of their true shapes, the misfit [15] has a minimum in the [111] direction and a maximum in the [113] direction. This is plotted in Fig. 2(c). A comparison with Figs. 2(a) and 2(b) proves that the tendency of the misfit with crystal orientation follows the predictions of the model: largest misfit of the one-line fit in directions where the spectra consist of several lines with strongly differing widths.

This agreement is, of course, not a proof that the α-γ model is the uniquely correct model, but it provides a strong indication that the model correctly describes what is going on. To test how significant the agreement between the α-γ model and the data is, we have studied the diffusion in off-stoichiometric iron-richer alloys where—as is evident and exactly determinable from the Zeeman split room temperature spectra—a fraction of iron atoms must occupy antistructure sites on the β sublattice. Figure 4(a) shows a spectrum for a [113] oriented crystal of $Fe_{80}Si_{20}$ measured at 900 °C in comparison to a spectrum of Fe_3Si also in the [113] direction measured at 800 °C [Fig. 4(b)]. Two observations are worth noting.

First, the fractional intensity of the broad Mössbauer line in the [113] direction (50%) is much smaller than for Fe_3Si, in striking disagreement with the predictions from the α-γ model (85%). Even a measurement of an $Fe_{76}Si_{24}$ alloy, i.e., only 1 at.% off stoichiometry, gave only 70% broad line.

These results imply that the α-γ model of diffusion via the three iron sublattices indeed describes the physics only close to stoichiometry. For off-stoichiometry, jumps of the iron atoms must be described by a system of four instead of three coupled rate equations, but that description suffers from too many free parameters and is not unambiguous. To turn the tables, the failure of the theory for off-stoichiometry indicates how sensitive the data are for a description with the α-γ model. The good agreement for the stoichiometric alloy on the other hand therefore implies that the α-γ model can correctly describe the diffusion in that alloy.

Second, the diffusional line broadening for $Fe_{80}Si_{20}$

[Fig. 4(a)] becomes significant only at temperatures from 900 °C on and even then it is much less than for Fe_3Si at 720 °C [Fig. 3(b)] and even more so for Fe_3Si at 800 °C [Fig. 4(b)]. We do not show the Fe_3Si spectrum at 900 °C since it is so broad as to be hardly measurable.

From the diffusional line broadening the diffusivity D can be estimated (neglecting correlation between jumps) by inserting the jump frequency ν—deduced from the line broadening according to $\Gamma_p = \hbar \nu M_p$—into the Einstein-Smoluchowski equation $D = d^2\nu/6$ with d the jump distance (NN distance).

For Fe_3Si the resulting value of the diffusivity is strikingly high: It amounts to 5×10^{-13} m^2/s already at 720 °C, but a factor of 5 to 10 lower for the off-stoichiometric alloy $Fe_{80}Si_{20}$. That means that several hundred degrees below the solidus temperature (1200 °C) the diffusivity of iron atoms in stoichiometrically ordered Fe_3Si reaches values which in pure metals are attained only close to the solidus temperature. This, however, is not a totally unknown phenomenon for the DO_3 structure: In tracer diffusion studies Heumann *et al.* [16] and Wever *et al.* [17] have found comparably high diffusivities of Ni and Cu for alloy compositions close to Ni_3Sb, Cu_3Sb, Cu_3Al, and Cu_3Sn, respectively, which increased with increasing concentration of the minority component. They ascribed the high diffusivities to an anomalously high fraction of structural vacancies (several percent) on the Ni or Cu sublattices.

The principal results and conclusions of this work are the following:

(a) Mössbauer spectroscopy permits for the first time a check of a model for the jump mechanism in an ordered intermetallic alloy in an atomistic way: For the stoichiometric alloy Fe_3Si at 720 °C the dominating mechanism is jumps via vacancies on the three Fe sublattices (α-γ model). (b) For the nonstoichiometric alloys a strong contribution comes from diffusion via antistructure sites (Fe on the β sublattice). (c) The diffusivity of iron atoms in Fe_3Si is extraordinarily high at temperatures far below the solidus line and *decreases* strongly when leaving stoichiometry versus the iron rich side. (d) Finding the reason for the remarkably high vacancy concentration close to stoichiometry and for the fast change in diffusivity when leaving stoichiometry appears as a challenge for theory. (e) The method can pave the way for deciding between competing models for diffusion in ordered structures.

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