

Monte Carlo simulations of Mössbauer spectra in diffusion investigations

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We study the diffusion process via a vacancy mechanism in an A - B binary alloy with $B2$ order. The starting point of our Monte Carlo simulations were experiments done recently by Mössbauer spectroscopy and nuclear resonant scattering on stoichiometric $B2$ ordered FeAl, which yielded a nonobvious jump model for the Fe atoms, namely a priority of effective jumps to third-nearest-neighbor sites over second-nearest-neighbor sites. In the simulations we chose ordering energies that ensured a phase diagram close to that of the real Fe-Al system. Allowing the vacancy to exchange with nearest-neighbor atoms exclusively, we obtained a perfect agreement between simulation and experiment for the case when an interaction between the vacancy and the atoms was included. We suggest that the remarkable features of Fe diffusion arise from highly correlated vacancy paths, which are due to an interaction of the vacancy with locally disordered areas in the $B2$ lattice created by the vacancy movement itself. [S0163-1829(99)10113-9]

I. INTRODUCTION

The high-temperature behavior of intermetallic phases depends to a large extent on diffusion properties. But, in spite of great experimental and theoretical effort, no consistent picture of the diffusion process in ordered intermetallic alloys has emerged until now. In most cases, diffusion corresponds to the exchange between a vacancy and a neighboring atom. When such exchanges between nearest-neighbor (NN) vacancy-atom pairs take place, e.g., in a $B2$ alloy, a random walk of vacancies via NN sites destroys the $B2$ order. That is why highly correlated vacancy sequences of NN jumps with a final restoration of the local lattice order have been proposed in the past and were observed and studied by Monte Carlo (MC) simulations.¹

In the case of ordered stoichiometric FeAl, an example of a $B2$ ordered intermetallic alloy considered throughout this work, both tracer diffusion (i.e., a “macroscopic” method)² and quasielastic Mössbauer spectroscopy (QMS) (i.e., a “microscopic” method)³ indicated that diffusion is, indeed, mediated by NN exchanges between atoms and vacancies. Mössbauer spectroscopy measures the Lorentzian shaped absorption spectrum of gamma radiation. As a result of the diffusion of the atoms at high temperatures, the linewidth of the Lorentzian is broadened.⁴ This effect, called diffusional line broadening, depends fundamentally on the orientation of the single-crystalline sample and thereby provides information on the atomic jump vector. These QMS studies as well as tracer diffusion experiments² have motivated *ab initio* calculations of vacancy concentrations on both sublattices, which yielded an extremely low vacancy concentration on the Al sublattice.⁵ Recently, the QMS results on FeAl have been confirmed by the new, powerful method of nuclear

resonant scattering (NRS) of synchrotron radiation.^{6,7} While a possible explanation for the observed effects is the existence of divacancies,^{3,8} it remains open whether a simpler mechanism involving the motion of single vacancies may also describe the phenomena.

For this reason, we have revisited the problem using a Monte Carlo (MC) method where A and B atoms (corresponding to Fe and Al atoms, respectively) are distributed on a bcc lattice and diffusion is mediated by a single vacancy.^{9,10} The papers of Kutner and Kehr,¹¹ Fultz,¹² and Athènes *et al.*¹ may be regarded as roots of the present work. Kutner *et al.*¹¹ have studied the diffusion of tagged particles in lattice gases analyzing the intermediate scattering function, which is also experimentally accessible. Fultz¹² showed the influence of the relative difference in strength of the A atom interactions and the B atom interactions (which result in an effective interaction between the vacancy and the atoms) on the kinetics of ordering. Athènes *et al.* were the first to attempt to explain an experimental result by taking into account this difference in interaction. The upward curvature of the Arrhenius plot of the diffusion constant observed experimentally in some intermetallic alloys [see, e.g., investigations of Stolwijk *et al.* of CoGa (Ref. 13)] was explained in this way.

Our MC model is characterized by two types of interaction: the exchange interaction $J^{(k)}$ between A and B atoms in the k th neighbor shell, which is essentially determining the equilibrium properties, that is, the phase diagram of the alloy, and the interaction $U^{(k)}$ between the vacancy and A or B atoms in the k th neighbor shell. The main goal of our work was to study the influence of $U^{(k)}$ on the diffusion process and, in particular, to investigate whether a suitable set of interaction parameters can reproduce the QMS/NRS results.

Using this approach, we show in the present paper that a single vacancy performs sufficiently correlated jumps to explain the experiments.

II. THE MODEL

The model we use for performing the simulations has been introduced earlier,¹⁰ and we give only a short summary here. We consider a rigid bcc lattice with periodic boundary conditions. The lattice sites are occupied by an equal number of *A* atoms and *B* atoms, and one vacancy. Taking into consideration pair interactions $\varepsilon_{AA}^{(k)}, \varepsilon_{BB}^{(k)}, \varepsilon_{AB}^{(k)}, \varepsilon_{AV}^{(k)}$, and $\varepsilon_{BV}^{(k)}$ up to the third nearest neighbors ($k=1$ to 3), the Hamiltonian can be written—alternatively to the well known Ising form—as

$$\mathcal{H} = \mathcal{H}_0 - 2 \sum_{k=1}^3 [J^{(k)} n_{AB}^{(k)} + U^{(k)} n_{AV}^{(k)}], \quad (1)$$

where $J^{(k)} = \frac{1}{4}(\varepsilon_{AA}^{(k)} + \varepsilon_{BB}^{(k)} - 2\varepsilon_{AB}^{(k)})$ and $U^{(k)} = \frac{1}{4}(\varepsilon_{AA}^{(k)} - \varepsilon_{BB}^{(k)}) - \frac{1}{2}(\varepsilon_{AV}^{(k)} - \varepsilon_{BV}^{(k)})$. \mathcal{H}_0 is a constant term and $n_{XY}^{(k)}$ denotes the number of *XY* pairs of *k*th neighbors. This equation clearly shows that the constant ordering energies $J^{(k)}$ essentially determine the ordering between *A* atoms and *B* atoms, while the constants $U^{(k)}$ are responsible for the behavior of the vacancy. In particular, if $U^{(k)} > 0$ (respectively, $U^{(k)} < 0$), the vacancy prefers *A* atoms (respectively, *B* atoms) in its *k*th neighbor shell. For $U^{(k)} = 0$ there is no preference. The chosen ordering energies ($J^{(1)} = 1$, $J^{(2)} = 0.167$, $J^{(3)} = -0.208$) are taken from diffuse neutron scattering experiments and ensure a phase diagram close to that of the Fe-Al system,¹⁴ with an order-disorder phase transition at $T_c = 7.9J^{(1)}/k_B$ in the stoichiometric case. All the dynamics was introduced by the movement of the single vacancy jumping to a nearest-neighbor position. The jump probability was calculated according to the usual Metropolis rule, $P = \min[\exp(-\Delta E/k_B T), 1]$, where ΔE denotes the energy difference between the final and the initial state. Since no reliable information about the height of the energy barriers between two states is available yet, additional energy barriers were completely neglected, although we are aware that energy barriers might have influence on the diffusion process.

III. RESULTS

Figure 1 shows the results of the NRS experiment published in Ref. 7 together with the QMS results from Ref. 3. The QMS data which had been obtained with a stoichiometric FeAl sample orientated between the [001] and the [110] direction are shown by full circles. Each data point corresponds to a measured Mössbauer spectrum followed by the determination of its linewidth. The overall result, as shown in Fig. 1, is the diffusional line broadening as a function of the sample orientation, $\Gamma = \Gamma(\mathbf{Q})$, where \mathbf{Q} denotes the wave vector of the gamma radiation relative to the crystal axes, or equivalently, $\Gamma = \Gamma(\theta)$, with θ being the rotational angle of the sample between the [001] and the [110] direction, $0^\circ \leq \theta \leq 90^\circ$. Noticeable are the strong minima, i.e., smaller diffusional line broadening, in [111] and [113] directions and four smaller secondary minima, which are marked by arrows. The NRS experiments shown by open circles⁷

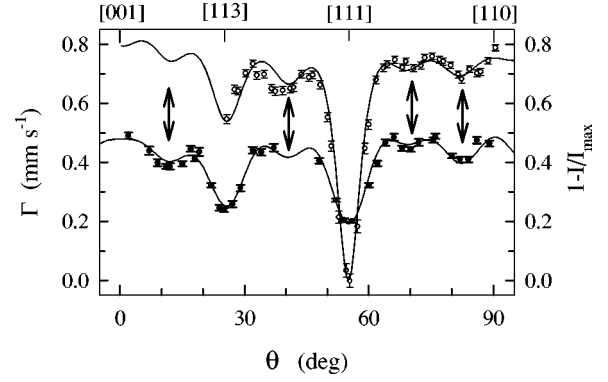


FIG. 1. Stoichiometric FeAl: orientational dependence of diffusional line broadening, $\Gamma(\mathbf{Q}) = \Gamma(\theta)$, from QMS experiment at 1065 °C (full circles, scale on the left side) and from an NRS experiment at 1030 °C (open circles, scale on the right side) normalized to be compared with QMS experiment. The two main minima are clearly visible, the four secondary minima are marked by arrows. Lines correspond to the analytical model [Eq. (2)] with the ratio of $W_3/W_2 = 1.9$ (see text).

completely confirmed the earlier data obtained by QMS.

For comparison with these data, we calculated Mössbauer spectra from our MC simulations in the following way: at a temperature comparable to the temperature of the QMS and NRS experiments ($T \approx 0.85T_c$), we waited until the system had attained thermal equilibrium, which was controlled by usual order parameters. In thermal equilibrium the determination of the autocorrelation function, $G_s(\mathbf{r}, t)$, of the *A* atoms was started. $G_s(\mathbf{r}, t)$ denotes the probability of finding an *A* atom, located at the origin at time $t=0$, at the lattice site \mathbf{r} after time t . $G_s(\mathbf{r}, t)$ is related to the experimentally obtained Mössbauer spectrum by a Fourier transformation in space (resulting in the so-called intermediate scattering function) and finally in time to arrive at a result comparable to QMS experiments. We calculated Mössbauer spectra at different orientations varying θ from the [001] to the [110] direction in steps of one degree. Finally, the simulated Mössbauer spectra went through the same evaluation procedure as the experimental ones, which means essentially a fit with a Lorentzian and a determination of its linewidth.

For the calculation it is necessary to convert simulation time [usually given in units of Monte Carlo steps (MCS), i.e., number of attempted interchanges per site] into physical time (given in seconds). We therefore computed the diffusion constant D_A in the model alloy by monitoring the movement of a tagged atom and determining its mean square displacement.¹⁰ The correspondence to the physical time is obtained by equating D_A with the experimentally determined diffusion constant.²

Figure 2 shows a comparison between the QMS data (full circles) and the results of MC simulations with different choices of the U parameters. If the U parameters in the MC simulation were set equal to zero for all three neighbor shells, i.e., $U^{(k)} = 0$, $k = 1, 2, 3$, the simulated diffusional line broadening, $\Gamma(\theta)$ (dashed line), agrees with the two main minima of the QMS data, but the further agreement is not satisfactory. However, with an appropriate choice of the U parameters, namely $U^{(1)} = 0$, $U^{(2)} = 8J^{(1)}$, and $U^{(3)} = -4J^{(1)}$, an almost perfect agreement between the QMS

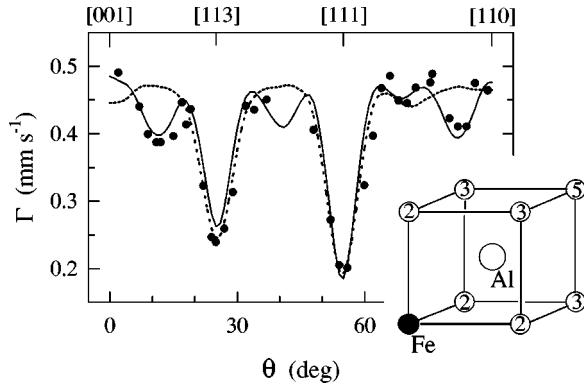


FIG. 2. Full circles: orientational dependence of diffusional line broadening, $\Gamma(\mathbf{Q}) = \Gamma(\theta)$, obtained by QMS experiment; the same data as the full circles in Fig. 1 but without error bars. Dotted line: MC simulations with $U^{(k)}=0$, $k=1,2,3$. Solid line: Monte Carlo simulation with $U^{(1)}=0$, $U^{(2)}=8J^{(1)}$, $U^{(3)}=-4J^{(1)}$. The inset shows different sites that the black Fe atom can reach with two consecutive nearest-neighbor jumps; numbers denote the neighbor shells of the sites.

data and the simulation results (solid line) is obtained: not only the two main minima, but also all four secondary minima are reproduced in the right way. Small deviations can be attributed to errors of the measurement, e.g., the width of the main minima, which is too small compared to the experimental data, is due to the inevitably inexact orientation of the FeAl sample.

IV. DISCUSSION

A first step in understanding our simulation results is to investigate a simple jump model, which is analytically tractable and motivated by the QMS experiments.³ The simple cubic sublattice of the bcc lattice with B2 order, which is mainly occupied by A atoms (respectively, B atoms) is denoted by A sublattice (respectively, B sublattice). We consider now a single A atom migrating on an otherwise empty bcc lattice via NN jumps with an infinitely short occupation time on the B sublattice. Two consecutive NN jumps can be integrated in one effective jump, which starts and ends on the A sublattice. As is shown in the inset of Fig. 2, one effective jump leads the atom back to the original site (zeroth-neighbor shell), or to the second-, third-, or fifth-neighbor shell.

According to Ref. 3, the line broadening Γ of this simple analytical jump model is given by

$$\Gamma(\mathbf{Q}) = \frac{2\hbar}{\tau} \left(1 - \sum_j W_j E_j \right). \quad (2)$$

Here τ denotes the mean residence time of an A atom on the A sublattice, W_j is the jump probability for an effective jump into a site in the j th neighbor shell and E_j —a kind of “structure factor” of the jump lattice—is defined as

$$E_j = \frac{1}{N_j} \sum_{n=1}^{N_j} \exp[i\mathbf{Q}\mathbf{I}_n^j], \quad (3)$$

where \mathbf{I}_n^j is the n th jump vector to a site in the j th neighbor shell and N_j is the number of lattice sites in the j th neighbor shell, e.g., $N_1=8$, $N_2=6$, etc. for a bcc lattice.

Under the special assumption that the jump probabilities from the B sublattice back to the A sublattice are equally distributed over all eight possible jump directions, the jump probabilities of an effective jump are as follows: for jumping back to the original site, $W_0 = \frac{1}{8}$; into a site in its second- or third-neighbor shell, $W_2 = W_3 = \frac{3}{8}$; and into a site in its fifth-neighbor shell, $W_5 = \frac{1}{8}$ (see the inset of Fig. 2).

The line broadening $\Gamma(\mathbf{Q}) = \Gamma(\theta)$ calculated with this choice of the W_j using Eq. (2) and the MC results for the case $U^{(k)}=0$, $k=1,2,3$ (Fig. 2) are almost identical. This shows that the computer simulations with $U^{(k)}=0$ can be well represented by a model where all jump probabilities to nearest-neighbor sites are equal, but the residence time of an A atom on the B sublattice is much smaller than on the A sublattice. Reasons for small differences are as follows: first, a short but not infinitely short occupation time of a site on the B sublattice, since an A atom has to wait at an antistructure site for the vacancy lending itself to a second jump back to its own sublattice; second, temporal and spatial correlation effects, as diffusion is mediated by exchanges with a single vacancy on an otherwise fully occupied lattice. Typical correlation effects are that an atom, which just exchanged with the vacancy, has a high probability for additional exchanges due to the proximity of the vacancy.

With the *ad hoc* assumption of a preference of effective jumps to third-nearest-neighbor sites over second-nearest-neighbor sites, specifically setting the ratio W_3/W_2 in our model equal to 1.9, Eq. (2) results in a line broadening $\Gamma(\mathbf{Q})$, which fits the experimental data very well (solid line in Fig. 1). This nonobvious jump model was reported in an earlier work,³ but its physical reasons remained unclear.

When $U^{(k)} \neq 0$ are allowed, we obtained with our MC simulations at least as good a fit of the QMS data (Fig. 2) as with the *ad hoc* model mentioned above. In order to understand this agreement between experiment and simulation, one has to ask how our choice of the U parameters, $U^{(1)}=0$, $U^{(2)}=8J^{(1)}$, and $U^{(3)}=-4J^{(1)}$, influences the movement of the vacancy and therefore the effective jumps of the A atoms. Because of the rather high simulation temperature and hence the large number of antistructure atoms (about 10%), the variety of different states of the system is immense. To simplify matters, let us reduce our considerations to a fully ordered state of the system and to minimal jump sequences of the vacancy, which allow an A atom to jump effectively on its own sublattice: the well known six-jump cycles (6JCs). We emphasize that these cycles are an extreme simplification. In fact, a manifold of different possible jump sequences is possible and the factorization into simple sequences has only an instructive purpose. One can distinguish between three different 6JCs, namely the so-called bended- and straight-(100) cycles, which lead to an effective jump to a second-nearest-neighbor site, and the (110) cycle, which leads to an effective jump to a third-nearest-neighbor site. Using Eq. (1), we calculated the maximal energy deviation from the energy of the totally ordered state for each 6JC. The statement that (110) cycles are energetically preferable to (100) cycles is equivalent to the inequality $-U^{(2)} + U^{(3)} < 0$. In our simulations we obtained good agreement with the

experimental data only in cases when this inequality was met clearly. Our choice of the U parameters results in $-U^{(2)} + U^{(3)} = -12J^{(1)}$, which corresponds to a maximal energy difference between (110) and (100) cycles of about $-25J^{(1)}$. Therefore the vacancy will prefer (110) cycles, leading to a jump model similar to the analytical model of Eq. (2) with $W_3/W_2 = 1.9$.

In summary, allowing the vacancy to exchange with nearest-neighbor atoms exclusively, we obtained a perfect agreement between simulation and experiment for the case when an interaction between the vacancy and the atoms was included. We understand our results in the following way: the vacancy migrates through the lattice destroying and restoring the lattice order. Since in our model the vacancy interacts with all atoms up to its third-nearest-neighbor shell, it particularly interacts with defects just created by its own movement, which causes different future paths of the vacancy to be energetically unequal. With our choice of the U parameters, the vacancy prefers such sequences of NN jumps, which result in effective jumps of A atoms preferably to third-nearest-neighbor sites.

With this attempt we have shown that interaction energies between atoms and vacancies play a crucial role in the microscopic diffusion mechanism of atoms in ordered alloys. Simulating the diffusion of Al atoms in the same way, we obtained a completely different orientational dependence of diffusional line broadening compared to that of the Fe atoms. Within our model we predict that the effective jumps of Al atoms are mainly to second-nearest-neighbor sites. The experimental determination of the Al diffusion mechanism will be hard to achieve, because none of the established quasi-elastic methods is capable of studying Al diffusion. In order to investigate correlated jumps of diffusion atoms experimentally, we therefore propose to investigate $B2$ alloys where both partners are accessible to methods which can determine the diffusional jump mechanism.

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