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KINETICS OF "ORDER-ORDER" RELAXATIONS IN Ni_3Al STUDIED BY COMPUTER SIMULATION

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The experimental investigations of "order-order" kinetics in Ni_3Al-based $L1_2$-ordered intermetallic compounds revealed the relaxation curves composed of two parallel processes considerably differing in relaxation rates. A simple Ising-type model based on a vacancy mechanism of atomic jumps was used to carry the Monte Carlo simulations of long-range-order relaxations in a binary A_3B system with $L1_2$-type superstructure. The simulated relaxation curves fitted weighted sums of two exponentials with significantly different relaxation times. It was found out that the fast relaxation process is controlled by the dynamics of the minority B-atom jumps.

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1. Introduction and general assumptions

By means of resistometry, two simultaneous processes were observed in "order-order" long-range-order (LRO) relaxations in Ni_3Al. The relaxation times of both processes significantly differed, but the related activation energies (reaching 4.6 eV) were nearly equal [1].

In the present study the Monte Carlo computer simulation technique (MC) was used in order to explain the origin of two LRO relaxation processes in $L1_2$ ordered A_3B binary systems.

The simulated $L1_2$ superlattice was composed of 256000 sites of A- and B-atoms. The fixed number of vacancies (usually 10) was initially distributed at random (vacancy formation process was not considered). The degree of LRO was determined by the parameter

$$\eta(t) = 1 - \frac{N_A^{(B)}(t)}{0.75 \times N^{(B)}}, \qquad (1)$$

where $N^{(B)}$ is the number of B-type sublattice sites, and $N_A^{(B)}$ is the number of A-antisites (A-atoms residing on the B-type sublattice).

The applied relaxation algorithm simulated the vacancy mechanism of elementary atomic jumps: an A- (or B-) atom chosen at random among the nearest--neighbours (nn) of a vacancy, jumps to this vacancy with a probability $P(\mathrm{A(B)})$, defined by the system configuration energy change ΔE due to a jump (standard Glauber-type term), and an appropriate saddle-point energy $E^{+}_{\mathrm{A(B)}}$ assigned exclusively to the jumping atom

$$P(\mathrm{A(B)}) = \frac{\exp\left[-\frac{\Delta E}{k_{\mathrm{B}}T}\right]}{1+\exp\left[-\frac{\Delta E}{k_{\mathrm{B}}T}\right]} \times \exp\left[-\frac{E_{\mathrm{A(B)}}}{k_{\mathrm{B}}T}\right], \tag{2}$$

where k_{B} is the Boltzmann constant and T is the absolute temperature. The energy $E^{+}_{\mathrm{A(B)}}$ selectively slows down the migration of A- (B-) atoms.

The configuration energy of the system is approximated by an Ising Hamiltonian with six energy parameters $V^{(1)}_{\mathrm{AA}}$, $V^{(1)}_{\mathrm{BB}}$, $V^{(1)}_{\mathrm{AB}}$, $V^{(2)}_{\mathrm{AA}}$, $V^{(2)}_{\mathrm{BB}}$ and $V^{(2)}_{\mathrm{AB}}$ describing pair-interactions of atoms in two coordination zones (marked by superscripts). Atom–vacancy and vacancy–vacancy pair-interaction energies are not taken into account. In order to approach the reality of $\mathrm{Ni_3Al}$ the parameters are evaluated according to the following criteria [2–4]:

$$V^{(j)}_{\mathrm{AA}} = 2 \times V^{(j)}_{\mathrm{BB}} \qquad [2], \tag{3a}$$

$$W^{(1)} = \frac{1}{4}\left[V^{(1)}_{\mathrm{AA}} + V^{(1)}_{\mathrm{BB}} - 2 \times V^{(1)}_{\mathrm{AB}}\right] = 0.035\ [\mathrm{eV}] \qquad [3], \tag{3b}$$

$$W^{(2)} = \frac{1}{4}\left[V^{(2)}_{\mathrm{AA}} + V^{(2)}_{\mathrm{BB}} - 2 \times V^{(2)}_{\mathrm{AB}}\right] = -0.0165\ [\mathrm{eV}] \qquad [4]. \tag{3c}$$

The sets of the pair-interaction energy parameters are thus definitely parameterized by two independent quantities: e.g. $V^{(1)}_{\mathrm{BB}}$ and $V^{(2)}_{\mathrm{BB}}$.

Each computer experiment began with a perfectly-ordered $\mathrm{A_3B}$ system (showing *no* antisite atoms) containing 10 vacancies. The perfect LRO corresponds to $T = 0$ K and $\eta = 1$. According to the jump algorithm the atomic configuration of the system is then relaxed to its equilibrium state at temperature $T_{\mathrm{f}} > 0$. The MC-time dependence of η, and MC-time dependence of *effective probabilities* $P_{\mathrm{A(B)}:i\to j}$ of A- or B-atom jumps from "i"- to "j"-type sublattice, are monitored. The $P_{\mathrm{A(B)}:i\to j}$ is defined as a number of jumps executed within a fixed MC-time period (usually 5000 MC steps per vacancy). About 75 snap-shots of the lattice per a single program run were saved on a disk for later use. All results were averaged over 20 independent lattices.

Thermal vacancies in $\mathrm{Ni_3Al}$ preferentially occupy the Ni-sublattice [2]. It was found out [4] that this behaviour is reproduced in the simulations only for a narrow range of pair-interaction parameters fulfilling the criteria (3). Consequently, the following values of $V^{(1,2)}_{ij}$ were assumed:

$$\text{set 1}: \quad V^{(1)}_{\mathrm{BB}} = -0.05\ \mathrm{eV} \quad \text{and} \quad +0.01\ \mathrm{eV} \le V^{(2)}_{\mathrm{BB}} \le +0.08\ \mathrm{eV}, \text{ or}$$

$$\text{set 2}: \quad V^{(1)}_{\mathrm{BB}} = -0.15\ \mathrm{eV} \quad \text{and} \quad -0.06\ \mathrm{eV} \le V^{(2)}_{\mathrm{BB}} \le +0.08\ \mathrm{eV}.$$

The simulations were carried out with saddle-point energies assigned either to A (majority) atoms ($E^{+}_{\mathrm{A}} > 0$, $E^{+}_{\mathrm{B}} = 0$) or to B (minority) ones ($E^{+}_{\mathrm{A}} = 0$,

$E_B^+ > 0$) — the same value of the saddle-point energy assigned to both atomic species results exclusively in an exponential slowing-down of the process.

2. Results

The simulation results reproduced the two experimentally observed parallel relaxation processes: weighted sums of *two* single exponentials fitted the best the $\eta(t)$ curves

$$\frac{\eta(t) - \eta_{EQ}}{\eta(t=0) - \eta_{EQ}} = C \exp\left(-\frac{t}{\tau_s}\right) + (1-C)\exp\left(-\frac{t}{\tau_l}\right), \qquad \tau_s \ll \tau_l. \tag{4}$$

Contrary to the experiment, however, only the long relaxation times τ_l obeyed the Arrhenius law.

The contribution of the fast relaxation process (i.e. the value of C) varied when particular parameters of the simulations were changed.

3.1. Simulations without saddle-point energies $E^+_{A(B)} = 0$

Figure 1 shows that the weight-factor C was generally lower in the case of $V_{BB}^{(1)} = -0.15$ eV than in the case of $V_{BB}^{(1)} = -0.05$ eV. Moreover, for both values of $V_{BB}^{(1)}$, C gradually decreased with an increase in $V_{BB}^{(2)}$.

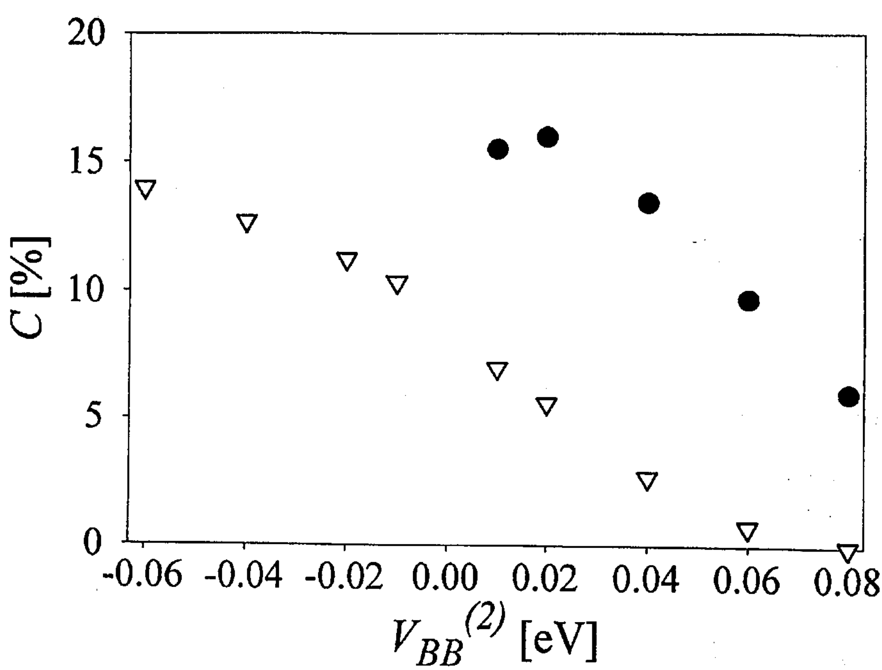

Fig. 1. The C factor as a function of $V_{BB}^{(2)}$. The results correspond to $E_A^+ = E_B^+ = 0$, the energy parameters arbitrary chosen from set 1 (•) and set 2 ($\bigtriangledown$) (see Sec. 3).

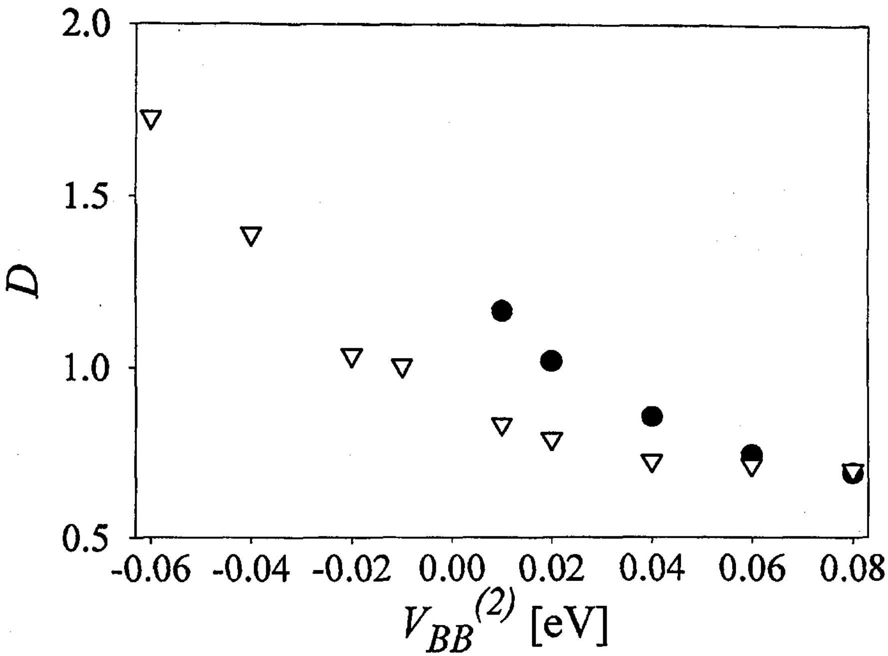

Fig. 2. The parameter D defined by Eq. (5) as a function of $V_{\mathrm{BB}}^{(2)}$. The results correspond to $E_{\mathrm{A}}^{+} = E_{\mathrm{B}}^{+} = 0$, the energy parameters arbitrary chosen from set 1 (•) and set 2 (▽) (see Sec. 3).

It was observed that in parallel with the systematic decrease in C, an increase in $V_{\mathrm{BB}}^{(2)}$ resulted in a gradual decrease in a parameter D defined as

$$D = \frac{P_{\mathrm{B:B}\rightarrow\mathrm{A}}}{P_{\mathrm{A:A}\rightarrow\mathrm{B}}} \qquad \text{(see Fig. 2).} \tag{5}$$

In the case of $C > 0.1$ the corresponding value of D exceeded 1, which meant a domination of B-atom jumps over the A-atom ones in the respective relaxations. On the other hand, the lowest values of C accompanied the domination of A-atom jumps ($D < 1$).

The decrease in D with increasing $V_{\mathrm{BB}}^{(2)}$ was naturally caused by a systematic variation of the averaged configurational energy changes ΔE corresponding to particular types of atomic jumps [4]: an increase in $V_{\mathrm{BB}}^{(2)}$ caused an increase in ΔE for B-atom jumps and a decrease in ΔE for A-atom jumps. Obviously, $P_{\mathrm{A(B)}:i\rightarrow j}$ is a decreasing function of ΔE (Eq. (2)).

3.2. Simulations with saddle-point energies: $E_{\mathrm{A(B)}}^{+} > 0$

Figure 3 shows the values of the weight-factors C resulting from the simulations performed for $V_{\mathrm{BB}}^{(1)} = -0.05$ eV and $V_{\mathrm{BB}}^{(2)} = 0.01$ eV at various combinations of E_{A}^{+} and E_{B}^{+} represented by their difference $\delta^{+} = E_{\mathrm{B}}{}^{+} - E_{\mathrm{A}}^{+}$. It is clearly visible that C decreased with decreasing δ^{+} (when A-atoms were immobilised).

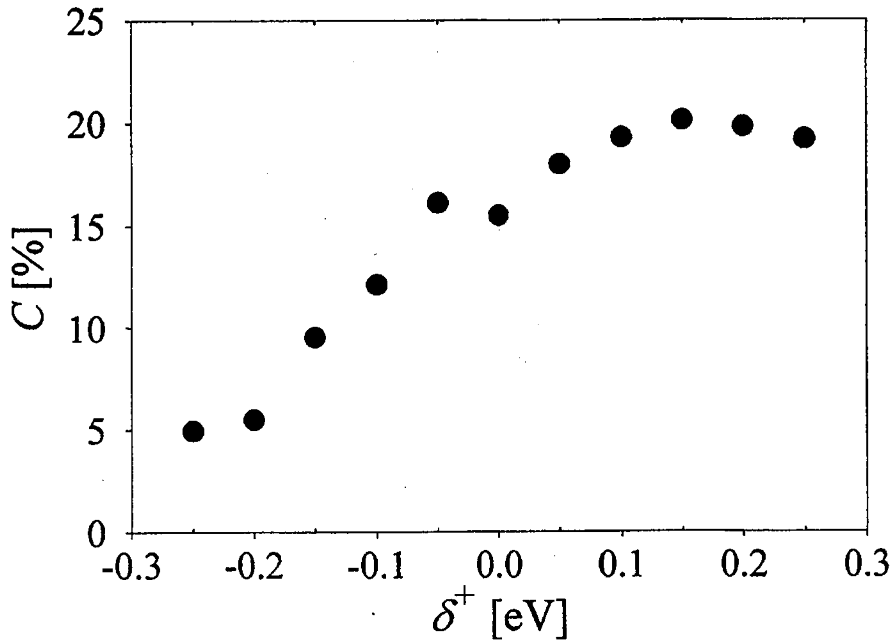

Fig. 3. The C factor as a function of δ^+.

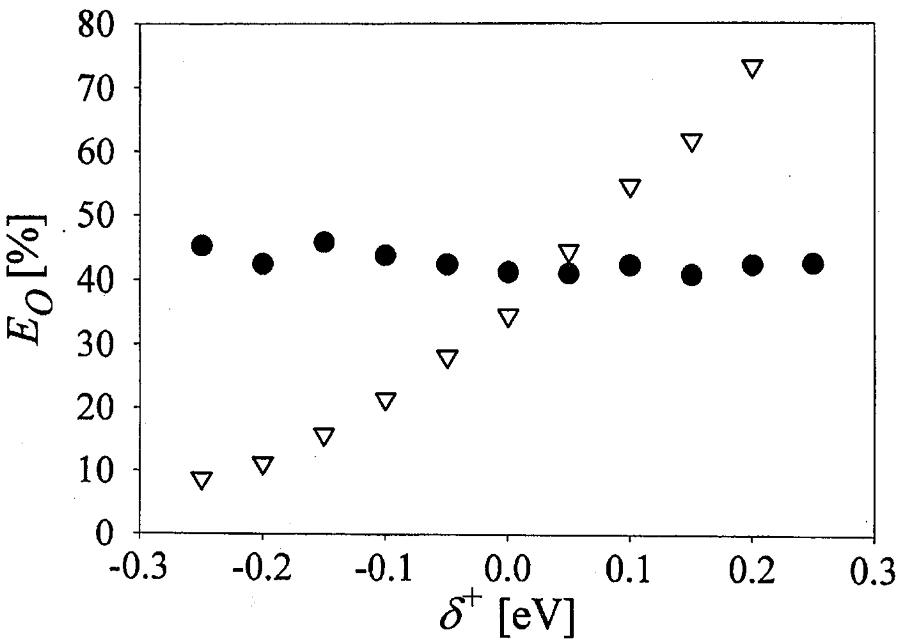

Fig. 4. The E_0^{A} ($\bullet$) and E_0^{B} (∇) as a function of δ^+.

It was found out that in parallel with the effect on C, the variation of δ^+ influenced the *efficiency* of B-atom jumps determined by the parameter E_0^{B}:

$$E_0^{\mathrm{B}} = \frac{P_{\mathrm{B:B}\to\mathrm{A}} - P_{\mathrm{B:A}\to\mathrm{B}}}{P_{\mathrm{B:B}\to\mathrm{A}}}, \tag{6}$$

which, in the same way as C, appeared an increasing function of δ^+ (Fig. 4). It is interesting that no effect was observed on the similarly defined A-atom jump efficiency parameter E_0^{A}. On the other hand, slowing-down of B-atoms ($\delta^+ > 0$) *increased* the value of the weight factor C, with respect to the case of $E^+_{\mathrm{A(B)}} = 0$ (Fig. 1), and significantly improved the efficiency E_0^{B}.

According to the recently proposed model [4], the sign and value of δ^+ controls directly the probability $P_{\mathrm{B:A}\to\mathrm{B}}$ of the reversed jumps of B-atoms back to their own sublattice. This probability, in turn, determines the value of E_0^{B}.

3.3. A- and B-antisite pair correlation (APC)

On the basis of the saved snap-shots of the lattice the value of APC defined as a probability of an A-antisite being a nearest-neighbour of a B-antisite was evaluated as a function of η and MC time. The results obtained for T = 1500 K and $E^+_{\mathrm{A(B)}} = 0$ and three different sets of energy (resulting in different weight factors C), are shown in Fig. 5.

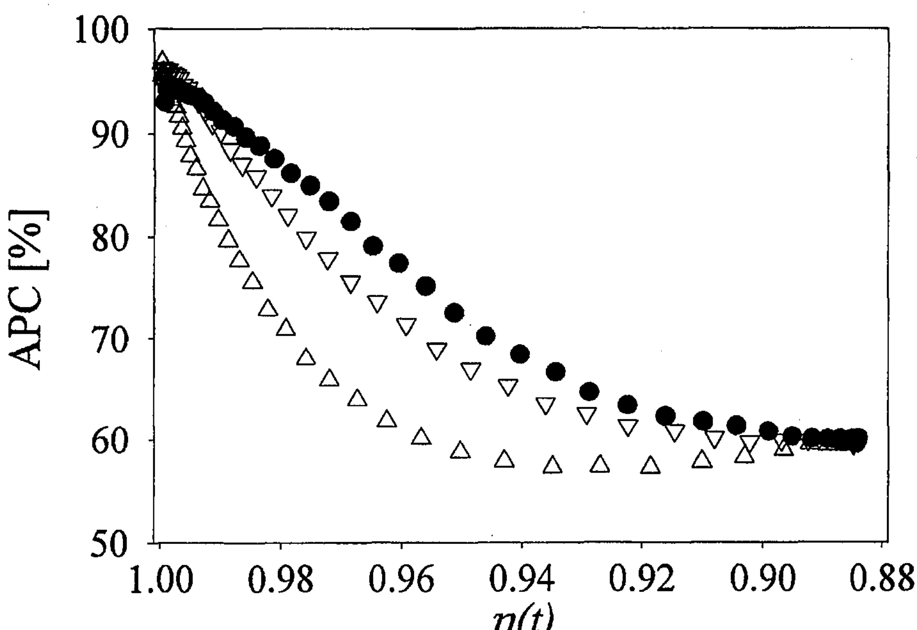

Fig. 5. The APC factor as a function of η: $C = 15.5\%$ (•), $C = 6\%$ (∇), $C = 0\%$ (Δ). Simulations done with $E_{\mathrm{A}}^+ = E_{\mathrm{B}}^+ = 0$.

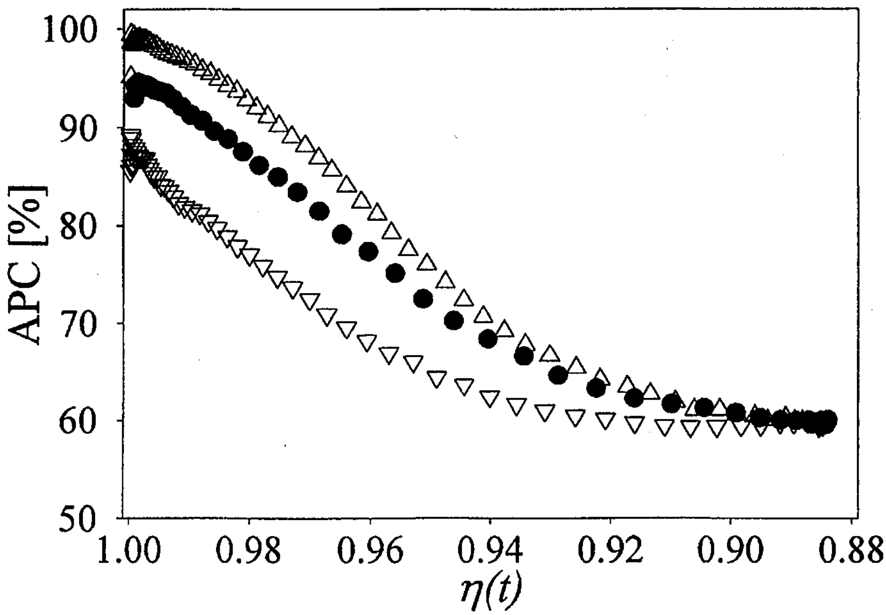

Fig. 6. The APC factor as a function of η: $\delta^+ = -0.25$ eV (∇), $\delta^+ = 0$ ($\bullet$), $\delta^+ = 0.25$ eV (Δ).

The APC reached always the same equilibrium value, but its kinetic paths were noticeably different in each case. During the relaxation the fraction of antisite pairs always decreased, but remained the larger, the larger was the value of the factor C. Similar result was obtained when C changed due to the variation of saddle-point energy values (Fig. 6).

4. Conclusions

The results of the MC simulations definitely indicated the correlation between the B-atom-jump dynamics and the contribution of the fast process to the "order-order" relaxations following an *increase* in temperature in an $L1_2$-ordered A_3B system. The simulated $\eta(t)$ curves showed different values of the weight factor C when the dynamics of B-atom jumps was varied by an appropriate change of the system parameters.

The previously proposed model [4] together with the present analysis of the evolution of the antisite-pair-correlations suggest that in the A_3B $L1_2$-ordered systems the degree of LRO decreases in two simultaneous processes: (i) nn pairs of A- and B-antisites form in a fast process controlled by B-atom jumps to nn vacancies, (ii) in a slow and complex cooperative process, involving all kinds of atomic jumps, further antisites are created and homogeneously distributed over the crystalline lattice (the nn antisite-pair density decreases).

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