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Atomic Migration on Ordering and Diffusion in Bulk and Nanostructured FePt Intermetallic

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“Order-order” kinetics was studied by means of in situ and quasi-residual resistometry in bulk polycrystal stoichiometric $L1_0$-ordered FePt and in epitaxially deposited FePt thin film. In addition, Fe diffusion in FePt thin film was examined by means of a combination of nuclear resonant scattering and nuclear tracer techniques. In bulk FePt, a discontinuous drop of the activation energy for chemical ordering (from 2.7-15 eV) was detected below 850 K, definitely away from the Curie point (735 K). The activation energy for Fe radiotracer diffusion in the FePt thin film studied below 900 K was found to be equal to 1.7 eV (in view of the value higher than 3 eV measured above 1100 K). Kinetic Monte Carlo simulations of order-order processes in bulk and nanolayered FePt reproduced their experimentally observed multi-time-scale character. In simulated FePt nanolayers, a reorientation of the initial *z*-variant $L1_0$ superstructure into a mixture of *x* and *y* variants was definitely a dominating process.

1. Introduction

The wide interest currently enjoyed by the $L1_0$-ordered FePt intermetallic stems from the high magnetic anisotropy and increased Kerr rotation, with both features following from the superstructure geometry, and making the intermetallic a promising candidate for magneto-optic recording media, especially as thin films.[1] The effects are directly connected with the chemical long-range order in the $L1_0$ superstructure, and it is thus of great importance to recognize in detail the conditions of superstructure formation enabling the understanding of ordering kinetics that are necessary when designing technologies of the system of interest.

Involving atomic migration, chemical ordering should always be considered with reference to diffusion, despite substantial differences between the two processes.[2] While tracer diffusion of the component atoms in FePt has for a long time been studied at temperatures above 1000 K,[3,4] a new method combining the advantages of nuclear resonant scattering (NRS) and conventional nuclear tracer techniques[5] appeared recently to be adequate for studying the process at lower temperatures and, thus, is applicable for the examination of epitaxially deposited thin film of FePt. Systematic investigations of ordering kinetics in FePt have been taken up only recently in a study of the present authors.[6]

The present article contains a review of the previous findings, and reports on the most recent experimental and simulation results.

2. Experimental

2.1 Samples

2.1.1 Bulk Material. An FePt polycrystal with nominal composition of 50 at.% Fe was cast in an arc furnace. The ingot was annealed for 10 h at 1223 K and was tested by x-ray diffraction (XRD), which revealed a highly ordered $L1_0$ tetragonal superstructure. Due to the lack of powdered material, only a rough estimation of the lattice parameters was possible, namely, $a \approx 0385$ nm and $c \approx 0371$ nm, which is in agreement with data from the literature.[7] Needle-like resistometry samples were spark-eroded from the ingot.

A more precise determination of the effective sample composition and additional verification of its homogeneity was performed by means of the electron microprobe and by checking the value of the Curie point T_{Currie} with in situ resistometry.[6] The resistometry result (Fig. 1) indicates that $T_{\text{Currie}} = (735 \pm 2)$ K, which is in agreement with the data from the literature for stoichiometric FePt.[8]

The value of T_{Currie} was checked before and after the measurement cycles, and its constant level was a probe for the structure stability and lack of any parasitic processes, which might occur in the sample due to long-time annealing at high temperatures.

2.1.2 FePt Multilayer. The FePt multilayer was grown by molecular beam epitaxy (MBE) codeposition at temperature of 823 K and was covered by 2 nm of Pt to avoid oxidation. The multilayer structure was Pt (20 Å)/[^{57}FePt (20 Å)/FePt (30 Å)] × 10/MgO (100) (inset in Fig. 5). The repeated bilayer structure was chemically homogeneous

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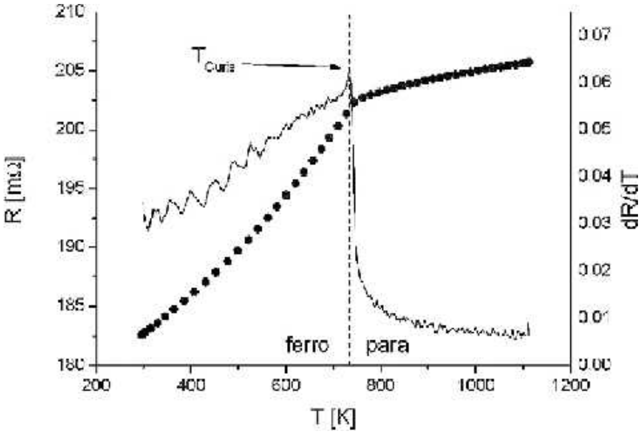

Fig. 1 In situ temperature dependence of electrical resistance of FePt

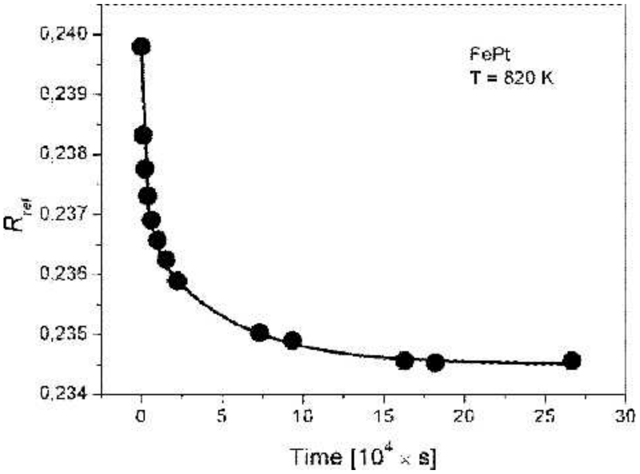

Fig. 2 Ordering $R_{\mathrm{rel}}(t)$ isotherm of FePt measured at 820 K

(i.e., all layers of FePt were of stoichiometric composition). The layer structure corresponded to the use of pure ^{57}Fe and natural Fe for every second layer, respectively. The chemical and magnetic orders were observed by XRD and Mössbauer spectroscopy as well as by conversion Mössbauer spectroscopy (CEMS). The z-variant L1_0 superstructure dominated in the material (i.e., the orientation of the c-axis of the unit cell was perpendicular to the surface of the thin film). 4.5(1)% mean (SD) of the layer volume was occupied by domains of x and y L1_0 variants (i.e., with the c-axis in the plane of the thin film), as detected by CEMS. In situ measurements of the electrical resistance of the multilayer also have been performed, and an anomaly on the $R(T)$ curve characteristic for T_{Currie} appeared smeared at about 700 K.

2.2 Measurement Technique

2.2.1 Resistometry. "Order-order" kinetics was studied by means of isochronal quasi-residual resistometry. The applied compact annealing-quenching line made it possible to perform isothermal annealing that were broken by quenching the sample in liquid nitrogen and measuring the quasi-residual electrical resistance $R_{77\mathrm{K}}$ without its reinstallation in a resistometric holder. All annealing were carried out in a 5 N Ar atmosphere at slight overpressure at temperatures stabilized within 0.5 K by means of the Eurotherm 2408/CP/system. The quasi-residual resistance measurements were performed using a classic four-probe method in relation to a resistance of a reference specimen, R_{ref}, residing all the time in a bath of liquid nitrogen.

Measured were the isothermal time evolutions of $R_{\mathrm{rel}} = R_{77\mathrm{K}}/R_{\mathrm{ref}}$ at temperatures T_{f} following a sudden change of temperature by $\Delta T = T_{\mathrm{f}} - T_{\mathrm{i}}$, where both the initial temperature (T_{i}) and the final temperature (T_{f}) were lower than the order-disorder transition point. The R_{rel} evolutions reflected the corresponding evolutions of the degree of long-range order (LRO).[2] The annealing temperature T_{f} was kept constant until R_{rel} saturated at a constant level. Then, it was changed again upward or downward by ΔT and the subsequent R_{rel} isotherm was measured.

2.2.2 Grazing Incidence Synchrotron Reflection (GINRS). The measurement of diffusion coefficients in the FePt multilayer was done at the European Synchrotron Radiation Facility by means of the ID22 device in air at room temperature for vacuum preannealed samples. The setup was similar to that used in conventional NRS experiments in grazing incidence geometry.[5] X-ray spectra were measured after annealing the FePt multilayer at temperatures of 773, 823, 848, and 873 K for time periods between 3600 and 7200 s. As successive annealing takes place, the isotopic bilayer structure is smeared out. The resulting intensity loss of the nuclear superstructure Bragg peak was observed. Information about diffusion coefficients for a certain annealing temperature was directly calculated from the decrease of intensity.[9]

3. Experimental Results

3.1 Order-Order Kinetics in Bulk FePt

The $R_{\mathrm{rel}}(t)$ isotherms of FePt were measured at temperatures between 700 and 950 K; a typical curve is shown in Fig. 2.

Similarly, as in previous papers,[6] the isotherms were analyzed by fitting weighted sums of two exponentials:

$$\frac{R_{\mathrm{rel}}(t) - R_{\mathrm{eq}}}{R_{\mathrm{rel}}(t=0) - R_{\mathrm{eq}}} = C \cdot \exp\left(-\frac{t}{\tau_{\mathrm{S}}}\right) + (1-C) \cdot \exp\left(-\frac{t}{\tau_{\mathrm{l}}}\right);$$

$$R_{\mathrm{eq}} = R_{\mathrm{rel}}(t \to \infty); \qquad \tau_{\mathrm{l}} > \tau_{\mathrm{S}}; \qquad 0 \le C \le 1 \qquad \text{(Eq 1)}$$

indicating the two-time-scale character of order-order kinetics. The weight factor C oscillated around 0.5.

The Arrhenius plot of the τ_{S} and τ_{l} relaxation times is shown in Fig. 3:

The most striking feature is a dramatic discontinuous change of ordering kinetics at 14 eV^{-1} < $(k_{\mathrm{B}}T)^{-1}$ < 14.5 eV^{-1} (corresponding to 800 K < T < 830 K). The change consisted of: (a) a drop of the activation energy E_{A} of the slow component of ordering kinetics by almost 50% (from 2.7 eV at T > 800 K to 1.5 eV at T < 830 K); and (b) an anomaly (break) of the temperature dependence of the equi-

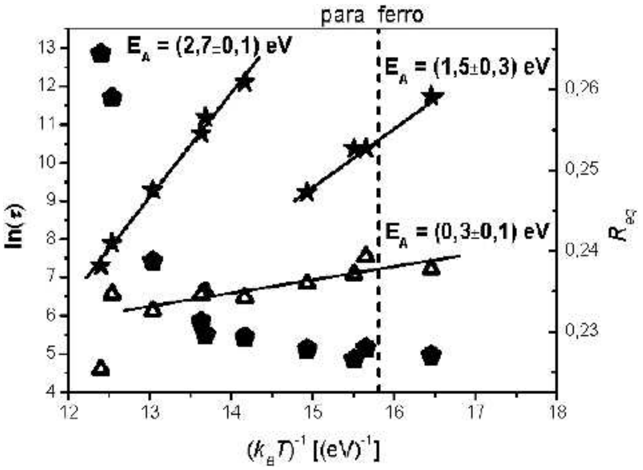

Fig. 3 Arrhenius plot of the relaxation times of order-order kinetics in FePt; open triangles, τ_S; solid asterisks, τ_l. $(k_BT)^{-1}$ dependence of R_{eq} is traced by solid pentagons

librium value R_{eq} of the quasi-residual electrical resistance. It is remarkable that the effect applied exclusively to τ_l (i.e., the slow relaxation component). The fast component, in turn, showed a very low activation energy of 0.3 eV, which was the same all over the temperature range of the measurements.

3.2 X-Ray Diffraction and Resistometric Examination of the FePt Multilayer

The structure of the multilayer Pt (20 Å)/[^{57}FePt (20 Å)/FePt (30 Å)] × 10/MgO annealed for 5 h at 823 K was examined by means of x-ray surface diffraction (grazing incidence geometry), and the diffraction pattern was compared with the one measured for the as-deposited material. In both cases, Pt and FePt diffraction lines were observed; however, after the annealing at 823 K the FePt diffraction lines were systematically shifted toward higher angles. After Klemmer et al.,[10] this might surprisingly indicate an increase of Fe content in FePt and, therefore, an escape of Pt atoms from FePt.

In situ resistometry of the as-deposited multilayer step-annealed at temperatures between 660 and 760 K showed a linear decrease of the resistance R at the subsequent annealing temperatures. The Arrhenius plot of the corresponding $R(t)$ slopes was linear and yielded a mean (± SD) activation energy of 1.8 ± 0.2 eV.

3.3 Fe Radiotracer Diffusion in FePt Multilayer

The results for iron (Fe) diffusion in L1$_0$ FePt thin film are summarized in an Arrhenius plot in Fig. 4.

The activation energy for Fe diffusion along the c-axis is about 1.65(29) eV. The diffusion coefficient and activation energy differ from the extrapolation from high-temperature tracer data. The authors suggest a change in the importance of different diffusion mechanisms at different temperature ranges as an explanation for the results (e.g., highly correlated six-jump cycles at low temperature and an antistructural bridge at high temperatures) as diffusion mechanisms.

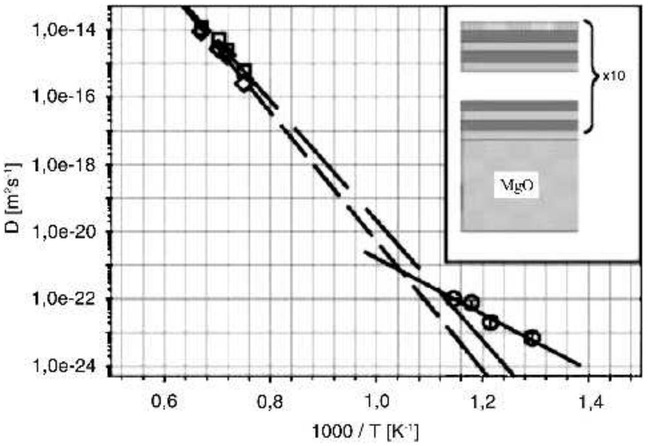

Fig. 4 Arrhenius plot for Fe diffusion in a Pt (20 Å)/[^{57}FePt (20 Å)/FePt (30 Å)] × 10/MgO (100) thin film, as shown on the inset. The GINRS data for the diffusion of Fe along the c-axis (open circles) are compared with recent radiotracer data for diffusion along the a-axis (open squares) and the c-axis (open diamonds), respectively.[11] The corresponding lines are guides for the eye.

Note that due to the geometry of the GINRS setup only Fe jumps perpendicular to the sample plane can be observed. Because the sample was prepared in z-variant, the performed experiment gives exclusive access to the diffusion of Fe along the c-axis of the FePt L1$_0$ structure.

4. Monte Carlo Simulations

4.1 Method

The simulated samples of an L1$_0$-ordered AB binary stoichiometric system consisted of 40^3 face-centered cubic cells. A single vacancy was introduced into the system by emptying one site that was randomly chosen. Similar to the method used in previous studies,[12] Glauber dynamics with the vacancy mechanism of atomic jumps has been used in the simulations. Pair interactions of Fe and Pt atoms in two coordination shells were evaluated on the basis of ab-initio calculations combined with the cluster-expansion technique.[13] The simulated isothermal order-order kinetics at temperatures T_{equ} followed sudden changes of temperature from T_{beg} to T_{equ}.

Among the monitored parameters were: a Bragg-Williams-type LRO parameter (η); specific short-range order parameters; and frequencies of particular atomic jumps. The simulated system showed a discontinuous order-disorder transition at a T_C close to the experimental one.

Thin layers of FePt with different variants of L1$_0$ superstructure were simulated by removing periodic boundary conditions in a direction parallel (z variant) or perpendicular (x and y variants) to the c-axis. The layer thickness was varied in a way that the vacancy concentration was fixed.

The simulations of bulk samples were performed for T_{beg}

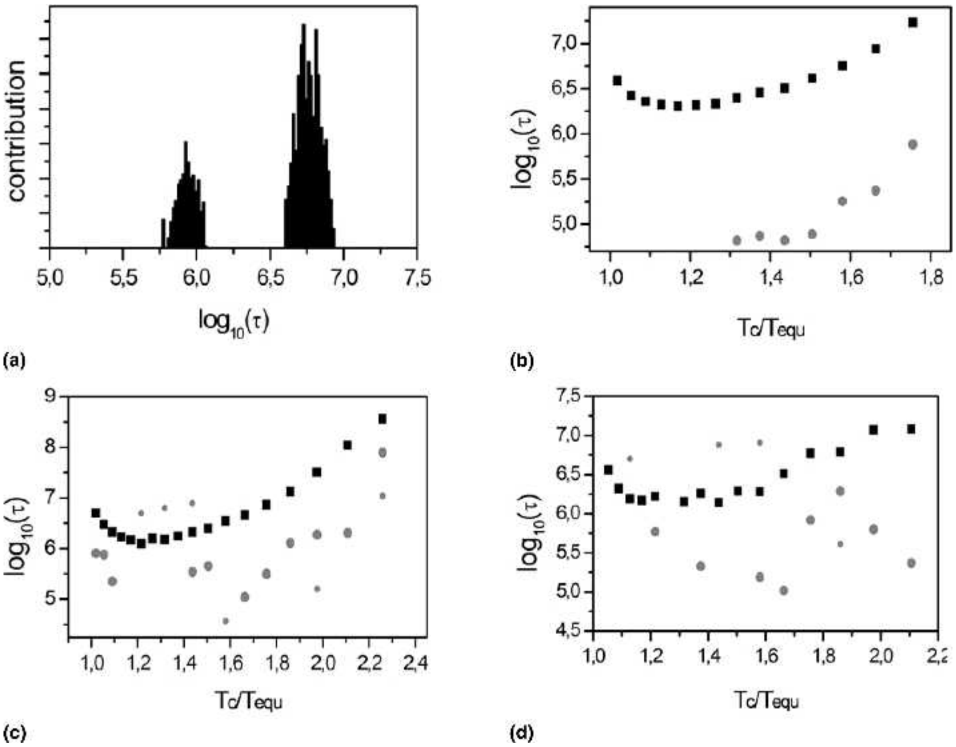

Fig. 5 (a) Example of a Laplace transform of the simulated $\eta(t)$ isotherm: contribution of the relaxation times τ to the ordering relaxation. (b-d) Arrhenius plots of the dominating (solid squares) and remaining (solid circles) relaxation times τ in FePt following from Laplace transforms of isotherms. (b) Disordering, $T_{\text{beg}} = 0$ K; (c) Disordering, $T_{\text{beg}} = T_{\text{equ}} - 100$ K; and (d) ordering, $T_{\text{beg}} = T_{\text{equ}} + 50$ K.

= (1) 0 K, (2) $T_{\text{equ}} - 100$ K, and (3) $T_{\text{equ}} + 50$ K. For thin layers only 0 K → T_{equ} simulations were performed, and the atoms were forced to remain in the initial box.

4.2 Results: Bulk Samples

It was observed that the vacancy resided preferentially on the Fe sublattice, which favored Pt-antisite diffusion within the Fe sublattice. However, in contrast with, for instance, Ni_3Al,[12] the ordering/disordering atomic jumps executed between different sublattices always outnumbered the antisite migration.

Laplace transforms of the η (Monte Carlo time) isotherms (Fig. 5a) revealed the multi-time-scale character of the order-order relaxations. Although the effect was definitely T_{equ}-dependent, and was usually different for ordering and disordering relaxations corresponding to the same T_{equ}, one particular relaxation component always dominated.

Due to the wide T_{equ} domain of critical slowing-down, the relaxation times τ corresponding to the main relaxation component obeyed the Arrhenius law only at low T_{equ} (Fig. 5b-d).

4.3 Results: Thin Layers

As reported in a previous communication,[14] two processes were observed in simulations of samples ordered initially in the z-variant $L1_0$ superstructure (Fig. 6): (a) homogeneous disordering generating antisites within the volume of the layer (as in the bulk material); and (b) the formation of x and y $L1_0$-variant domains nucleating at the Fe surface and growing inward the layer.

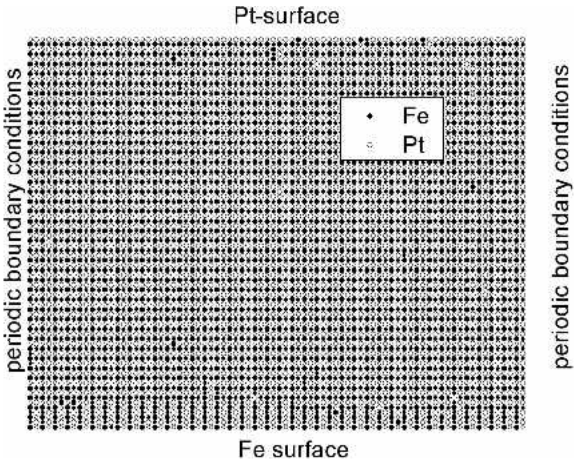

Fig. 6 Projection of the nth (larger circles) and $(n + 1)$th (smaller circles) (010)-type atomic planes in $L1_0$-ordered FePt layer disordering at $T_{\text{equ}} = 1200$ K

Experimental evidence of the effect has recently been reported.[15] The Pt surface layer definitely stabilized the initial variant of the $L1_0$ superstructure, and the phenomenon is now a subject of extensive investigation.

The disordering in FePt layers that was initially ordered in the *x* variant of $L1_0$, occurred similarly to that in the bulk material. The process was, however, slowed down while decreasing the layer thickness.

5. Conclusions

- The discontinuous change of order-order kinetics in bulk FePt at about 800 K correlates with the change of Fe* diffusion kinetics in a multilayer of this system reflected by the difference between the activation energy for Fe* diffusion measured classically above 1000 K (about 3 eV) and recently around 800 K by means of GINRS reflection (1.65 eV). In situ resistometry of the multilayer revealed a linear process showing the activation energy of the same range.
- Monte Carlo simulations of order-order kinetics in $L1_0$-ordered bulk FePt reproduce the experimentally evidenced multi-time-scale character of the relaxations and may elucidate the atomistic origin of the phenomenon.[6] The applied simulation algorithm based on the Glauber dynamics implemented with the vacancy mechanism of atomic jumps appeared very efficient and adequate in the presented study. As was demonstrated,[16] the application of other algorithms, and those involving saddle point energies, leads to results showing perfect qualitative agreement (multi-time-scale relaxations) with the ones obtained within Glauber dynamics.
- Analogous Monte Carlo simulations of an $L1_0$-ordered thin layer of FePt revealed a process of spontaneous reorientation of the initial *z*-variant $L1_0$ superstructure into a system of *x*-variant and *y*-variant domains.

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References

1. A. Cebollada, D. Weller, J. Sticht, G.R. Harp, R.F.C. Farrow, R.F. Marks, R. Savoy, and J.C. Scott, Enhanced Magneto-Optical Kerr Effect in Spontaneously Ordered FePt Alloys: Quantitative Agreement between Theory and Experiment, *Phys. Rev. B: Condens. Matter,* Vol 50, 1994, p 3419-3422
2. R. Kozubski, Long-Range Order Kinetics in Ni_3Al-Based Intermetallic Compounds with $L1_2$-type Superstructure, *Prog. Mater. Sci.,* Vol 41, 1997, p 1-59
3. J. Kucera and B. Million, Diffusion of Platinum in the Fe-Pt System, *Phys. Status Solidi A,* Vol 31, 1975, p 275-282
4. Y. Nose, T. Ikeda, H. Nakajima, K. Tanaka, and H. Numakura, Fe Tracer Diffusion in $L1_0$ Ordered FePt, *Mater. Res. Soc. Symp. Proc.,* Vol 753, 2003, p BB5.36.1-6
5. A. Gupta, M. Gupta, S. Chakravarty, R. Rueffer, H.C. Wille, O. Leupold, and M. Horisberger, Study of Self-Diffusion of Iron in Amorphous Fe-Zr Alloys Using Nuclear Resonance Reflectivity, *Proceedings to Workshop on Nuclear Resonant Scattering* March 2004, ESRF Grenoble
6. R. Kozubski, M. Kozlowski, V. Pierron-Bohnes, and W. Pfeiler, "Order-Order" Relaxations in Intermetallics, *Z. Metallkd.,* Vol 95, 2004, p 880-887
7. K. Wanatabe, Permanent Magnet Properties and Their Temperature Dependence in the Fe-Pt-Nb Alloy System, *Trans. Jpn. Inst. Metall.,* Vol 32, 1991 p 292-298
8. Y. Nose, A. Kushida, T. Ikeda, H. Nakajima, K. Tanaka, and H. Numakura, Re-Examination of Phase Diagram of Fe-Pt System, *Mater. Trans., JIM,* Vol 44, 2003, p 2723-2731
9. H.E. Cook and J.E. Hillard, Effect of Gradient Energy on Diffusion in Gold-Silver Alloys, *J. Appl. Phys.,* Vol 48, 1969, p 2191-2198
10. T.J. Klemmer, N. Shukla, C. Liu, X.W. Wu, E.B. Svedberg, O. Mryasov, R.W. Chantrell, D. Weller, M. Tanase, and D.E. Laughlin, Structural Studies of $L1_0$ FePt Nanoparticles, *Appl. Phys. Lett.,* Vol 81, 2002, p 2220-2222
11. A. Kushida, K. Tanaka, and H. Numakura, Chemical Diffusion in $L1_0$-Ordered FePt, *Mater. Trans., JIM,* Vol 44, 2003, p 59-62
12. P. Oramus, R. Kozubski, V. Pierron-Bohnes, M.C. Cadeville, and W. Pfeiler, Monte Carlo Computer Simulation of "Order-Order" Kinetics in $L1_2$-Ordered Ni_3Al Binary System, *Phys. Rev. B: Condens. Matter,* Vol 63, 2001, p 174109/1-14
13. T. Mohri and Y. Chen, First Principles Investigation of $L1_0$-Disorder Phase Equilibrium in Fe-Pt System, *Mater. Trans., JIM,* Vol 43, 2002, p 2104-2109
14. M. Kozlowski, R. Kozubski, V. Pierron-Bohnes, and W. Pfeiler, $L1_0$-Ordering Kinetics in FePt Nano-Layers: Monte Carlo Simulation, *Comput. Mater. Sci.,* Vol 33, 2005 p 287-295
15. Ch. Issro, W. Püschl, W. Pfeiler, P. Rogl, W. Soffa, R. Kozubski, and V. Pierron-Bohnes, Temperature Driven Changes of Order and Magnetism in FePd Thin Film and Thin Foil, *Scripta Mater.,* Vol 53, 2005, p 449-454
16. P. Oramus, R. Kozubski, V. Pierron-Bohnes, M.C. Cadeville, C. Massobrio, and W. Pfeiler, Computer Simulation of Long-Range Order Relaxation in Homogeneous Systems, *Mater. Sci. Eng. A,* Vol 324, 2002, p 11-15