Atomic Ordering and Magnetism in $L1_0$ Ordered FePd Alloys

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Intermetallic compounds due to their promising corrosion resistance and high-temperature mechanical strength give hope for their application as high-temperature structural materials. Intermetallics of $L1_0$ type structure in recent years in addition have attracted great interest as potential recording media. These alloys are ferromagnetic and display marked mechanical and magnetic anisotropy with the tetragonal *c*-axis of the ordered domains as the ''easy axis'' of magnetization. High-density magnetic recording may be achieved by a preferential domain orientation with the *c*-axis perpendicular to the surface, if these materials can be stabilized as low-dimensional magnetic structures. Knowledge of kinetic parameters that determine alloy stability is essential for alloy design, technical application, and performance of materials. We used FePd as a model system for this class of $L1_0$-ordered intermetallics and have studied the changes of long-range order during heat treatments in the bulk and in thin films produced by different techniques. Results of X-ray diffraction (XRD), resistivity measurement, Mößbauer spectroscopy, and measurement of magnetization in both geometries are compared.

I. INTRODUCTION

INTERMETALLIC compounds below a characteristic ordering temperature $T_{O/D}$, frequently right up to the melting point, show a tendency to distribute the different sorts of atom preferentially on certain sublattices of the original atomic lattice of the disordered alloy. This state of long-range order (LRO) is a consequence of the atomic interaction energies, in this case, favoring unlike atoms as nearest neighbors. The new crystal structure can remain unchanged (for example, in Ni_3Al, where the ordered $L1_2$ structure fully corresponds to the original fcc structure) or can be distorted as in $L1_0$-ordered TiAl, where the fcc structure changes into tetragonal. In particular, ferromagnetic $L1_0$-ordered alloys display a marked mechanical and magnetic anisotropy with the tetragonal *c*-axis of the distorted ordered domains being the ''easy axis'' of magnetization. Due to this high magnetic anisotropy, these alloys have a potential as magnetic and magneto-optical recording media, and a very high recording density may be achieved, if these materials can be stabilized as low-dimensional magnetic structures.[1,2]

It is known that atom jump processes can be considerably changed in low-dimensional structures such as thin films due to increased crystal defect density and by processes of surface diffusion or interdiffusion with substrate, buffer, or capping layers that may start at comparatively low temperatures. Having investigated ordering kinetics in massive samples, we recently began to apply our successful techniques to intermetallic thin films. Within the interesting group of $L1_0$-ordered ferromagnetic alloys, FePd, FePt, CoPt, with their mechanically and magnetically anisotropic ordered phases, we used FePd as a model system. It shows a lower order-disorder transition temperature than FePt and CoPt but a similar or even larger saturation magnetization.[3,4]

In view of the great technological importance, there is only little detailed knowledge on the basic atomistic properties of these interesting alloy films. Therefore, the current study pays attention to the kinetics of ordering and the corresponding changes of the magnetic and structural properties of FePd alloy films. We compare results of X-ray diffraction (XRD), resistivity measurements, Mößbauer spectroscopy, and measurements of magnetization hysteresis loops in two geometries: in cold-rolled thin foils and two types of thin films. FePd films were either sputtered on Si or deposited by molecular beam epitaxy (MBE) on MgO and investigated in the as-prepared state and after specific heat treatments.

The detailed knowledge of ordering kinetics in this model system shall give us indications on the limits of alloy stability, which is a precondition for materials design and alloy development.

II. EXPERIMENTAL

FePd polycrystalline foil was cold rolled at room temperature (RT) to a thickness of about 10 μm from bulk

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material. This bulk polycrystalline material was alloyed by arc melting in an argon atmosphere with a nominal concentration of 50 at. pct Fe and 50 at. pct Pd by the Department of Materials Science and Engineering, University of Pittsburgh. By a detailed investigation using electrical resistivity measurement and scanning calorimetry, the actual composition was determined to be 49.8 at. pct Fe and 50.2 at. pct Pd with an accuracy of ± 0.5 at. pct.[5]

A 50-nm FePd thin film (composition 50 ± 5 at. pct Fe) was nonepitaxially deposited at RT on Si(100) substrate by dc and rf magnetron cosputtering.

Epitaxial FePd thin films (composition 50 ± 2 at. pct Fe) were deposited on MgO(001) substrates by MBE at a substrate temperature of 773 K. A 50-nm epitaxial FePd film was grown either without buffer, with or without capping layer, or with both buffer (30 nm) and capping (5 nm) layers. For more details of sample preparation, refer to Reference 5.

During the annealing treatments in vacuum at a pressure below 3×10^{-6} Torr between 473 and 873 K, the samples were wrapped in a Nb foil to protect them from oxidation.

The structural state of order was investigated by XRD using Cu K_α radiation. Electrical resistivity was measured in-plane with van-der-Pauw geometry on samples directly immersed in liquid nitrogen (REST). Mößbauer spectroscopy was studied at RT using a 10 mCi ^{57}Co source in a Rh matrix. The magnetic properties were monitored with an alternating gradient field magnetometer either perpendicular or parallel to the film plane. Changes in size of magnetic domains were studied by magnetic force microscopy (MFM) perpendicular to the film surface.

III. CHANGES OF ORDER AND MAGNETISM IN THE COLD-ROLLED THIN FOIL

Isochronal annealing ($\Delta T = 20$ K, $\Delta t = 1200$ s) of massive specimens in the as-rolled state resulted in a higher degree of LRO than applying the same heat treatment to fully recrystallized samples.[6] Figure 1 shows the shift of the resistivity "equilibrium line" to lower resistivity values for the rolled specimen. This surprising finding could be explained by differences in microstructural changes during the "combined reaction"[7] of defect annealing and ordering when starting from the as-deformed state.[8]

As a bulk limit, a FePd foil cold rolled to about 10 μm was investigated prior to thin film material by REST measurements, XRD, Mößbauer spectroscopy, and measurement of magnetization hysteresis loops. Results of resistivity measurement during isochronal annealing ($\Delta T = 20$ K, $\Delta t = 1200$ s) are shown in Figure 2.

The usual interpretation of the curve in Figure 2 is that, as soon as atomic mobility is enabled *via* a vacancy mediated atomic diffusion process during heating (▲), two (simultaneous) processes start to run: defect recovery and long-range ordering. When defect recovery is completed and when the state of order of the sample corresponds to the equilibrium value for the current annealing temperature, a minimum in the curve is observed. For higher annealing temperatures, the degree of order decreases in thermodynamic equilibrium (increase of resistivity). When subsequently *decreasing* the annealing temperature isochronally (▼), the points reflect the change of LRO with temperature

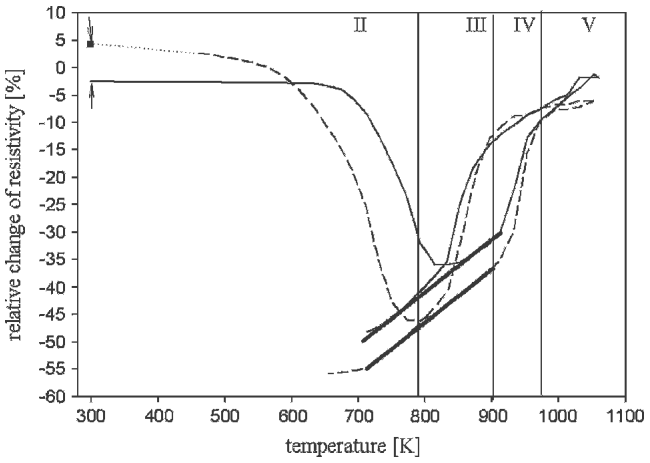

Fig. 1—Relative change of resistivity of massive FePd during isochronal annealing ($\Delta t = 1200$ s, $\Delta T = 20$ K) as a function of temperature. Full line: fully recrystallized sample; and dashed line: sample cold rolled to ≅60 pct thickness reduction. Thick lines: sample states in thermal equilibrium ("equilibrium line") of recrystallized and deformed samples.

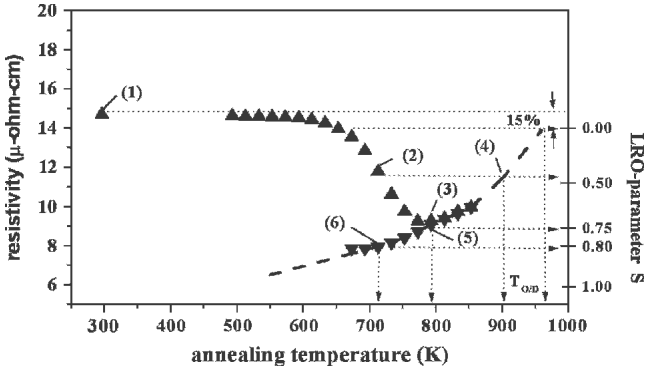

Fig. 2—Changes of REST as a function of temperature of a polycrystalline FePd foil (10-μm thickness). Initial state (1): as-rolled; states (2) through (4): isochronal annealing ($\Delta T = 20$ K, $\Delta t = 1200$ s); and states (5) and (6): 40 h at 793 and 713 K, respectively. Dashed line: equilibrium curve reflecting changes of LRO parameter in thermodynamic equilibrium (scaling on the right). Arrows correlate with XRD measurements (refer to text).

in thermodynamic equilibrium as long as atomic mobility is high enough (not frozen in). Figure 3 represents XRD measurements at the temperatures indicated in Figure 2 showing the change in the degree of LRO of the as-rolled foil with isochronal annealing temperature. Starting from the disordered state (1) ($S = 0$, Figure 3(1)), LRO develops after annealing for 1200 seconds at 713 K (state (2), $S = 0.49$, Figure 3(2)), 793 K (state (3), $S = 0.69$, Figure 3(3)), and 900 K (state (4), $S = 0.65$, Figure 3(4)). Long-time annealing for 40 hours at 793 K (state (5)) changes the LRO parameter only slightly ($S = 0.75$, Figure 3(5)), whereas 40 hours at 713 K (state (6)) results in a marked increase of order up to a value of $S = 0.81$ (Figure 3(6)). This is in excellent correspondence with the measured resistivity changes and allows a scaling of REST in degree of order. From an earlier investigation,[6] we know that the resistivity change due to defect recovery is between 10 and 15 pct (compare arrows in Figure 1). If we take a value of 15 pct in the present case of heavy cold rolling (10 μm) and extrapolate the equilibrium curve (dashed in Figure 2) to $S = 1$ at $T = 0$ and to $S = 0$ at $T_{O/D} = 963$ K, we

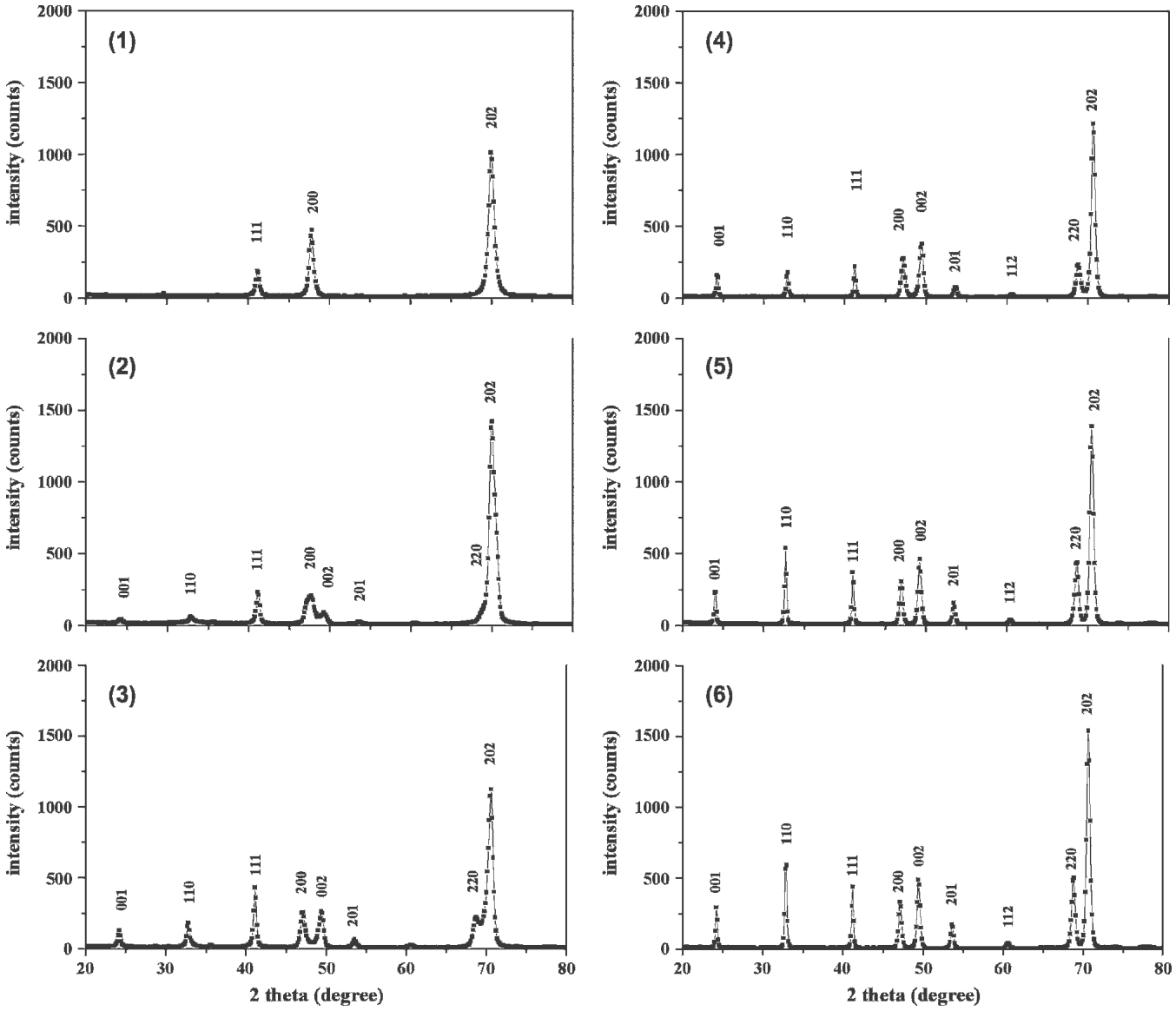

Fig. 3—Changes in the degree of LRO of a FePd foil (10-μm thickness) during isochronal annealing (ΔT = 20 K, Δt = 1200 s) as measured by XRD: (1) cold-rolled initial state, (2) 713 K, (3) 793 K, and (4) 900 K. Additional long-time annealing of 40 h: (5) 793 K and (6) 713 K.

get a corresponding range of resistivity values. Using the approximate law $\rho \propto (1 - S^2)$,[9] a scaling in S is obtained (Figure 2, right axis), which corresponds very well to the values as determined from XRD (arrows in Figure 2).

From Mößbauer spectra taken for corresponding states of isochronal annealing treatment (Figure 4), the hyperfine field distribution was obtained using the RECOIL fit program with the Voigt-based method.[10] The peaks of the hyperfine field distribution (Figure 5) can be correlated with the numbers of nearest-neighbor Fe-Fe atom pairs[11] and states of LRO can be estimated.[12] State (1): complete disorder; state (2): highly ordered domains develop with $H_{hf} >\cong 26$ T; state (3): an almost maximum state of LRO during isochronal annealing is reached and an iron-rich, less-ordered component with $< H_{hf} > 35$ T appears; state (4): the contribution of highly ordered domains (26 T) decreases, but the second ordered component at 27.5 T increases; states (5) and (6): the ordered components (26 T and 27.5 T) grow, and the disordered, iron-rich

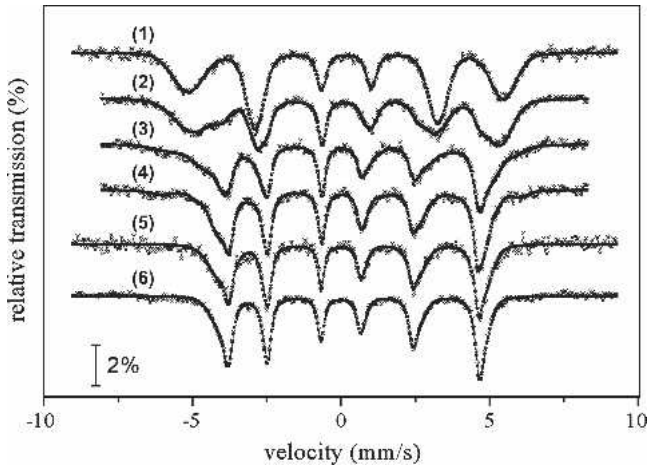

Fig. 4—Evolution of Mößbauer spectra of FePd foil after different annealing treatments numbered as in Figs. 2 and 3.

component disappears completely. From a comparison with TEM work on highly deformed FePd, it can be concluded that the splitting of the ordered components is correlated with the occurrence of different ordered structures, that is, twin-free grains originating from massive transformation and the formation of polytwinned volume, respectively.[8]

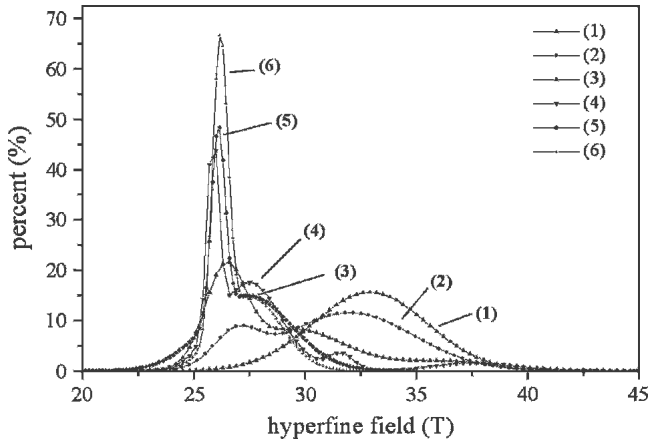

Fig. 5—Hyperfine field distribution for annealing treatments 1 through 6 numbered as in Figs. 2 and 3.

Measurements of magnetization hysteresis loops were carried out on the cold-rolled thin foil for four stages of treatment: as-deformed and isochronally annealed to 713, 773, and 1003 K (above $T_{O/D}$). Figure 6(a) shows that a strong shape anisotropy of magnetization is observed in the as-rolled state as a consequence of magnetostatic interaction in flat geometry. The increasing magnetic coercivity with thermal treatment is a consequence of magnetocrystalline anisotropy due to increasing degree of $L1_0$-LRO (Figures 6(b) and (c)). The coercive field of the foil annealed at 713 K is slightly smaller for the magnetic field in the foil plane (//) than normal to it ($\perp$), showing a small preference to form the $L1_0$ phase with the concentration modulation perpendicular to the film plane. This can be related to the stresses induced by cold rolling. Actually, in a single crystal, a compressive stress favors the variant with the concentration modulation along the stress when $c < a$.[13,14] For the 773 K annealed foil, the coercive field is equivalent for the magnetic field lying in the foil plane (//) and normal to it ($\perp$), showing the random character of the $L1_0$ variants in the grains. At 773 K, the stresses may already be relaxed completely due to the higher

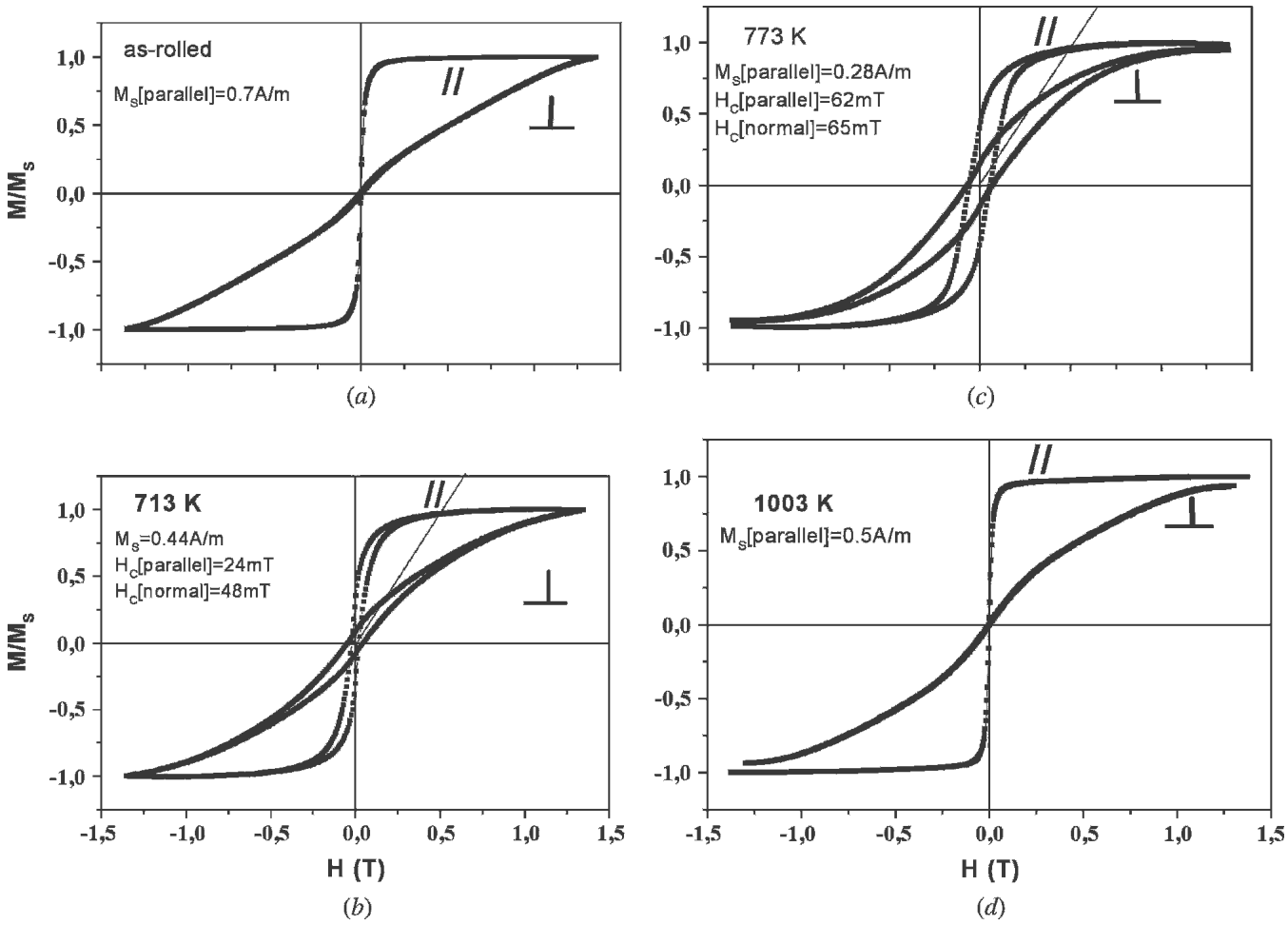

Fig. 6—Hysteresis loops of FePd (*a*) in the as-rolled state and after isochronal annealing for 1200 s at (*b*) 713 K, (*c*) 773 K, and (*d*) 1003 K. The straight line gives an indication of the demagnetizing field.

temperature. Annealing above $T_{O/D}$ restores the disordered state (Figure 6(d)).

IV. CHANGES OF ORDER AND MAGNETISM IN THIN FILMS

A. *Film Sputtered at RT on Si*

The XRD measurements (not shown here) provided evidence that the film sputtered at RT initially is polycrystalline and completely disordered fcc with a very fine grain size of about 15 nm.

In-plane REST measured during subsequent isochronal annealing yields a similar picture as for the thin foil (Figure 7). At a comparable temperature of about 600 K, atomic mobility is enabled and a two-stage decrease of resistivity is observed. Since we know from magnetization measurements that ordering does not start below 673 K (Figure 8), the first stage is attributed to grain growth of the fine-grained material starting at about 600 K; the second, smaller stage at about 750 K then corresponds to $L1_0$ ordering. The drastic increase of resistivity above 830 K may be due to the beginning of disordering with increasing temperature when attaining equilibrium values of LRO and even more to the onset of interdiffusion between substrate and film.[15]

Mößbauer measurements on thin film FePd samples (natural Fe) did not yield reliable results within reasonable measuring times. An enrichment of ^{57}Fe may be a solution.

Figure 8 shows the results of magnetization hysteresis measurements on the sputtered FePd film. The results

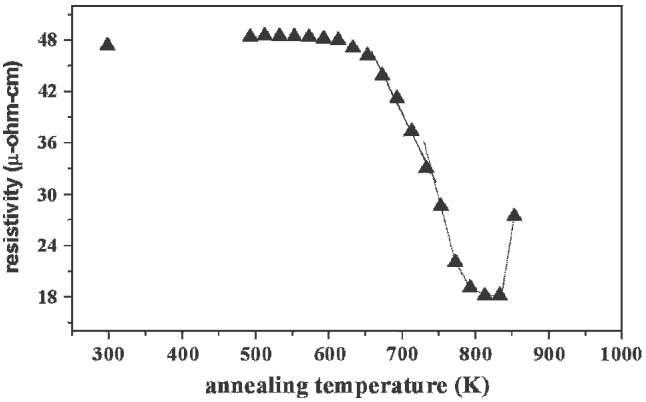

Fig. 7—REST measurement during isochronal annealing of 50-nm films of FePd sputtered on Si (ΔT = 20 K, Δt = 1200 s).

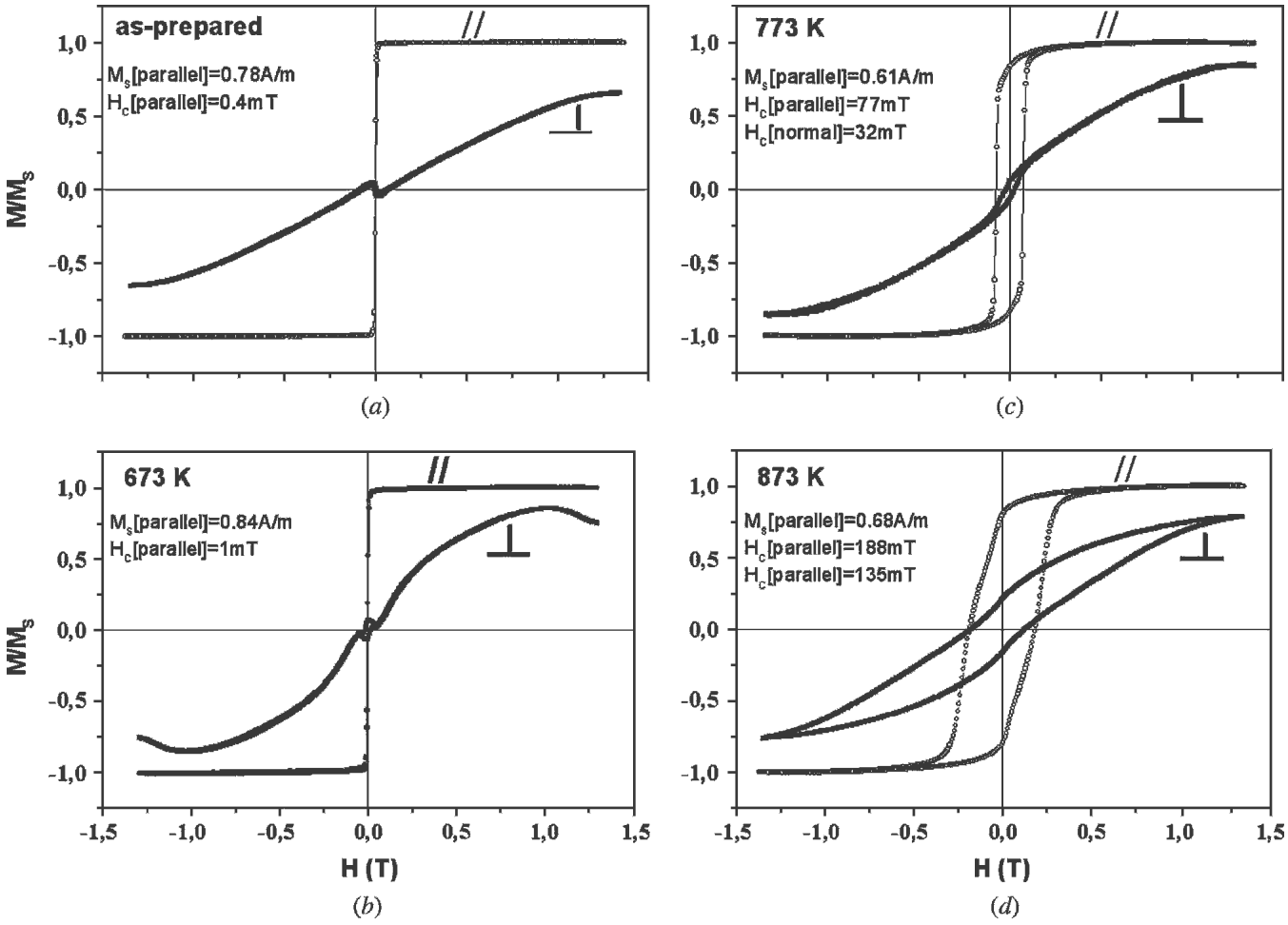

Fig. 8—Hysteresis loops of FePd thin film on Si substrate: (*a*) as prepared and annealed for 1200 s at (*b*) 673 K, (*c*) 773 K, and (d) 873 K.

obtained are very similar to those of the foil (Figure 7). For the as-prepared disordered film, the difference between magnetization in-plane (//) and perpendicular to the sample surface ($\perp$) is due to the shape anisotropy. This finding remains practically unaffected by the isochronal annealing treatment up to 673 K. At 773 K, the onset of $L1_0$-ordering generates some ordered domains, hereby increasing coercivity.

The *c*-axis of easy magnetization is slightly more often oriented in the in-plane direction (parallel), giving rise to a larger coercive field in that direction. Some regions are still disordered, their magnetization remaining isotropic and quite easy in all directions. Annealing at 873 K further increases coercivity, with a randomly oriented *c*-axis as shown by the equivalent coercivity in both directions showing the continuing development of $L1_0$-ordered domains with all possible variants.

B. *Film MBE Deposited at RT on MgO*

A nearly single crystalline character of the thin film produced by MBE deposition at 773 K was deduced from XRD measurement (not shown here; see Reference 5) with some mosaic structure and a well-developed $L1_0$ LRO with $S = 0.83$.[5]

Since the degree of order of the sample in the as-prepared state is already comparatively high, the change during isochronal annealing is expected to be only small. This is exactly what we found by REST (Figure 9): the resistivity change is less than 1/3 of that of the sputtered film (Figure 7) and reflects a slight further increase of order toward its thermal equilibrium value. Unlike the sputtered

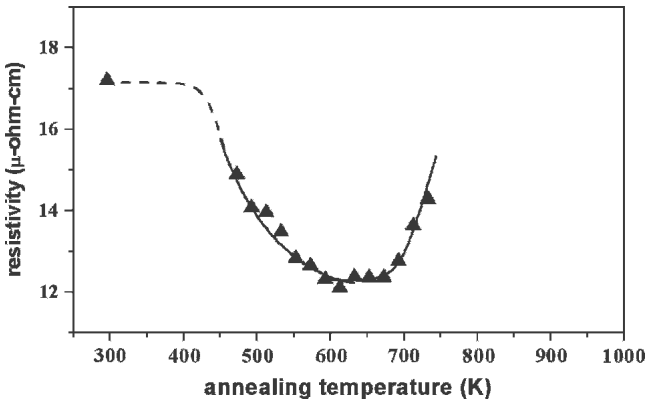

Fig. 9—REST measurement during isochronal annealing of 50-nm films of FePd grown by MBE on MgO ($\Delta T = 20$ K, $\Delta t = 1200$ s). The variation is less than 1/3 of that shown in Fig. 7.

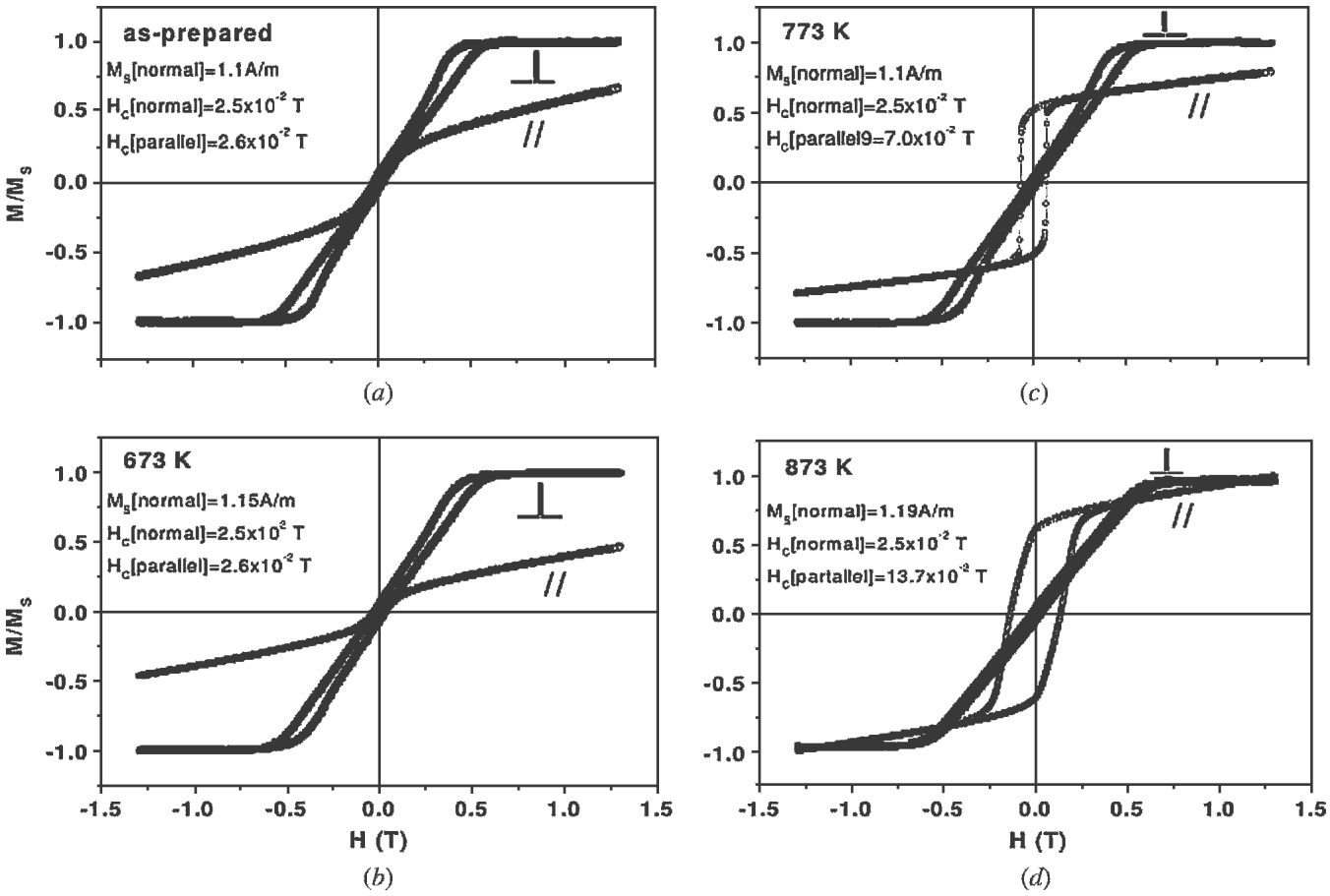

Fig. 10—Hysteresis loops of FePd thin film on MgO substrate with buffer and capping layers: (*a*) as prepared and annealed for 1200 s at (*b*) 673 K, (*c*) 773 K, and (*d*) 873 K.

sample, the decrease of REST here starts below 600 K. This is due to quenched-in vacancies and to other defects generated in the MBE-deposited samples arising from mismatch strains.

Magnetization measurements on MBE-deposited samples (with buffer and capping layers) showed a completely different picture (Figure 10) from those on sputtered samples. Surface effects during the growth (segregation and surface mobility) favor the formation of the *z*-variant among the three possible variants of ordered domains; therefore, the easy axis of magnetization is perpendicular ($\perp$) to the sample surface. The high magnetic anisotropy for all heat treatments, in correspondence to our XRD results, indicates that a high degree of $L1_0$ LRO exists already in the as-prepared state. The $\perp$ magnetization behavior remains practically unchanged for all states. This corresponds well to the MFM pictures taken after the same heat treatments and showing a practically constant domain structure after $\perp$ demagnetization by field cycling (Figure 11). From the hysteresis loop with the field parallel to the plane, it can be concluded, however, that for a small part of the sample, the easy axis is not perpendicular to the film surface. This can be attributed to growth defects due to the columnar growth induced by the lattice mismatch. Annealing at 673 K results in an even more pronounced prevalence of the easy axis in the *z* direction leading to an increased anisotropy due to a progressive disappearance of the growth defects. A surprising result was obtained during the heat treatment at 773 and 873 K: An ever increasing number of magnetic domains start to order in *x*- and *y*-variants so that more and more grains with in-plane easy magnetization axis appear. This is accompanied by a large coercive field because different ordered variants represent magnetic inhomogeneities that are strong traps for the domain wall migration. Such an in-plane rotation of magnetic domains actually proceeds in the direction toward thermodynamical equilibrium and was indeed found by MC simulations of ''order-order'' kinetics in $L1_0$-ordered FePt nanolayers:[16] Annealing a FePd multilayer originally completely ordered with *c*-axis in the *z* direction ($\perp$ film surface) resulted in the formation of *x*- and *y*-variants, nucleating on the Fe surface layer and growing into the structure (Figure 12). An additional strong effect favoring in-plane reorientation of the magnetic domains is the reduction of the associated magnetostatic energy not included in the MC simulations.

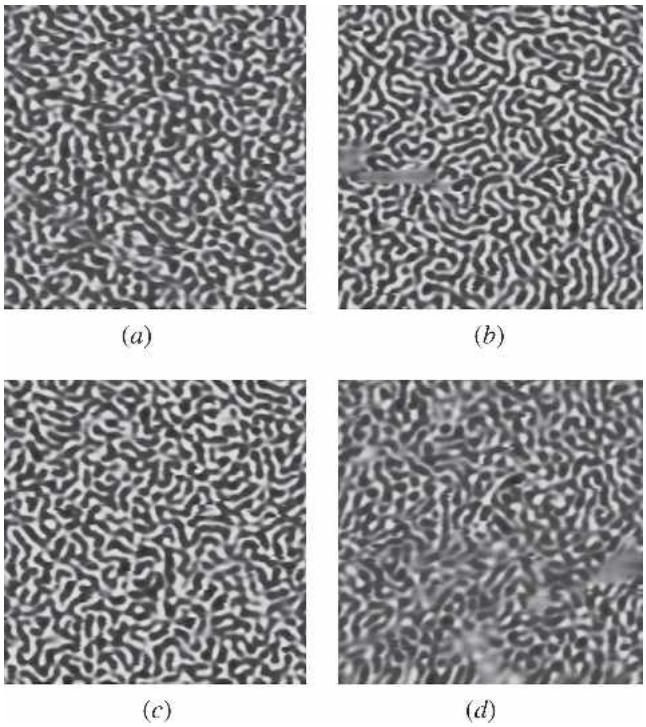

Fig. 11—MFM image of FePd film of 50 nm on MgO with 30-nm Pd buffer and 5-nm Pd capping: (*a*) as prepared and after isochronal annealing to (*b*) 673 K, (*c*) 773 K, and (*d*) 873 K. The image size is 5 μm $\times$ 5 μm.

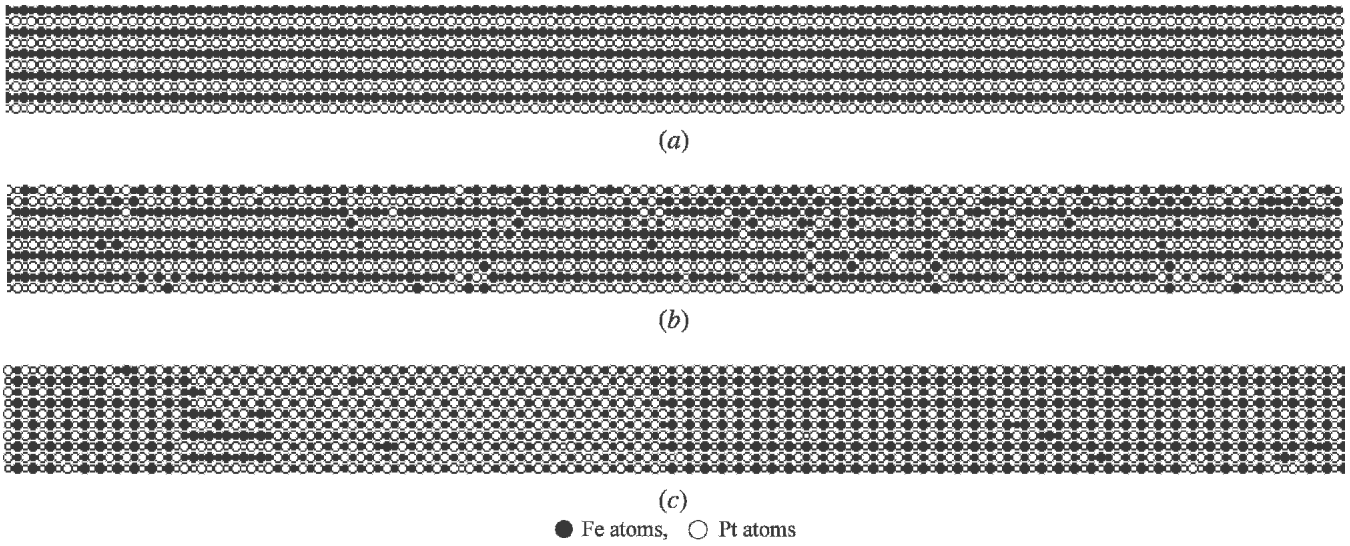

Fig. 12—Results of Monte Carlo simulations of atomic relaxation in FePt nanolayers (10 planes).[16] $L1_0$ domains initially ordered in *z*-variant only relax into *x*- and *y*-variants as a stable final configuration. (*a*) initial state: *c*-axis normal to film surface, (*b*) 10^7 MC steps at 1200 K, and (*c*) 5×10^8 MC steps at 1200 K.

V. CONCLUSIONS

The conclusions can be summarized as follows.

1. A very good correspondence is obtained for changes in the degree of LRO of a 10-μm FePd foil, as measured by XRD, REST, Mößbauer spectroscopy, and magnetization measurement. This suggests application of these well-approved methods to thin film material. It turns out that REST measurement is well suited for detection of atom jumps in intermetallic thin films due to its high resolution for configurational changes.
2. For our model system FePd, comparable results on ordering kinetics are observed for bulk material and polycrystalline thin films. Atom jumps in these thin films seem to occur in a similar manner as long as surface effects are not predominant. FePd thin films resist temperature treatments up to about 800 K.
3. Mößbauer spectroscopy gives additional insight into structural processes during ordering. For thin films, the signal has to be amplified by enrichment of ^{57}Fe in the material.
4. As expected, FePd films sputtered at RT initially are completely disordered and order during a subsequent temperature treatment below $T_{O/D}$. The MBE-deposited films are highly ordered from the beginning and only slight subsequent changes of LRO are obtained.
5. The MBE-deposited FePd film with an initial high preference for *z*-variants (normal to film surface) when annealed shows an ever increasing contribution from *x*- and *y*-oriented domain variants (in-plane). Indeed, this effect has been found by MC simulations in $L1_0$-ordered FePt nanolayers.

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