



Full Tunability of Strain along the fcc-bcc Bain Path in Epitaxial Films and Consequences for Magnetic Properties

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Strained coherent film growth is commonly either limited to ultrathin films or low strains. Here, we present an approach to achieve high strains in thicker films, by using materials with inherent structural instabilities. As an example, 50 nm thick epitaxial films of the Fe₇₀Pd₃₀ magnetic shape memory alloy are examined. Strained coherent growth on various substrates allows us to adjust the tetragonal distortion from $c/a_{\text{bct}} = 1.09$ to 1.39, covering most of the Bain transformation path from fcc to bcc crystal structure. Magnetometry and x-ray circular dichroism measurements show that the Curie temperature, orbital magnetic moment, and magnetocrystalline anisotropy change over broad ranges.

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Strain effects on functional materials are of great current interest for improving materials properties. By strained epitaxial film growth, physical properties can be controlled and improved, e.g., in semiconductors [1], multiferroic materials [2], and ferromagnets [3–7]. Moreover, there are even materials which exhibit functional properties such as ferroelectricity only in strained films [8].

During epitaxial growth, the film orientation is controlled by the substrate onto which the material is deposited. In addition, a thin film may also adapt its in-plane lattice parameters to the substrate, even if its equilibrium lattice parameters differ considerably. The particular case in which the lattice parameters of the film material are strained such that they are identical to those of the substrate is called strained coherent film growth. In common rigid metals, straining of the crystal lattice by coherent film growth requires substantial elastic energy. As a consequence, already at strains of a few percent, coherent growth is limited to ultrathin films with thicknesses of up to several atomic layers. For the growth of coherent epitaxial films with high strains and large thickness soft materials should be used, as suggested by van der Merwe [9]. Such softening is observed in crystals with lattice instabilities, e.g., in materials with a martensitic transformation. As an example how to exploit such a martensitic instability, Godlevsky and Rabe [10] predicted the possibility to induce a cubic to tetragonal distortion with c/a ratios from 0.95 to 1.25 in the magnetic shape memory material Ni₂MnGa. In fact, in experiments Dong *et al.* [11] demonstrated a considerable epitaxial strain of 3% in a Ni-Mn-Ga film.

This shows that for improved tunability of crystal lattice and functional properties in thicker films, it is advantageous to exploit lattice instabilities. Here, we report the preparation of seven evenly distributed stages along the

Bain path, between face centered cubic (fcc) and body centered cubic (bcc) structure in 50 nm thick Fe₇₀Pd₃₀ films (Fig. 1). The martensitic and ferromagnetic Fe₇₀Pd₃₀ alloy is well known for anomalous magnetomechanical effects such as the magnetic shape memory effect [12]. We demonstrate the inverse magnetomechanical behavior of this compound: By varying c/a_{bct} , Curie temperature, orbital magnetic moment, and magnetocrystalline anisotropy are tuned in wide ranges. The approach can be extended to a multitude of materials with ferroelastic or martensitic lattice instabilities enabling large strains. In particular, the possibility to stabilize intermediate lattice geometries and vary smoothly between stable phases along Bain transformation paths offers new routes to adjust and understand structure-property relations in functional materials.

Fe-Pd has been suggested as a model system for martensitic transformations, already in 1938 [13]. For the present experiments, it is favorable that the Fe₇₀Pd₃₀ alloy exhibits a structural instability resulting in softening of the crystal lattice near room temperature [14]. In addition, growth at ambient temperature frequently enables preparation of coherent films with larger thickness due to the reduced mobility of dislocations [15]. In the composition range from Fe₇₀Pd₃₀ to Fe₇₅Pd₂₅ and in the vicinity of room temperature four phases with different tetragonal distortions have been observed in quenched, chemically disordered bulk: fcc, “fct,” bct, and bcc [16]. These structures follow the Bain transformation path [17]. The Bain path is a geometrical description for the transformation from fcc to bcc lattice. Considering a body centered tetragonal (bct) unit cell with the lattice parameters a_{bct} and c_{bct} [marked by colored atoms and thicker lines in Fig. 1(b)] one can describe the transformation from

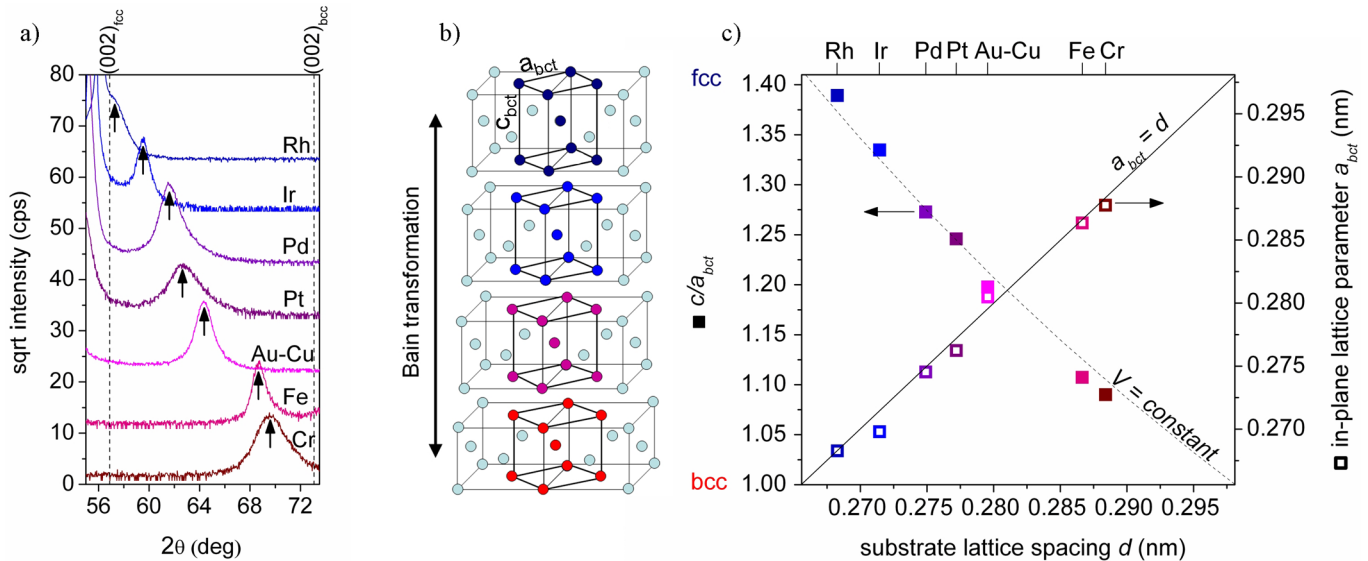


FIG. 1 (color online). (a) A considerable shift of the Fe₇₀Pd₃₀ (002)_{bct} peak (arrow) is observed in x-ray diffraction patterns that have been measured on the films grown on different substrate materials (CoK_α). Peak positions expected for fcc and bcc structure are marked by dotted lines. They represent the boundaries of the Bain transformation. (b) Sketch of the different stages during the Bain transformation between fcc (top, dark blue) and bcc structure (bottom, red). The black lines mark the bct unit cell used to describe this transformation. (c) Variation of the Fe₇₀Pd₃₀ crystal lattice (substrate materials are marked on top). The in-plane lattice parameter a_{bct} (open symbols) follows the straight line representing identity with the substrate's lattice spacing d . The c/a_{bct} ratio (solid symbols) is varied almost from fcc to bcc structure by the coherent epitaxial growth. The dotted curve illustrates the expected change of c/a_{bct} at constant volume of the unit cell.

fcc (top) to bcc lattice (bottom) by a continuous variation of the tetragonal distortion c/a_{bct} from $\sqrt{2}$ to 1. In accordance with Bain, we use the bct description of the unit cells here. The four phases are described by c/a_{bct} ratios of 1.41 (fcc), 1.33 (“fct”), 1.02 (bct), and 1 (bcc).

Fe₇₀Pd₃₀ films of 50 nm nominal thickness were deposited onto different substrates at room temperature by magnetron sputtering from a 2 inch Fe₇₀Pd₃₀ alloy target. The substrates consist of a MgO(100) single crystal with different epitaxial metallic buffer layers (Rh, Ir, Pt, Pd, Au-Cu, Fe, and Cr). Details on the growth of the epitaxial films are described in the auxiliary material available online [18]. The epitaxial growth on the different substrates induces considerable distortion of the crystal lattice. X-ray diffraction (XRD) was measured at room temperature. As an overview over the crystal structure, $\theta - 2\theta$ diffraction patterns were recorded in Bragg-Brentano geometry (Co K_α, 0.1789 nm). The diffraction patterns show a (002)_{bct} reflection of the epitaxial Fe₇₀Pd₃₀ film [Fig. 1(a), reflection marked by an arrow]. When varying the substrate, this reflection shifts by 12.3 degrees. However, it always lies within the boundaries of the Bain transformation between the reflection positions expected for fcc and bcc structure. Intensity measured at $2\theta \leq 56^\circ$ is due to the (002) reflection of the fcc Au-Cu, Pt, Pd, Ir, or Rh layer.

Determination of the lattice constants was performed in a 4-circle setup with Euler stage (Cu K_α, 0.1540 nm) [18].

The in-plane lattice parameters of the films are identical to the substrate lattice spacings [Fig. 1(c)]. This proves a coherent epitaxial growth in spite of a large variation of the substrate lattice spacing. The epitaxial strain reaches a maximum value of 8.3% relative to the Fe₇₀Pd₃₀ fcc lattice [19]. Because of the coherent growth, our films are in a single variant state with both in-plane lattice parameters a_{bct} of the crystal structure's basal plane fixed by the cubic substrate lattice, while no constraint exists for the lattice parameter c_{bct} in the out-of-plane direction. The measured c/a_{bct} ratio ranges from $c/a_{\text{bct}} = 1.09$ to 1.39, covering most of the Bain path from bcc to fcc. This corresponds to a variation of tetragonal distortion by 27% which we could stabilize in films with a remarkable thickness of 50 nm. The dotted line in Fig. 1(c) represents the ideal behavior at constant unit cell volume ($c/a_{\text{bct}} = V_{\text{bct}}/2a^3$, $V_{\text{bct}} = 0.0265 \text{ nm}^3$ [19]). The experimental data points show that the assumption of constant volume is justified even for such large deformations.

The achieved strained film growth indicates very low energy differences between the crystal structures along the Bain path. For the present material, this is confirmed by density functional calculations [Fig. 2(a)]. Electronic structure calculations for disordered Fe-Pd alloys were performed with the full potential local orbital (FPLO) code [20] in the framework of density functional theory. Disorder was treated in the coherent potential approxima-

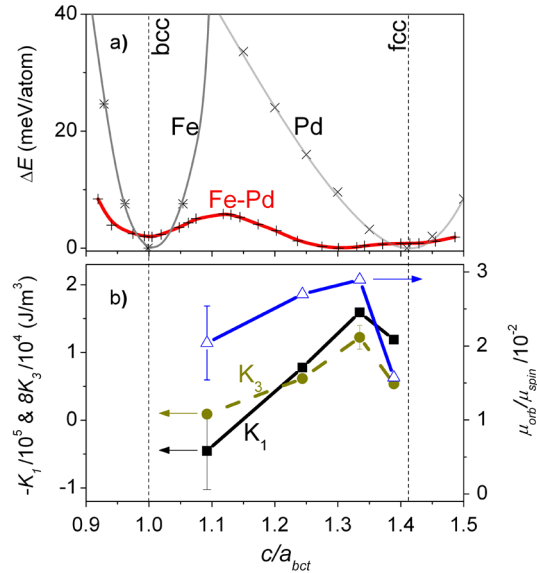


FIG. 2 (color online). (a) Calculated energy required to induce tetragonal distortions (c/a_{bct}) along the Bain path. Compared to literature data of the common metals Fe [23] and Pd [24] only little elastic energy is required for a tetragonal distortion of Fe-Pd. (b) Change of the magnetocrystalline anisotropy constants K_1 and K_3 and the ratio of orbital to spin momentum ($\mu_{\text{orb}}/\mu_{\text{spin}}$) of Fe 3d electrons along the Bain path. For each quantity, the experimental error is represented by an error bar.

tion (CPA) [21] and the exchange and correlation potential was treated in the local spin density approximation (LSDA). In the calculations, the c/a_{bct} ratio is varied, while the volume of the unit cell is held constant, as justified by our experiments. Numerical details of the calculations are identical to those given in Ref. [22]. In comparison to the rigid pure Fe [23] and Pd [24], the energy landscape is very flat along the entire Bain path; i.e., energy differences between the different c/a_{bct} ratios are indeed small. Hence, the film-substrate interaction is sufficient to stabilize large tetragonal distortions in films of bulklike thickness.

The key property of magnetic shape memory alloys is their magnetocrystalline anisotropy. Strained epitaxial growth holds the promise of adjusting this property, beyond what is possible by conventional inverse magnetostriction. On the atomic scale, the origin of the magnetocrystalline anisotropy is the spin-orbit coupling of the valence electrons in combination with exchange-splitting and with the particular electronic structure. We studied the effect of lattice distortion on the spin-orbit related properties by measuring the ratio of orbital-to-spin magnetic momentum ($\mu_{\text{orb}}/\mu_{\text{spin}}$) of the iron 3d electrons by means of x-ray magnetic dichroism along the [001] crystal direction of four films with considerably different tetragonal distortion. In addition, we determined the anisotropy constants K_1 and K_3 of these films by magnetometer measurements along different crystallo-

graphic directions [001]; [100]; [110] [Fig. 2(b)]. Magnetic measurements with both methods were performed at 300 K [18]. While K_1 defines the work required to magnetize the material along the hard magnetization axis [001], K_3 is a measure of the anisotropy in the basal plane of the tetragonal unit cell. All three quantities ($\mu_{\text{orb}}/\mu_{\text{spin}}$ and K_1, K_3) show considerable changes along the Bain path but similar trends. At $c/a_{\text{bct}} = 1.33$, maximum anisotropy is observed. This value of tetragonal distortion coincides with the “fct” phase that exhibits high magnetocrystalline anisotropy and shows the magnetic shape memory effect in bulk. For the magnetic shape memory effect, the anisotropy constant K_1 is a crucial quantity. We find that due to the strain and tetragonal distortion, K_1 considerably varies in our series of epitaxial films. When approaching cubic structures, the magnetic anisotropy is reduced as expected due to their high symmetry. The maximum value of $K_1 = 1.5 \times 10^5 \text{ J/m}^3$ at $c/a_{\text{bct}} = 1.33$ is identical with the literature value that has been reported at $T = 100 \text{ K}$ for a “fct” single crystal with $c/a_{\text{fct}} = 0.945$ (corresponding to $c/a_{\text{bct}} = 1.33$) [25].

Moreover, the tetragonal distortion of the lattice also significantly changes the Curie temperature. Temperature dependent spontaneous magnetization was measured in the film plane (Fig. 3). The applied field of 1 T is sufficient to saturate the sample along this direction. Increase in curvature is observed with increasing c/a_{bct} ratio. To explain this behavior, the Curie temperature T_C was evaluated. According to Kuz’min’s model [26], T_C can be determined by a fit of the relative magnetization curves (inset in Fig. 3). The additional shape parameter s that is included in this model depends on the spin wave stiffness [27]. While the shape parameter does not vary significantly

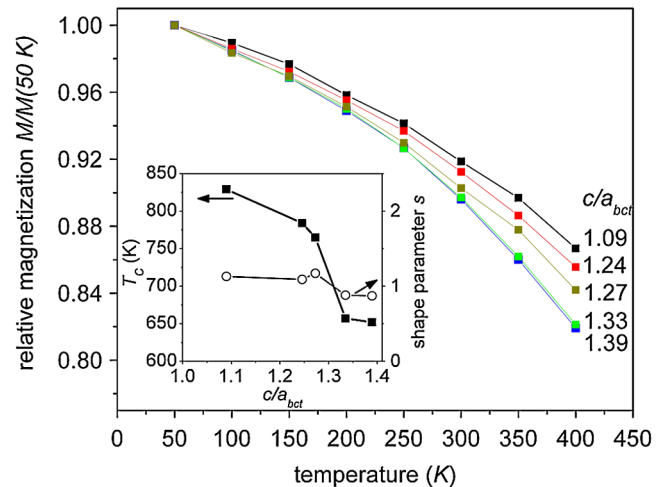


FIG. 3 (color online). The curvature of the relative spontaneous magnetization versus temperature decreases with increasing tetragonal distortion. *Inset*: Curie temperature T_C and shape parameter s that have been extracted using Kuz’min’s model [26]. T_C increases considerably when approaching the bcc structure. The shape parameter only shows minor changes.

with tetragonal distortion, the ferromagnetic transition temperature increases remarkably from 652 K at $c/a_{\text{bct}} = 1.39$ to a value of 829 K at $c/a_{\text{bct}} = 1.09$. The extrapolated value of $T_C = 650$ K at $c/a_{\text{bct}} = 1.41$ (fcc) is similar to the literature value of 600 K reported for the fcc phase in $\text{Fe}_{70}\text{Pd}_{30}$ bulk [28,29].

In conclusion, by strained coherent growth of 50 nm thick $\text{Fe}_{70}\text{Pd}_{30}$ films with inherent structural instability, we achieve a quasi-continuous variation of the lattice distortion along the Bain path. The magnetic properties of the $\text{Fe}_{70}\text{Pd}_{30}$ films display considerable changes: The Curie temperature is increased more than 25% with respect to the value for $\text{Fe}_{70}\text{Pd}_{30}$ with fcc structure. The ratio of orbital vs spin magnetic momentum changes by a factor of two. This is accompanied by an increase of the magnetic anisotropy from near zero to values close to those of “fct” bulk $\text{Fe}_{70}\text{Pd}_{30}$. Softening of the crystal lattice and a flat energy landscape along the Bain path are not a unique feature of this alloy. Similar lattice instabilities may be exploited in various functional materials including (magnetic) shape memory, ferroelectric, multiferroic, or magnetocaloric materials for extended adjustability of their crystal structure in strained epitaxial films. This should cause severe changes in the electronic structure of the materials and, thus, should allow us to tune magnetic, transport, optical, or even catalytic properties in a wide range.

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- [1] J. C. Bean, *Science* **230**, 127 (1985).
 [2] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).
 [3] C. Thiele, K. Dörr, S. Fähler, L. Schultz, D. C. Meyer, A. A. Levin, and P. Paufler, *Appl. Phys. Lett.* **87**, 262502 (2005).
 [4] A. Winkelmann, M. Przybylski, F. Luo, Y. Shi, and J. Barthel, *Phys. Rev. Lett.* **96**, 257205 (2006).
 [5] X. W. Li, A. Gupta, and Xiao Gang, *Appl. Phys. Lett.* **75**, 713 (1999).
 [6] M. J. Pechan, C. Yua, D. Carr, and C. J. Palmstrøm, *J. Magn. Magn. Mater.* **286**, 340 (2005).
 [7] A. R. Kwon, V. Neu, V. Matias, J. Hänisch, R. Hühne, J. Freudenberger, B. Holzapfel, L. Schultz, and S. Fähler, *New J. Phys.* **11**, 083013 (2009).
 [8] J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, *Nature (London)* **430**, 758 (2004).
 [9] J. H. van der Merwe, *J. Appl. Phys.* **34**, 123 (1963).
 [10] V. V. Godlevsky and K. M. Rabe, *Phys. Rev. B* **63**, 134407 (2001).
 [11] J. W. Dong, J. Lu, J. Q. Xie, L. C. Chen, R. D. James, S. McKernan, and C. J. Palmstrøm, *Physica E (Amsterdam)* **10**, 428 (2001).
 [12] R. D. James and M. Wuttig, *Philos. Mag. A* **77**, 1273 (1998).
 [13] R. Hultgren and C. A. Zapffe, *Nature (London)* **142**, 395 (1938).
 [14] R. Oshima, S. Muto, and F. E. Fujita, *Mater. Trans. JIM* **33**, 197 (1992).
 [15] R. Hull and J. C. Bean, *Crit. Rev. Solid State Mater. Sci.* **17**, 507 (1992).
 [16] M. Sugiyama, R. Oshima, and F. E. Fujita, *Trans. Jpn. Inst. Met.* **25**, 585 (1984).
 [17] E. C. Bain, *Transactions of the American Institute of Mining and Metallurgical Engineers* **70**, 25 (1924).
 [18] See EPAPS Document No. E-PRLTAO-103-002947 for experimental details of the film deposition. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
 [19] J. Cui, T. W. Shield, and R. D. James, *Acta Mater.* **52**, 35 (2004).
 [20] K. Koepnik and H. Eschrig, *Phys. Rev. B* **59**, 1743 (1999); <http://www.FPLO.de>.
 [21] K. Koepnik, B. Velicky, R. Hayn, and H. Eschrig, *Phys. Rev. B* **55**, 5717 (1997).
 [22] I. Opahle, K. Koepnik, U. Nitzsche, and M. Richter, *Appl. Phys. Lett.* **94**, 072508 (2009).
 [23] S. L. Qiu, P. M. Marcus, and H. Ma, *Phys. Rev. B* **64**, 104431 (2001).
 [24] F. Jona and P. M. Marcus, *Phys. Rev. B* **65**, 155403 (2002).
 [25] T. Kakeshita, T. Fukuda, and T. Takeuchi, *Mater. Sci. Eng. A* **438–440**, 12 (2006).
 [26] M. D. Kuz'min, *Phys. Rev. Lett.* **94**, 107204 (2005).
 [27] M. D. Kuz'min, M. Richter, and A. N. Yaresko, *Phys. Rev. B* **73**, 100401 (2006).
 [28] A. Kussmann and K. Jessen, *J. Phys. Soc. Jpn.* **17**, 136 (1962).
 [29] M. Matsui, T. Shimizu, H. Yamada, and K. Adachi, *J. Magn. Magn. Mater.* **15**, 1201 (1980).