# Magnetic properties of Fe-Pd magnetic shape memory alloys: Density functional calculations and epitaxial films

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The magnetic properties of Fe-Pd magnetic shape memory alloys with different Pd contents are investigated in epitaxial films and by means of density functional calculations. The magnetocrystalline anisotropy energy (MAE) of ordered and disordered Fe-Pd alloys is calculated as a function of c/a ratio and Pd concentration. Disorder is found to be essential for the experimentally observed easy *a*-axis anisotropy in fct-Fe<sub>70</sub>Pd<sub>30</sub>. The MAE of disordered fct-Fe-Pd not only increases with decreasing c/a but also increases with increasing Pd concentration for fixed c/a. Epitaxial Fe-Pd films deposited on MgO (100) exhibit (with increasing Pd concentration from 25 to 37 at. % Pd) bcc, bct, and fct structures at room temperature. Temperature dependent magnetic properties are studied by using hysteresis, saturation magnetization, and susceptibility measurements. The coercivity and MAE at room temperature in the fct films is higher than in bct and/or bcc films. Increasing MAE is observed with increasing Pd concentration within the fct phase. Due to the nanocscale microstructure, the magnetocrystalline anisotropy energy in the fct films is reduced compared to bulk. Furthermore, it is observed that the fct Fe-Pd films with Pd < 33 at. % continuously transform to the bct phase during cooling. In contrast to bulk materials, this transformation is found to be reversible in thin films.

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# I. INTRODUCTION

Disordered Fe-Pd alloys have been well known for their invar behavior for a long time.<sup>1</sup> Another anomaly, i.e., unconventionally high magnetic field induced strain, was observed in single crystals around the composition Fe<sub>70</sub>Pd<sub>30</sub> in the disordered Fe-Pd fct phase by Matsui and Adachi.<sup>2</sup> The underlying mechanism of this effect was identified by James and Wuttig<sup>3</sup> and is now known as magnetic shape memory (MSM) effect.

The MSM effect in disordered Fe<sub>70</sub>Pd<sub>30</sub> is attributed to the reorientation of martensitic twins in a magnetic field and requires, besides a high mobility of twin boundaries, a sufficiently large magnetocrystalline anisotropy energy (MAE). The magnetocrystalline anisotropy (MCA) depends in a complicated fashion on structural properties, composition, and chemical order. Experimentally, it is difficult to distinguish between the different effects on the MCA since structure and composition are intimately connected. The c/a ratio in bulk Fe-Pd strongly depends on the composition and temperature, and the fct phase is only observed in a narrow composition range around 30 at. % Pd.<sup>4</sup> In contrast, in epitaxial films, the fct phase is extended over a wider composition range and the c/a ratio shows only a moderate dependence on the Pd concentration.<sup>5</sup> Density functional calculations allow us to independently estimate the effect of structure, composition, and chemical order and can thus provide valuable information for the interpretation of the experimental trends.

The Fe-Pd fct phase exhibits an easy plane MCA in a general case. However, due to the fourfold symmetry of the basal plane, some deviation from idealized easy plane behavior is observed, which can more precisely be described by a two-axis behavior with both easy axes aligned along the *a* axes of the unit cell.<sup>6,7</sup> Calculations of the MCA are compu-

tationally demanding since they require a high accuracy and a careful convergence of numerical parameters. For the Fe-Pd alloys considered here, these calculations are further complicated by the need for a suitable model to simulate the disordered lattice. Calculations for the MCA of disordered alloys have been performed within the coherent potential approximation<sup>8,9</sup> (CPA) and with supercell approaches.<sup>10,11</sup> The CPA allows for an efficient and overall good description of the electronic and magnetic properties of disordered alloys but does not capture the effects of the local arrangement of atoms, such as a charge transfer deviating from the average, which could be of importance for the MCA. This might explain why, in contradiction to experiment, the CPA calculations of Stern *et al.*<sup>12</sup> for disordered fct-Fe<sub>70</sub>Pd<sub>30</sub> yielded an easy c axis. Alternatively, supercell approaches allow for a treatment of local order (including relaxations) but are computationally demanding, as they require a large cell and/or a sufficiently large ensemble. In practice, the calculations are restricted to relatively small cells but can nevertheless provide results in reasonable agreement with the CPA calculations.<sup>11</sup> A drawback of the supercell approach is that the distribution of atoms is only to a certain degree random since it is a periodic arrangement of a limited number of atoms. The MCA is highly sensitive to chemical order. For example, in the hard magnetic  $L1_0$ -FePt alloys, the large MCA is mainly due to the chemical order (i.e., the layered structure), whereas the small tetragonal lattice distortion is of minor importance.<sup>13</sup> Thus, special care has to be taken that the arrangement of atoms in the supercell does not introduce spurious contributions to the MCA. This can, for example, be achieved by an ensemble average over the properly chosen ensemble members, as it is done in this work.

The structure of Fe-Pd alloys, having a major impact on the MCA, has been experimentally investigated and is accessible in literature. According to "metastable phase diagrams"



FIG. 1. Schematic diagram of the metastable phases in the Fe-Pd films around the composition  $Fe_{70}Pd_{30}$  and their magnetocrystalline anisotropy.

of quenched Fe-Pd bulk,<sup>6,14</sup> the Pd-rich alloys exhibit a fcc structure and the Fe-rich alloys exhibit a bcc structure. The transition from fcc to bcc occurs around the composition  $Fe_{70}Pd_{30}$ . At this composition, the fcc and the bcc phase have similar free energy and intermediate phases are observed. The phase transformation follows the Bain transformation path. With decreasing temperature fcc, fct, bct, and, at lower Pd content, bcc phases are observed. [Note that fct and bct denote the same centered tetragonal structure. In accordance with the notation in related literature, the structure is called fct (although no crystallographically defined structure) if the c/a ratio is closer to fcc than to bcc; otherwise, the structure is called bct here.]

Here, the magnetic properties of Fe-Pd alloys are experimentally investigated on epitaxial films. In a previous publication, the structure and microstructure of roomtemperature deposited epitaxial Fe-Pd films with Pd content from 22 to 43 at. % has been described in detail.<sup>5</sup> epitaxial relationship for the fct The films is MgO(100)[001]||Fe-Pd(100)[001] (cube on cube), and for the bct and/or bcc films, it is  $MgO(100)[001]\parallel$ Fe-Pd(100)[011] (45° rotation of the unit cell with respect to the substrate). With varying Pd content, three different phases are observed in the films at room temperature: fct phase for  $\geq 29$  at. % Pd, bct for 28 at. % Pd, and bcc for <28 at. % Pd. Compared to bulk, severe stress caused by pulsed laser deposition (PLD) leads to a stabilization of the fct phase over an extended composition range up to the investigated 43 at. % at room temperature. Recently, the film stress could be measured in situ during deposition.<sup>15</sup> In order to compensate stress, the fct phase splits up into fine variants by (110) twinning. Since the capability of stress compensation by this mechanism is exhausted in the films, further (111) twinning occurs during film growth. Magnetic measurements at elevated temperatures indicate that the fct phase can be stable up to 600 K in a film containing 33 at. % Pd.<sup>16</sup>

By using the above composition ranges as an isothermal cut at room temperature and the upper temperature limit for the stability of the fct phase, a metastable phase diagram for films is sketched in Fig. 1 where the low temperature part will be established in this work. The aim of this paper is to use the temperature dependent magnetic measurements to investigate the magnetic properties of the films, to correlate magnetic and structural information both in experiment and in theory, and to examine the characteristics of the transformations.

## **II. EXPERIMENTAL AND THEORETICAL DETAILS**

Fe-Pd films were prepared on chemically inert MgO (100) substrates at room temperature in UHV by using the PLD method from high purity Fe (99.995%) and Pd (99.995%) targets.<sup>5</sup> Temperature dependent magnetic measurements were performed in a Quantum Design vibrating sample magnetometer and superconducting quantum interference device (SQUID) magnetometer. In-plane measurements were made along MgO[100]. The samples were measured in fields up to 3 T. The field sweep rates were 1 mT/s below 0.5 T and 5 mT/s above. The temperature sweep rate in temperature dependent measurements was 2 K/min. Room-temperature hysteresis measurements along different in-plane directions were performed in a hysteresis loop tracer (SHB Instruments, Inc.). The absolute film thickness is 250 nm with an accuracy of about 10% and was determined by using atomic force microscopy step measurement on a reference sample. The rigid substrate is expected to block any elongation: thus, different to single crystals, no additional device is needed to avoid reorientation of the variants during magnetic measurements.<sup>17</sup>

The MAE of disordered fct Fe-Pd alloys was calculated as a function of c/a ratio and composition using the relativistic version<sup>18</sup> of the full potential local orbital method.<sup>19</sup> For this purpose, one special 32 atom supercell with 22 Fe atoms and 10 Pd atoms (corresponding to 31.25 at. % Pd) was constructed in such a way that it matches the nearest neighbor patterns of the completely disordered alloy as closely as possible. This choice is guided by the idea that the local environment of an atom will have the most significant influence on the electronic structure.

The special arrangement of the atoms in the cell will, however, cause spurious contributions to the MAE. This problem has been circumvented by taking the average over a symmetry adapted ensemble of similar cells. In a completely random alloy, the probabilities to find a certain atomic pattern and a related one by application of the symmetry operations of the space group are identical. Thus, in the cubic parent structure, an ensemble with 48 members is the smallest appropriate entity to ensure proper symmetrization. This ensemble has been constructed by applying the 48 symmetry operations of the cubic group to the original (at first cubic) supercell. The total energy of these 48 different structures is the same if spin-orbit coupling is neglected (scalar relativistic approach).

Next, the supercells of the ensemble are distorted along the *c* axis to achieve the intended c/a ratio. For c/a deviating from unity, three different total energies are obtained in the scalar relativistic approach, as the 16 tetragonal operations applied to the distorted cell do not change the energy if spin space and real space are not coupled.

Switching on spin-orbit coupling keeps this property only if the magnetization points along the c axis. Else, if the magnetization points along one of the a axes, six different ener-

gies are found due to the remaining eight orthorhombic operations. This means that full-relativistic calculations have to be carried out for only nine different combinations of structure and magnetic moment orientation in order to get the complete information to evaluate the ensemble averaged energy difference between c- and a-axis orientations of the magnetic moment. The average has the correct properties that it vanishes for c/a=1 and that both a axes are equivalent.

For the numerical calculation of the MAE, the so-called magnetic force theorem has been used. Starting from a charge density obtained by the scalar relativistic approach, the MAE for each supercell has been obtained in a full-relativistic one-step calculation from the related band energy differences between magnetization directions along *c* and *a* axes, respectively. These axes correspond to the experimental hard and easy axes in disordered fct-Fe<sub>70</sub>Pd<sub>30</sub>.<sup>6,7</sup> The MCA was then calculated from the ensemble average  $\Delta E = 1/N\Sigma_i \Delta E_i = 1/N\Sigma_i E_i - E_i(100)$ , where *N* is the number of ensemble members and the index *i* runs over the supercells generated by the rotation of the original cell.

Up to 32 768 k points in the full Brillouin zone (BZ) were used for the MCA calculations and 64 k points for the selfconsistent scalar relativistic calculations. Additionally, the MCA for hypothetical  $L1_2$ -ordered Fe<sub>3</sub>Pd was calculated to check the influence of disorder on the MCA. Here, up to 11 0592 k points in the full BZ were used. All of the MCA calculations were performed in the local spin-density approximation (LSDA) with the Perdew–Wang<sup>20</sup> parametrization of the exchange and correlation potential. Orbital moments were evaluated from single self-consistent relativistic calculations. Here, in addition to the LSDA calculations, orbital polarization corrections (LSDA+OP<sup>21</sup>) were applied to the Fe 3d states. The basis set in all of the calculations consisted of Fe 3d and 4sp and Pt 5d and 6sp states and the volume of the unit cell in the calculations was kept fixed to the experimental value for Fe<sub>70</sub>Pd<sub>30</sub>.

# **III. RESULTS**

The calculated MAE as a function of c/a ratio for (hypothetical)  $L1_2$ -ordered Fe<sub>3</sub>Pd and disordered fct-Fe<sub>68.75</sub>Pd<sub>31.25</sub> is shown in Fig. 2. Also shown is the MAE of Fe<sub>70</sub>Pd<sub>30</sub> in the  $L1_2$  structure, assuming a rigid band shift. For the ordered systems, it is observed that the MAE depends in a nonmonotonous way on the c/a ratio. Close to cubic symmetry (c/a=1), the MAE is almost proportional to (1-c/a) and the absolute value strongly increases with decreasing c/a ratio in all of the three cases. For tetragonal systems, the MAE is generally much higher than for cubic symmetry. This can be understood from perturbation theory: the contribution of spin-orbit coupling, which is the dominating and the only considered term in the present calculation, is of second order for tetragonal systems, whereas it is of fourth order for cubic systems.

Ordered  $Fe_3Pd$  can be considered the simplest prototype for the simulation of the electronic structure of disordered  $Fe_{70}Pd_{30}$  with a similar concentration and a related structure. Indeed, the overall density of states (not shown) and the



FIG. 2. (Color online) Calculated MAE as a function of c/a ratio for  $L1_2$ -ordered Fe<sub>3</sub>Pd (squares) and disordered Fe<sub>68.75</sub>Pd<sub>31.25</sub> (diamonds). Also shown is the effect of a change of the band filling on the MAE in the  $L1_2$  structure (circles) with an electron number corresponding to Fe<sub>70</sub>Pd<sub>30</sub>. Experimental data points (crosses) are taken from a temperature dependent measurement published for bulk Fe<sub>68.8</sub>Pd<sub>31.2</sub> (Ref. 22).

calculated atomic spin moments  $\mu_{\rm Fe}=2.7\mu_B$  and  $\mu_{\rm Pd}$ =0.25 $\mu_B$  are already quite close to the results of CPA calculations for the disordered alloy.<sup>23</sup> The orbital moments, which are obtained from self-consistent calculations, contribute  $0.08\mu_B$  (Fe) and  $0.05\mu_B$  (Pd) to the total moment in LSDA. Upon inclusion of orbital polarization corrections (LSDA+OP),<sup>21</sup> which provide usually a more realistic value for the orbital moment of 3d atoms, the orbital moment of Fe is about 0.14 $\mu_B$ . The MAE, however, is very sensitive to the details of the electronic structure and, thus, also to the atomic order. In the case of Fe<sub>3</sub>Pd, the MAE exhibits a maximum around c/a=0.94 with an absolute value that is more than two times larger than the experimental value of the disordered alloy.<sup>7</sup> More severe, the easy axis is the c axis in contrast to the experimentally observed easy a axis in disordered  $Fe_{70}Pd_{30}$  (i.e., the sign of the MAE is opposite).

By only considering the composition, a part of this difference can be attributed to the different electron count in Fe<sub>3</sub>Pd compared to Fe<sub>70</sub>Pd<sub>30</sub>. This can be best seen from the MAE calculated in the  $L1_2$  structure with a band filling corresponding to that of Fe<sub>70</sub>Pd<sub>30</sub>. The MAE decreases (except for c/avalues very close to 1), i.e., the *c* axis becomes energetically less favorable with increasing Pd concentration. However, the tetragonal *c* axis remains the easy axis for the c/a values of interest. Thus, disorder is essential for the sign of the MAE in Fe<sub>70</sub>Pd<sub>30</sub>.

The importance of disorder on MAE is confirmed by the results of our supercell calculations. The average spin moments are almost unchanged in comparison to the ordered structure,  $\mu_{Fe}=2.75\mu_B$  ( $\pm 0.05\mu_B$  depending on the local environment) and  $\mu_{Pd}=0.25\mu_B$ . The same holds for the orbital moments that amount to about  $0.08\mu_B$  (Fe) and  $0.04\mu_B$  (Pd) in the LSDA calculations, and  $(0.13\pm0.02)\mu_B$  (Fe) and  $0.04\mu_B$  (Pd) in the LSDA+OP calculations. The calculated values for the MAE of the disordered alloy have an appreciable uncertainty, which is mainly due to the limited number of ensemble members available for averaging and the limited size of the cell (the variations between different ensemble members are comparable to the size of the MAE). However, the results should be sufficient for a qualitative discussion of the different influences on the MAE. The calculated easy



FIG. 3. (Color online) Calculated MAE for disordered fct-Fe-Pd as a function of band filling for fixed c/a ratio of 0.95.

axis for disordered Fe<sub>70</sub>Pd<sub>30</sub> is the tetragonal *a* axis, which is in agreement with the experiment. The absolute values of the MAE are close to the experimental literature values. The MAE strongly increases with decreasing c/a but is expected to saturate for lower values since the symmetry becomes cubic again for c/a=0.71 (bcc structure).

The concentration dependence of the MAE for fixed c/a=0.95, which is calculated under the assumption of a rigid band shift, is shown in Fig. 3. The MAE strongly increases from a Pd concentration of 25 at. % to a maximum at around 32 at. %. A further increase in Pd content results in a decrease in MAE to a local minimum at 37 at. % Pd. The changes of the MAE with concentration and c/a ratio are both comparable in size. Both effects compete in bulk since the c/a ratio increases with increasing Pd concentration. In epitaxial films, where c/a has only a weak concentration dependency, the Pd concentration should be dominant, leading to an increase in MAE with increasing Pd content.

In order to experimentally assign the structure and magnetic properties at room temperature, in-plane hysteresis curves of epitaxial Fe-Pd films with different Pd contents were measured (Fig. 1). At low Pd content, the hysteresis exhibit a steplike switching behavior. At higher Pd content, the open hysteresis with increased coercivity  $H_C$  is observed, and after hysteretic switching, a nearly linear increase in magnetization toward saturation occurs. This kind of hysteresis is expected for a multivariant martensite state exhibiting magnetocrystalline anisotropy. Variants with the easy axis along the field direction show irreversible switching with an open hysteresis. Variants with the hard axis along the field direction exhibit reversible rotation of magnetization instead, which results in a continuous increase in magnetization until saturation. The saturation field  $H_S$  is estimated from the intersection of the linear extrapolations of J from low field and high field, respectively, as indicated in Fig. 4. By considering the existence ranges of the different phases at room temperature, the changes in the magnetic hysteresis can be attributed to the structural changes (films with 33 at. % Pd and 29 at. % Pd forming in fct and 28 at. % Pd forming in bct and 25 at. % Pd forming in bcc structure). The bcc films show low coercivity and low saturation field due to the highly symmetric structure. The bct films behave similar to that of the bcc films but exhibit slightly higher coercivity and slightly reduced saturation field. Compared to the bcc and



FIG. 4. Hysteresis curves for different Pd content measured at room temperature.

bct films, the fct films exhibit a different loop shape with highest coercivity and highest saturation field. Although no sample exhibited the fcc phase, due to the high symmetry of fcc, again low coercivity and low saturation field are expected. In the following, if not differently stated, structural descriptions such as fct, bct, and bcc assign the structure of the films at room temperature.

Temperature dependent hysteresis measurements during cooling of films with different Pd contents are applied to investigate phase transitions in the range of 400–50 K. The low-field region of the in-plane hysteresis is depicted in Fig. 3. The insets in Fig. 5 show the full hysteresis loops measured along the out-of-plane and in-plane directions. It is observed that in low fields, the shape of the hysteresis exhibits a significant composition and temperature dependence. The temperature dependent changes of the in-plane hyster-



FIG. 5. Hysteresis curves for the Fe-Pd films with different Pd contents. The main graphs show in-plane measurements (along MgO[100]) at different temperatures. The insets show the comparison of hysteresis curves measured in plane and out of plane at 300 K up to higher magnetic fields.

esis loops can be best seen in the extracted values of  $H_C$  and  $H_{\rm s}$  [Figs. 6(a) and 6(b)]. It is observed that films with bct or bcc structure (≤28 at. % Pd) constantly exhibit low coercivity and low saturation field over the whole temperature range. The bcc films exhibit slightly higher  $H_S$  compared to the bct films. No indication of a phase transformation is observed. Compared to this, the fct films ( $\geq 29$  at. % Pd) behave differently. At 300 K and above, the fct films with 29 at. % Pd exhibit an open hysteresis loop having high  $H_C$ and  $H_{\rm S}$ . When reducing temperature below 300 K, a continuous decrease in  $H_S$  and  $H_C$  is observed down to 50 K. The same behavior of  $H_C$  and  $H_S$  has been reproduced in a second experiment on the same sample (dashed line), which indicates a reversible behavior of this transition. The fct films with slightly increased Pd content of 33 at. % Pd exhibit a similar magnetic behavior. The transition in  $H_S$  and  $H_C$  is



FIG. 6. Temperature dependence of (a) in-plane coercivity  $\mu_0 H_C \parallel$  and (b) saturation field  $\mu_0 H_S \parallel$  and (c) out-of-plane coercivity  $\mu_B H_C \perp$ . For the sample with 29 at. % Pd, the measurement was repeated (dotted line). No indication of irreversible changes are observed. All of the measurements were performed during cooling.



FIG. 7. SQUID magnetization measurement at an applied field of 1 T (in plane, along MgO[100]).

shifted to lower temperatures of about 200–250 K. When further increasing Pd content to 37 at. % Pd, no transition is observed in contrast to the other two fct films. In this case,  $H_C$  shows an almost linear increase with decreasing temperature.  $H_S$  only shows minor changes and a weak maximum between 200 and 250 K.  $H_C$  and  $H_S$  are the highest of all the examined films.

Along the in-plane direction, all of the films are fully saturated at a field of 0.5 T. In the out-of-plane direction, the shape anisotropy dominates the magnetization behavior. As expected for a demagnetization factor of 1, the extrapolation of the curve for the out-of-plane direction intersects the curve of the in-plane direction at  $\mu_0 H \approx J_s$ . The magnetization curve, however, does not go straight into saturation. As for the in-plane measurements, this can be attributed to the rotation of magnetization to the hard axis. In the out-of-plane data, a small hysteresis is also observed. Since the rotation of magnetization cannot explain this, this indicates that a small fraction of the variants has their easy axes partially aligned out of to the film plane. The development of  $H_C$  of the outof-plane hysteresis for different Pd contents is summarized in Fig. 6(c). The observed trends are similar to  $H_C$  measured in plane.

Since at a Pd content of 29 at. %, the most pronounced changes were observed in magnetic hysteresis measurements, more detailed investigations were performed. SQUID magnetization measurements [Fig. 7(a)] indicate that between 290 and 270 K, a small but visible hysteretic change in saturation magnetization occurs. This temperature range coincides with the temperature where  $H_C$  and  $H_S$  begin to decrease.

Due to single-crystal-like microstructure, epitaxially grown films often allow us to identify the easy magnetization directions by measuring the angular dependent hysteresis curves within the film plane.<sup>24</sup> Hysteresis measurements were performed along different in-plane directions at room temperature (not shown). It is observed that bcc films have preferred magnetization directions in plane along  $\langle 100 \rangle_{bcc}$ . In contrast, the bct films can be magnetized easiest along the in-plane  $\langle 110 \rangle_{bct}$  directions. For the fct films, however, no preferred in-plane magnetization axes are observed. This unexpected behavior of the fct films is explained in the following.

#### **IV. DISCUSSION**

The experimentally observed increase in MAE during tetragonal distortion from fcc to fct could be verified by the presented density functional theory (DFT) calculations. The MAE versus tetragonal distortion calculated for disordered Fe<sub>70</sub>Pd<sub>30</sub> here revealed an almost linear relationship. This shows that this intuitively expected behavior is even valid for a distortion of several percent and allows identifying the proportional constant as magnetoelastic coupling coefficient. For the Ni-Mn-Ga system, this concept has been differently used and the MAE of martensitic phases with different c/aratios that were compared by Chernenko *et al.*<sup>25</sup> gives an idea of the MAE versus c/a ratio in Ni-Mn-Ga. Although the linear dependence in Fe-Pd suggests the importance of magnetostriction, one can still unambiguously distinguish between conventional (anisotropic) magnetostriction (where the origin of the tetragonal distortion is the magnetic field) and the magnetic shape memory effect (where the origin of the tetragonal distortion is the martensitic transformation, which induces the magnetocrystalline anisotropy).

The maximum magnetic stress of the magnetic shape memory effect achieved in a field exceeding the anisotropy field is  $\sigma_M = \text{MAE}/(1-c/a)$ .<sup>26</sup> Accordingly, the linear behavior of MAE ~ (1-c/a) suggests that  $\sigma_M$  is constant and thus independent of the c/a ratio. To obtain any twin boundary movement, however,  $\sigma_M$  must exceed the twinning stress  $\sigma_{\text{TW}}$ . Since in Fe-Pd the c/a ratio strongly varies with temperature,<sup>22</sup> it will be interesting to perform temperature dependent measurements of the MSM effect, which is similar to those made for the Ni-Mn-Ga system.<sup>27</sup>

Furthermore, DFT calculations predict an increase in MAE with increasing Pd content up to 32 at. % in the fct phase. In order to observe these changes in magnetic anisotropy, in-plane hysteresis loops of Fe-Pd films have been measured. The extracted values  $H_C$  and  $H_S$  show similar temperature dependent behavior (with an exception at 37 at. % Pd). Although  $H_C$  is an extrinsic property, depending also on the microstructure, its origin is the magnetocrystalline anisotropy. It is thus justified to take the temperature dependence of both  $H_C$  and  $H_S$  as indicators for the temperature dependence of MAE. A low coercivity, as observed in the present case, is common for a system with an easy plane anisotropy.

At room temperature,  $H_S$  indicates highest magnetic anisotropy in the fct samples. When measuring hysteresis curves with the field applied in plane, internal and external fields are equal due to shape anisotropy. This allows identifying the in-plane saturation field with the anisotropy field,  $H_S = H_A$ ; one can use  $\langle K \rangle = H_S \cdot J_S/2$  to estimate the MAE. This approach is valid for single crystal films without restrictions when magnetizing along the hard magnetization directions, whereas for polycrystalline films, this approach typically underestimates  $H_A$ . The MAE of the fct films increases with increasing Pd content: it is 11.2 kJ/m<sup>3</sup> for 29 at. % Pd, 14.9 kJ/m<sup>3</sup> for 33 at. % Pd, and 31.9 kJ/m<sup>3</sup> for 37 at. % Pd. Since the fct films exhibit only a weak variation of c/a(around 0.95–0.96), the influence of c/a on MAE should be comparably small.<sup>5</sup> For comparison, the following absolute MAE values for Fe-Pd fct bulk were reported in literature: 35 kJ/m<sup>3</sup> (Ref. 6) and 80 kJ/m<sup>3</sup>, (Ref. 22) which were obtained at T=273 K, 29.8 at. % Pd and T=200 K, 31.2 at. % Pd, respectively (c/a=0.96). Compared to the calculations and to literature values, the absolute value of MAE of the fct phase in the films is significantly reduced.

Contrary to the calculations describing the situation at 0 K, bulk and film experiments have been performed at finite temperatures. Nonetheless, bulk and theory show reasonable agreement. This is not unexpected since all of the measurements have been performed at temperatures significantly below  $T_c$ .<sup>1</sup> The c/a ratio slightly varies in this comparison since it cannot be independently controlled in the experiments. However, the error arising from this should be negligible. In order to explain the remaining (significant) MAE differences between bulk and films, the microstructure needs to be considered.

It was shown that the bcc, bct, and fct films epitaxially grow on MgO substrates. While the texture of the bcc and bct films remains constant throughout the entire film thickness, it was observed that in the fct films, only the first 20 nm grow highly textured. At higher film thickness, stress induced (111) deformation twinning was observed.<sup>15</sup> Deformation twinning is in common for all of the investigated fct films and occurs in addition to the (110) twins expected from martensitic transformation.<sup>5</sup> Thus, deformation twinning disturbs the texture and leads to misalignment of the easy axes compared to a single crystal configuration. This explains the magnetically isotropic behavior observed in the fct films for different in-plane directions. For the fct films with 29 at. % Pd, a coherence length as low as 3 nm was observed in x-ray diffraction, suggesting a high density of martensitic and deformation twins.<sup>5</sup> When identifying the coherence length with the grain (or variant) size, one has to consider the nanoscale microstructure in the fct films for the interpretation of magnetic measurements. Although magnetocrystalline anisotropy is typically considered as an intrinsic property only depending on the crystal structure, this concept must be adapted for nanostructured materials. According to the random-anisotropy model,<sup>28</sup> the externally observable average magnetic anisotropy  $\langle K \rangle$  is determined by exchange coupling of neighboring nanocrystalline ferromagnetic grains. This becomes important once the grain size is below the exchange length  $l_{\text{exch}} = 2\sqrt{A\langle K \rangle^{-1}}$ . By using the exchange constant for stoichiometric FePd  $[A=2\times10^{-11} \text{ J/m}]$  (Ref. 29)] and the measured magnetocrystalline anisotropy in the films, one obtains exchange lengths in the range of 18-85 nm for the fct films (with 37 and 29 at. % Pd, respectively), which is significantly above the observed coherence length of 3-8 nm.<sup>5</sup> Since for grain sizes D, which are below the exchange length, the effective anisotropy vanishes with  $D^{6,28}$ a significantly lower anisotropy is observed in these films compared to single crystals. Since the driving force for magnetically induced reorientation is the magnetocrystalline anisotropy energy,<sup>30</sup> it is suggested that the exchange length is a lower limit for the grain size where the MSM effect should be observable. Since the observed grain size<sup>5</sup> is significantly lower compared to the film thickness, the influence of a possible surface anisotropy can be neglected.

In the fct films with 29 and 33 at. % Pd, a continuous reduction in  $H_S$  and  $H_C$  is observed below 300 and 250 K, respectively, and indicates decreasing anisotropy. This is opposite to what is expected for a simple ferromagnet and opposite of what is typically observed in bulk Fe-Pd within the fct phase.<sup>22</sup> This suggests the occurrence of a phase transition that could explain this unexpected behavior. Continuous,

second-order-like phase transformation has been reported for the martensitic transition from fcc austenite to fct martensite.<sup>6,31</sup> This transition, however, can be excluded since the films with  $\geq 29$  at. % Pd are already in the tetragonally distorted fct phase at room temperature.<sup>5</sup> Instead, in bulk, at low temperatures, the occurrence of a fct bct transition is observed.<sup>6</sup> In our room-temperature hysteresis measurements, it was observed that the bct (and bcc) films exhibit both lower  $H_S$  and  $H_C$  compared to the fct films. In the temperature dependent measurement, an fct film with 29 at. % Pd exhibited reduction of both  $H_S$  and  $H_C$  to values similar to that of the bct phase at low temperatures. Furthermore, in agreement with the fct-bct transition in "metastable phase diagrams" for bulk,  $^{6,14}$  the onset of  $H_S$  and  $H_C$  reductions shifts to lower temperature with increasing Pd content. It is thus suggested that the observed transition is a gradual transformation from fct to bct at low temperatures. The composition dependent onset of the fct-bct transformation is sketched in the metastable phase diagram for the Fe-Pd films (Fig. 1). In bulk experiments, this transition was reported to be irreversible.<sup>6</sup> In contrast, this transformation is reversible in films. Irreversible martensitic transformations usually originate from unfavorable habit planes<sup>32</sup> or volume changes during the transition. In contrast to bulk systems, thin films can easily compensate a volume change by a change of film thickness. This might explain the observed reversible behavior.

In contrast to the continuous change in  $H_S$  and  $H_C$ , the temperature dependent measurement of saturation magnetization exhibits a steplike hysteretic change at the beginning of the fct-bct transformation in SQUID measurements. Although the step is small, it indicates that the bct phase has a slightly higher magnetization compared to fct and that this transformation is of first order. The saturation magnetization is a purely intrinsic magnetic property. In contrast, both  $H_S$  and  $H_C$  are extrinsic properties (microstructure dependent). One may speculate that the fct-bct transformation is indeed of sharp first order, but the adaption of the microstructure is continuing below the transformation temperature. A continuous adaption of microstructure may be necessary since elastic properties may strongly vary around a martensitic transformation.<sup>33</sup>

When comparing bct to bcc films, a slight increase in  $H_S$  is observed even though symmetry increases. The in-plane easy magnetization directions are  $\langle 110 \rangle$  for bct films and  $\langle 100 \rangle$  for bcc films. In both films, [110] is aligned parallel to MgO[100] and thus parallel to the measurement direction in the temperature dependent measurements. The slightly harder magnetization behavior along [110] observed in the bcc films is thus a consequence of the modified easy axis direction and not of an unexpected increase of MAE.

## **V. CONCLUSION**

Magnetic properties of Fe-Pd alloys have been studied by using DFT calculations and by measurements on epitaxially grown films. The magnetic behavior of Fe-Pd films with fct, bct, and bcc structure has been studied in the temperature range from 400 to 50 K. At room temperature, it is observed that the fct films have higher coercivity and magnetocrystalline anisotropy compared to the bct and/or bcc films. This allows phase identification by magnetic measurements. In agreement with bulk data, an almost linear increase in MAE with decreasing c/a ratio is predicted for disordered Fe<sub>70</sub>Pd<sub>30</sub> from theory. Additionally, the composition influence on MAE was examined in DFT and thin films. Thin film experiments and calculations significantly differ in the magnitude of MAE. The difference could be attributed to the nanoscaled film microstructure, which is in accordance with the random anisotropy model. According to temperature dependent hysteresis measurements, Fe-Pd fct films with Pd <33 at. % continuously transform to the bct phase during cooling. It is suggested that the continuous change in coercivity and saturation field are due to continuous adaptation of martensitic microstructure. In contrast to bulk materials, this transformation is reversible in thin films.

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