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Citation: *J. Appl. Phys.* **91**, 7818 (2002); doi: 10.1063/1.1449443

View online: <http://dx.doi.org/10.1063/1.1449443>

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Electronic and structural properties of Fe₃Pd–Pt ferromagnetic shape memory alloys

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Ferromagnetic shape memory (FSM) alloys are scientifically and technologically interesting materials that combine ferromagnetism with a reversible martensitic phase transformation. Fe₇₀Pd₃₀ has recently been shown to display a FSM effect at usable temperatures and low fields. Reported here are results of experimental studies on Fe₇₀Pd₃₀ and electronic structure calculations on Fe₇₀Pd_{30-x}Pt_x. The calculations show that additions of Pt by 6 at % to Fe₇₀Pd₃₀ can triple the magnetocrystalline anisotropy. There is, however, a large discrepancy between the measured and calculated anisotropy values of Fe₇₀Pd₃₀, suggesting the presence of significant disorder in the measured samples. Other calculated structural and magnetic properties are in close agreement with experimental values. © 2002 American Institute of Physics. [DOI: 10.1063/1.1449443]

INTRODUCTION

Ferromagnetic shape memory alloys (FSMA) are ferromagnetic materials exhibiting a reversible symmetry-breaking structural phase transition. This combination of properties allows the material to change its shape with application of an external magnetic field. There are three currently known mechanisms that can produce the shape change. First, the structural transition can be induced, as in Fe–Ni alloys,¹ although this requires very large fields, about 10 T for a 20 °C shift. Second, the magnetization can be rotated with respect to the crystal lattice, as in Terfonol-D.² This requires negligible magnetocrystalline anisotropy (MCA), so that there is little or no energy cost for rotating the magnetization. Finally, structural domains can be rearranged through domain wall motion, as in Ni₂MnGa (Ref. 3) and the Fe₇₀Pd₃₀ (Ref. 4) alloys considered here. This third mechanism requires high domain wall mobility, large magnetizations, and large MCA. The large MCA essentially pins the magnetization along the crystalline easy axis, ensuring a significant driving force on the domain walls.

Here we report upon a joint theoretical and experimental study of the relatively new Fe₃Pd-based FSMA. The theoretical work involves a study of structural, elastic, and magnetic properties of Fe₇₀Pd_{30-x}Pt_x using first principles electronic structure calculations. Experimental results include measurements of magnetic and structural properties of Fe₇₀Pd₃₀, along with an ongoing ordering study and preliminary magnetic force microscopy images of relevant domain structures.

RESULTS

We first focus on the two ordered compounds Fe₃Pd and Fe₃Pt. Density functional calculations on these materials were performed using the Vienna *Ab Initio* Simulation Package (VASP) (Ref. 5) with ultrasoft pseudopotentials⁶ and the generalized gradient approximation (GGA) to the exchange and correlation energy.⁷ This full potential program allows us

to study magnetic and structural properties of the martensite and austenite structures. Elastic constants and bulk moduli for each stable phase were calculated by performing appropriate lattice distortions and fitting the variation in total energy to the standard equation of state.⁸

In both the cubic and tetragonal phases of ordered Fe₃Pd and Fe₃Pt, the Pd and Pt atoms are located at the vertices of a cubic lattice, while the Fe atoms occupy the face centers. Completely ordered Fe₃Pt is cubic, and does not exhibit a martensitic transformation. Only when the crystal is disordered does a martensitic phase appear, with the martensitic transition occurring between 80 and 100 K, depending on the degree of order.⁹ Consistent with this are the results of our calculations, indicating the existence of two stable phases of Fe₃Pt, a cubic phase and a tetragonal phase, which are nearly degenerate in energy. On the other hand, Fe₃Pd is calculated to have only a stable tetragonal phase; the cubic phase is unstable with respect to tetragonal distortions. The very small negative value of C₁₁–C₁₂ obtained for the cubic phase of Fe₃Pd along with the positive value of C₄₄ suggests the tetragonal phase might indeed be stabilized by additions of Pd, as was found to be the case experimentally.

Calculated lattice constants are in close agreement with measured results, and elastic constants appear reasonable, although we have not found experimental values with which to compare. A summary of computational and experimental results is given in Table I. Figure 1 shows the variations in total energy of the stable phases as a function of the unit cell volumes for isotropic distortions. The near-degeneracy of stable phases for Fe₃Pt is obvious.

Next we turn to the alloy Fe₇₀Pd₃₀ which was studied experimentally. Three samples were cut from a single crystal boule, obtained by the Bridgman method. After stress biasing the sample to ensure a single variant, M–H curves were measured by vibrating sample magnetometry (VSM). A detailed description of both the samples and experimental techniques can be found in Ref. 12. The sample on which anisotropy

TABLE I. Structural, elastic, and magnetic constants of Fe₃Pd and Fe₃Pt.

	Structure	<i>a</i> -axis (Å)		<i>a/c</i>		Bulk Mod	<i>C</i> ₁₁ – <i>C</i> ₁₂	<i>C</i> ₄₄	Magnetization (emu/cm ³)	
		Calc.	Expt.	Calc.	Expt.				Calc.	Expt.
Fe ₃ Pt	tet	3.822	3.820 ^a	1.047	1.059 ^a	1.66	0.544	0.642	1523	1539 ^b
Fe ₃ Pt	cubic	3.762	3.730 ^c	1.000	1.000	1.82	0.106	0.596	1512	
Fe ₃ Pd	tet	3.791	...	1.030	...	1.72	0.295	0.645	1519	
Fe ₃ Pd	cubic	...	3.818 ^c	...	1.000 ^c				...	
Fe ₇₀ Pd ₃₀	tet	...	3.8375		1.0843				1362	1200 ± 20 ^d
Fe ₇₀ Pd ₃₀	cubic	...	3.7534		1.000				1362	1200 ± 20 ^d

^aReference 9.
^bReference 10.
^cReference 11.
^dReference 4.

measurements were performed was heat treated at 900 °C for 2 h, followed by a rapid quench into a 10% by weight solution of NaOH at –8 °C. This rapid quench was done to raise the austenite/martensite transformation temperature, which is very sensitive to precipitation.

First principles electronic structure calculations were done using the layered Korringa–Kohn–Rostoker (LKRR) (Ref. 13) approach within the coherent potential approximation (CPA).¹⁴ This is one of the few approaches that can treat substitutionally disordered random alloys. However, this method is based upon the atomic sphere approximation (ASA) and uses spherical potentials, hence this technique is less accurate than the full potential VASP approach. We used this method to calculate magnetizations and magnetocrystalline anisotropies at the experimental volumes, but not lattice or elastic constants.

The magnetization values presented in Table I are consistent with the magnetic moment being associated primarily with the Fe atoms. The smaller magnetization found in Fe₇₀Pd₃₀ compared with that of Fe₃Pd simply reflects the decreased Fe content. Measured experimental magnetizations as a function of external field are shown in Fig. 2.

MCA calculations were performed for the series of alloys of the form Fe₇₀Pd_{30–x}Pt_x, with *x* ≤ 0 ≤ 6.25. Pt atoms were distributed on the Pd site. Figure 3 displays the results

as a function of the Pt composition, *x*. We found that the alloys all had a uniaxial MCA. Additions of Pt by 10% increase the MCA by a factor of 3, a consequence of the greater spin–orbit coupling of Pt as compared to Pd. However, the calculations reveal anisotropy constants an order of magnitude greater than those found in the laboratory; experimental MCA values extracted from hysteresis loops yield a value of 0.031 MJ/m³. For comparison, the calculated MCA values are about 0.30 MJ/m³. In addition, although the calculated easy axis is the [001] axis, the sample does not appear to be uniaxial; there exists substantial magnetic anisotropy in the *a*–*b* plane. Following the first principles results reported here, we later confirmed that x-ray diffraction scans of this sample showed no evidence of superlattice peaks associated with the accepted ordering of Fe₃Pd. These discrepancies suggest the presence of significant disorder in the sample, produced by rapid quenching during sample preparation. A partial source of this disorder may be the presence of an irreversible BCT martensite phase. A complete ordering study is currently in progress.

CONCLUSIONS

First principles electronic structure calculations have been performed on a series of Fe₃Pd–Pt alloys in an effort to understand the FSM effect in these materials. We have found

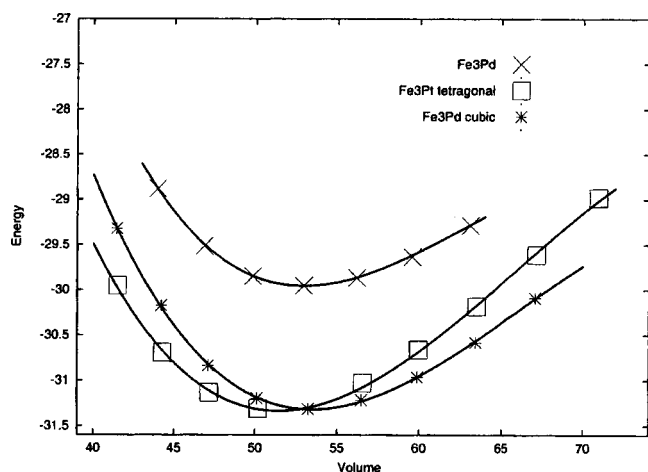


FIG. 1. Ground state energy in eV as a function of volume in Å³, for isotropic expansions.

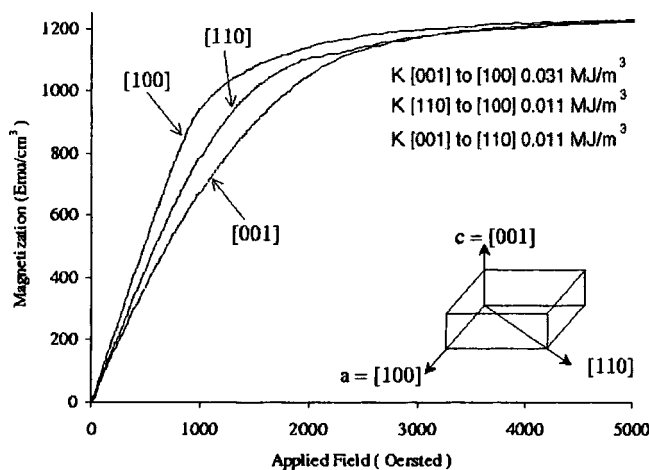


FIG. 2. Magnetization vs external field for Fe₇₀Pd₃₀.

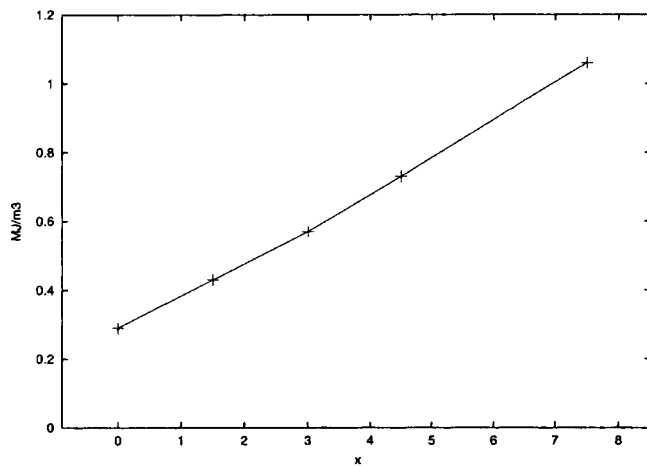


FIG. 3. Magnetocrystalline anisotropy in MJ/m^3 as a function of x for $\text{Fe}_{70}\text{Pd}_{30-x}\text{Pt}_x$.

that additions of Pt dramatically increase the MCA, although the anisotropy may be reduced by an order of magnitude by rapidly cooling the samples. Increasing the anisotropy implies a smaller external field can be used to reorient the variants, although structural disorder is necessary to raise the martensitic transition temperature to a useful range. If it is

not reasonable to increase the order in these materials, then perhaps alloying with Pt can maintain a large magnetocrystalline anisotropy.

ACKNOWLEDGMENTS

The work at Tulane was supported by the Office of Naval Research Award No. N000149910924 and the National Science Foundation Award No. DMR-9971573. The work at the University of Minnesota was supported by the Office of Naval Research under Award No. N000149910925.

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