

Competition between ferromagnetism and antiferromagnetism in FePtG. Brown,^{1,2,3} B. Kraccek,⁴ A. Janotti,^{1,5} T. C. Schulthess,^{1,2} G. M. Stocks,^{1,5}
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FePt in the $L1_0$ (tetragonal) phase is of interest due to its ease of synthesis as nanoparticles and because superparamagnetism is suppressed by the large magnetoanisotropy energy (MAE) of the $L1_0$ phase. Here we present the results of first-principles electronic-structure calculations that reveal a competition between ferromagnetic (FM) and antiferromagnetic (AFM) ordering of the alternating Fe planes, with energy differences less than room-temperature thermal energy. We find that the FM state is stabilized relative to the AFM state as $L1_0$ tetragonal distortion decreases or chemical (antisite) disorder increases on Pt planes. Inherently, then, there is a competition between stabilizing the FM state and maintaining the large MAE in FePt, and optimally maximizing both is important for nanomagnetic applications.

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Equiatomic FePt is a material of great promise for nanoscale magnetic applications because it can be synthesized chemically as monodisperse particles with tunable diameters from 3 to 10 nm (Refs. 1 and 2) and its high magnetoanisotropy energy (MAE) suppresses superparamagnetism at these volumes. Experiments find both bulk and nanoparticle samples to be ferromagnetic, and first-principles electronic-structure calculations agree quantitatively for such properties as the average atomic magnetic moment. However, these calculations have *a priori* assumed a symmetry for the magnetic moments consistent with the ferromagnetic state. Here we present first-principles calculation results that do not assume such high symmetry and find near degeneracy between ferromagnetic (FM) and antiferromagnetic (AFM) ordering of the alternating Fe layers in FePt. In fact, our calculations indicate that ferromagnetism is observed experimentally only because of imperfect long-range ordering in sample crystals.

FePt orders from the disordered fcc ($A1$) structure to the $L1_0$ (face-centered tetragonal) structure, in which the Fe and Pt atoms form layers occupying alternating (001) planes of the original fcc lattice. The [001] direction acts as both the tetragonal symmetry axis (hereafter the c axis) and the magnetic easy axis. The ordering is accompanied by a contraction along the c axis, changing the ratio c/a from the cubic value of 1. Thermodynamically, real crystals are subject to chemical disorder with substitution of Fe(Pt) atoms into Pt(Fe) sublattice without changing the stoichiometry. The degree of chemical ordering can be characterized by a long-range order parameter $\eta = c[\text{Fe}] - c[\text{Pt}]$ where $0 \leq \eta \leq 1$ and $c[\text{Fe}]/(c[\text{Fe}] + c[\text{Pt}])$ is the site composition (or site probability) of Fe on the Fe (Pt) sublattice.

Experiments in equiatomic FePt thin films have found that chemical disorder, c/a , coercivity and magnetic anisotropy are related to one another: as η increases, c/a decreases and the coercivity and magnetoanisotropy for moments parallel to the c axis increase.^{3,4} These properties can be controlled

by annealing temperature for films deposited in the $A1$ phase⁴ or substrate temperature for films which order during deposition.^{3,5} The relative volume of FePt to B_2O_3 matrix in nanocomposite films has also been found to change c/a .⁶ Furthermore, c/a is affected by the relative composition of Fe and Pt, although the minimal value $c/a = 0.966$ is found at 50 at% Fe.⁷ Coercivity and MAE are also affected by composition, with maxima in samples which are shifted towards the Fe-rich $L1_0$ stoichiometries.^{2,7,8} The coercivity has also been shown to be strongly dependent on the defect structure of the samples,^{9,10} which can be controlled by processing.

For magnetic materials with a single, easy anisotropy axis MAE is determined from the difference in total energy between magnetic moments oriented parallel and perpendicular to the c axis. Since the energy difference between these states is much smaller than their individual values, first-principles calculations of MAE require extremely high precision. The computational resources for such calculations in FePt have only recently become available, but several calculations have now been completed.¹¹⁻¹⁵ These calculations find that the large anisotropy of FePt is related to its $L1_0$ structure. Willoughby *et al.* found that the calculated anisotropy energy is linearly related to c/a for equiatomic FePt,¹³ and similar behavior has been measured in thin films.³ However, these MAE calculations have all implicitly assumed perfect FM order. In calculating exchange energies in FePt, Zeng *et al.* used a method which does not constrain moments to point in the same direction⁶ and found AFM order for c/a less than about 0.95. However, the authors categorized these results as “erroneous,” presumably since only FM order has been observed experimentally. In this letter, we investigate the competition between FM and AFM in FePt, and particularly the stabilization of FM order via substitutional disorder which is present in all materials.

We performed first-principles calculations based on the local spin-density approximation (LSDA) to density-

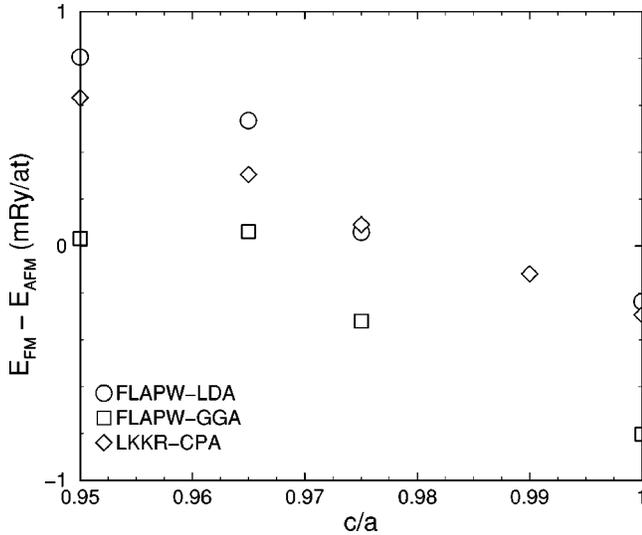


FIG. 1. Total-energy difference between ferromagnetic, E_{FM} , and antiferromagnetic, E_{AFM} , states vs. c/a . The FM state is more favorable as $c/a \rightarrow 1$. The AFM state is most favorable for nonideal c/a . All results are for perfectly ordered $L1_0$ FePt with $\eta = 1$, i.e., in the absence of chemical disorder.

functional theory¹⁶ as implemented in the approximate bulk Korringa-Kohn-Rostoker^{17,18} (KKR) and layered-KKR¹⁹ (LKKR) methods, which use the atomic sphere approximation (ASA), and the more accurate full-potential linearized augmented plane wave²⁰ (FLAPW) methods. The generalized-gradient approximation²¹ (GGA) was used within the FLAPW as a check, but it was found to have no qualitative difference to the LSDA results.²² In general, GGA is not more accurate than LSDA for magnetic calculations,²³ and specific cases exist where LSDA results are closer to experiment, see, e.g., Refs. 24 and 25. The KKR calculations use a new, variational definition of potential-energy zero that often dramatically improves agreement with respect to full-potential results,²⁶ which we quantify below. Both KKR methods were used in combination with the coherent-potential approximation (CPA) to investigate the effects of disorder on stability and structural properties.²⁷ Charge-correlation effects within (partially) disordered configurations were included within the bulk KKR-CPA calculations to improve the CPA description of the configurationally averaged Coulomb energy.²⁸

We calculated the difference in the total energies, $E_{FM} - E_{AFM}$, between the FM and AFM state in FePt as a function of c/a . The LKKR and FLAPW (both LSDA and GGA) results are presented in Fig. 1, where positive (negative) energy differences indicate stability of the AFM (FM) states. We find that the energy difference separating the FM and AFM states is less than room temperature for all c/a considered here. Both the FLAPW and LKKR calculations find the FM state is stabilized as $c/a \rightarrow 1$, which is the same trend found by Zeng *et al.* However, the present LSDA results find AFM order stable for significantly higher c/a . Combined with the fact that relaxing $c/a \rightarrow 1$ is known to reduce the MAE,^{3,13} it is clear that the magnetic ordering of FePt thin films depends sensitively on the substrate lattice parameters.

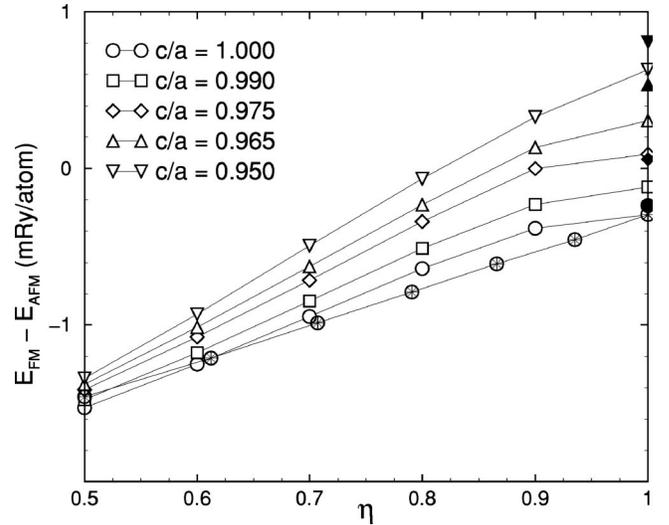


FIG. 2. Total-energy differences between ferromagnetic, E_{FM} , and antiferromagnetic, E_{AFM} , states vs the long-range order parameter η for LKKR-CPA (open symbols) and bulk KKR-CPA (star-filled symbols) methods. Details are found in text, but several c/a with fixed unit-cell volume are used. The lines are a guide to the eye. The solid symbols are for FLAPW-LSDA results.

The impact of chemical disorder, i.e., the antisite substitution of Fe(Pt) into Pt(Fe)-rich layers, is calculated via the KKR-CPA method,²⁷ which also can be related to characterization experiments; see, e.g., Ref. 29. In Fig. 2, $E_{FM} - E_{AFM}$ versus η is shown. The LKKR-CPA results (bulk KKR) are the open (star-filled) symbols. The FLAPW-LSDA results at $\eta = 1$ (solid symbols) are included for comparison. We note in passing that, for $c/a = 1$, the KKR-ASA calculation with the improved definition of energy zero²⁶ shifts $E_{FM} - E_{AFM}$ down by 1 mRy/atom, favoring the FM state and bringing it in very good agreement with FLAPW. The KKR-CPA calculation finds the FM state becomes more favorable as the chemical disorder increases, i.e., $\eta \rightarrow 0$. In fact, the FM state is favored at $\eta \leq 0.8$ for all the c/a considered here, corresponding to antisite substitution of only 10%.

The reason for enhanced ferromagnetism due to chemical disordering can be readily understood by investigating pairwise interactions between atomic moments. Intuitively, for example, Fe antisites on the Pt layer are expected to couple ferromagnetically to the neighboring Fe in an Fe layer, as seen in an alloy-expanded fcc lattice (see Ref. 30). More quantitative statements can be made. In the limit of infinitesimal fluctuations in the moment orientations, the pairwise magnetic interaction energies can be calculated within the KKR³¹ and KKR-CPA formalisms.³² It is often useful to map these energies onto the Heisenberg Hamiltonian

$$E = - \sum_{ij, i \neq j} J_{ij} \hat{s}_i \cdot \hat{s}_j, \quad (1)$$

where J_{ij} is the interaction energy between the i th and j th moments, and \hat{s}_i is a unit vector describing the orientation of the i th moment. LKKR calculations for the FM state at $\eta = 1$ and $c/a = 0.965$, near the bulk value, have found strong

ferromagnetic coupling between Fe within the Fe-rich (001) layers. Nearly equal energies are contributed by the (100) and (110) neighbors, with $J \sim 1$ mRy. The coupling between Fe and Pt neighbors along the (101) direction is also ferromagnetic as well, but significantly weaker, $J \sim 0.15$ mRy. However, the coupling between neighboring Fe-rich planes is antiferromagnetic, the dominant contribution coming from Fe-Fe interactions along the (101) direction with $J \sim -0.5$ mRy.

Thus, within KKR and FLAPW formalisms, the perfectly ordered FePt ($\eta=1.0$) with $c/a=0.965$ has the lowest energy when the Fe layers have alternating magnetic orientation and there is negligible moment on the Pt atoms.³³ However, as the chemical order is reduced (i.e., thermal antisites with $\eta \neq 1$), some Fe atoms are found in Pt-rich layers. In this case, using the KKR-CPA method, we find that the interaction along the $\langle 101 \rangle$ direction between an antisite substituted Fe atom and the neighboring Fe in the Fe-rich layers is strongly ferromagnetic, $J \sim 1$ mRy. These Fe atoms provide a much stronger FM coupling between the Fe-rich layers than Pt atoms provide. As the chemical disorder increases ($\eta \rightarrow 0$), the FM coupling due to the antisite Fe becomes stronger and can dominate otherwise AFM coupling.

Neutron scattering experiments have found a similar dependence on chemical order in FePt₃.³⁴ There, disordered (A1) FePt₃ is ferromagnetic, while it occurs in one of two antiferromagnetic states in the perfectly ordered $L1_2$ crystal, where the Fe atoms form a cubic sublattice in which no Fe are nearest neighbors. The observed FM state can be explained by FM coupling between the neighboring Fe atoms that occur through antisite substitution. We note in passing that, in agreement with the calculations presented here, Pt has negligible magnetic moment in AFM states.³⁴

First-principles calculations suggest some ways that the FM state is stabilized. We note that all these methods will likely decrease the MAE, so it is likely that some combination would be best. First, as discussed above, thermodynamically favored chemical (antisite) disorder stabilizes FM. This further suggests that FM stability may be enhanced by changing the composition to be slightly Fe-rich. That is, Fe_{0.5+ δ} Pt_{0.5- δ} with $0 < \delta < 0.2$ would help stabilize the FM state with Fe antisites mediating the FM coupling between Fe layers. Calculations using the bulk KKR method confirm this, finding $E_{\text{FM}} - E_{\text{AFM}} = -1.1$ mRy/atom for Fe_{0.6}Pt_{0.4} for $c/a=1.0$ and no Pt on Fe sites, compared to -0.3 mRy/atom for perfectly ordered $L1_0$ FePt, see Fig. 1. We anticipate that this will have a similar effect on the MAE to increasing the chemical disorder, and that MAE will decrease with increasing δ . Finally, the FM is strongly favored over AFM in CoPt, so substituting a small percentage of Co

for Fe may further stabilize the FM state. In CoPt with $\eta = 1.0$ and $c/a=1.0$, we find $E_{\text{FM}} - E_{\text{AFM}} = -2.0$ mRy/atom using the bulk KKR method, compared to -0.3 mRy/atom for FePt in Fig. 1. Equiatomic CoPt is found experimentally to have a MAE of 4.9×10^7 erg/cm³ at its minimum c/a , 0.972, compared to 6.6×10^7 erg/cm³ in FePt at $c/a = 0.966$.¹⁰ Using a (Fe_{1- x} Co _{x})Pt alloy with $x \sim 0.1 - 0.25$ should maintain the high anisotropy of FePt while strengthening the FM coupling. Kanazawa *et al.* have experimental evidence that for $x < 0.43$ the MAE approaches that of FePt as $x \rightarrow 0$.^{3,35} Bulk KKR-CPA calculations show that this is also true for $E_{\text{FM}} - E_{\text{AFM}}$. With $c/a=1$ and no Pt antisites, we calculate $E_{\text{FM}} - E_{\text{AFM}} = +0.7$ mRy/atom for (Fe_{0.75}Co_{0.25})Pt, i.e., disordered Fe-Co layers between pure Pt layers with an effective two atoms per cell, indicating that FM is not favored. With $c/a=1$ and fully ordering (Fe_{0.75}Co_{0.25})Pt to eight atoms per cell Fe₃Co₁Pt₄, however, we calculate $E_{\text{FM}} - E_{\text{AFM}} = -0.5$ mRy/atom, where, of course, by symmetry there are antisites. Although this is not an exhaustive thermodynamic search, it does indicate that antisite disorder is key to the stability of the FM state.

In summary, we have presented FLAPW and KKR results showing a near degeneracy between FM and AFM order in alternating Fe layers in FePt previously undetected in calculations that *a priori* assumed FM order consistent with experimental observations. We find that the relative stability of FM order is enhanced by increasing chemical disorder, either via thermal Pt antisites (with $\eta \rightarrow 0$) or ordering that creates Pt antisites by symmetry, and FM order is enhanced by decreasing the tetragonal distortion of $L1_0$ (i.e., $c/a \rightarrow 1$). Experimentally, the effects of processing temperature favor antisite disorder in FePt and, hence, ferromagnetism. On the other hand, in finite-sized (supported) FePt nanoparticles (with single c domains), there will be an inherent tetragonality (bond contraction, i.e., $c/a < 1$) in order to increase metallic density, which favors antiferromagnetism. In general, there is an antagonistic relation between the stability of the ferromagnetic state and the increased magnetoanisotropy energy desired in magnetic recording, which appears to be somewhat mollified by the unavoidable occurrence of antisite defects. Even for FM FePt, the magnetic recording properties may be affected if the AFM state provides a magnetic reversal mode different from coherent rotation.

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