

State-Tracking First-Principles Determination of Magnetocrystalline Anisotropy

Ding-sheng Wang

*Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208-3112
and Institute of Physics, Academia Sinica, Beijing 100080, China*

Ruqian Wu and A. J. Freeman

*Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208-3112
(Received 8 September 1992)*

A state-tracking method is proposed for the determination of the magnetocrystalline anisotropy (MCA) energy, in which the spin-orbit coupling perturbed occupied states are defined according to their wave functions as related to the unperturbed occupied states, instead of their energies. This ensures that the force theorem is well satisfied—a very important feature in all non-self-consistent perturbative procedures. In calculations for the effect of strain on the MCA of an Fe monolayer (using the full-potential linearized augmented plane-wave method), highly stable results were obtained even with a small number of k points (10^2 in the full Brillouin zone) versus the 10^4 points needed previously.

PACS numbers: 75.30.Pd, 75.70.Ak

Recent experiments revealed that due to their reduced dimensionality many thin overlayer and superlattice systems show perpendicular magnetic anisotropy and so appear to be promising candidates for high-density magneto-optical storage media [1,2]. They have also called attention to the strong desire for an *ab initio* theoretical approach that can explain the underlying physics and, more importantly, predict new systems with desired properties in advance of experiments. Unfortunately, despite enormous advances in local-spin-density electronic structure theory and computational power in the last decade, the theoretical understanding of magnetocrystalline anisotropy (MCA) for 3d magnetic transition metals (TM) still remains a great challenge. Earlier pioneering tight binding and even recent first-principles theoretical studies for MCA actually resulted in seemingly more controversy than success [3–5]. This is not surprising, given the complexity of the fundamental challenge of finding a stable and precise way to isolate the tiny spin-orbit coupling (SOC) contribution in a first-principles calculation that still takes account of all the complexities existing in a real material.

This Letter presents a new method based on state tracking that provides, for the first time, a stable and precise way to determine from first principles the magnetocrystalline anisotropy energy. The method ensures that the force theorem is well satisfied and gives highly stable results even for a small number of k points, 100–421 in the full Brillouin zone (BZ) in the test case of an Fe monolayer. These results agree overall with the earlier pioneering work of Gay and Richter [4] who used 7744 k points. Application to the determination of the effect of strain on the MCA energy of an Fe monolayer shows, surprisingly, that while the magnetic moment is enhanced the anisotropy constant decreases with increasing lattice parameter.

As proposed by Van Vleck [6] more than 50 years ago, the magnetocrystalline anisotropy is thought to originate

from the SOC, included in relativistic theory by the Hamiltonian term $H^{sl} = \xi \boldsymbol{\sigma} \cdot \mathbf{L}$, where the coupling constant ξ depends on the gradient of the potential around each atom. In TM systems, the SOC becomes extremely weak because of the quenching of the orbital angular momentum, and the MCA energy is very small (10^{-5} to 10^{-4} eV), i.e., much smaller than the total energy difference between final self-consistent iterations. A perturbative (rather than self-consistent) treatment based on a force theorem [7] is usually adopted in MCA calculations, in which the SOC induced change of total energy is approximated by the difference of the single-state energies summed over all occupied states, namely,

$$E^{sl}(\theta) = \sum_{O'} \epsilon'_i - \sum_O \epsilon_i, \quad (1)$$

where the prime denotes SOC perturbed states, energies, etc.

In Eq. (1) the sets $\{O\}$ and $\{O'\}$ of occupied states are independently defined according to Fermi statistics by their own eigenenergies, ϵ_i and ϵ'_i , respectively, regardless of the possible relation between the unperturbed and perturbed states (wave functions). Now, this is correct if the SOC perturbed system is also calculated self-consistently—since through iterations the ϵ'_i can undergo changes depending on the effect of SOC on their wave functions. Otherwise, mistakes will arise for perturbative calculations as was done by almost all previous authors because, for example, although an unperturbed empty state $\epsilon_j(k_2)$ has nothing to do with the occupied state $\epsilon_i(k_1)$, it may still become occupied if $\epsilon'_i(k_1)$ is raised above E_F by SOC at the specified moment direction. Since the difference $\epsilon'_j(k_2) - \epsilon_i(k_1)$ which contributes to the total energy change may chance to range from zero to the SOC strength ($\sim 10^{-2}$ eV), this “blind” Fermi filling results in a strong stochastic variation of MCA and spikes as high as $\epsilon'_j(k_2)$ and $-\epsilon_i(k_1)$ in the distribution of the MCA energy in the BZ at k_2 and k_1 , respectively [8]. Moreover, Strange *et al.* [9] and Daalderop, Kelly, and

Schuermans [10] argued that even a ± 0.01 electron filling may also change the sign of the MCA energy, and concluded that only 10^{-2} (or even fewer) electron at E_F contribute to the MCA. Both assertions are obviously in contrast to the experimental fact that the MCA is a short-ranged intrinsic property of ferromagnetic materials and that it can hardly be affected by a small amount (a few percent) of impurities. Furthermore, the blind Fermi filling also violates the basic assumption required by the correct application of the force theorem, i.e., minimal change of the charge and spin densities, since the wave function of $\epsilon'_j(k_2)$ may differ totally from that of $\epsilon_i(k_1)$. This is the main reason why many thousands of k points in the BZ had to be used in previous MCA calculations to suppress the randomness by reducing the weight of each such "abnormal" k point. In addition to the fact that the results still contain large uncertainties, the high cost of computer time also frustrates the application of this kind of MCA calculation to systems of experimental interest.

Based on this analysis, we propose a state tracking method to determine the set of occupied states $\{O\}$ which can ensure the stability of the calculated MCA energy with respect to the number of k points, electron filling, and even the SOC scaling factor. After obtaining highly precise eigenvalues, ϵ_i , and eigenfunctions, Ψ_i , of the unperturbed Hamiltonian, H^0 , using the local-density full-potential linearized augmented plane-wave (FLAPW) method, we treat H^{st} in a second variational way (convenient for but not required by the state tracking scheme) in the space expanded by $\{\Psi_i\}$, i.e.,

$$\langle \Psi_i | H^0 + H^{st} | \Psi_j \rangle = \epsilon_i \delta_{ij} + \langle \Psi_i | H^{st} | \Psi_j \rangle, \quad (2)$$

and solve for the SOC perturbed state

$$\Psi'_i = \sum_j C_j^i \Psi_j. \quad (3)$$

Each perturbed state Ψ'_i is tracked by defining a probability of finding it in the unperturbed occupied states $\{O\}$ (determined by Fermi filling),

$$P_i^{\text{occ}} = \sum_{j \in \{O\}} |C_j^i|^2. \quad (4)$$

Now, rather than minimizing the total eigenvalue energy by filling the lowest ϵ'_i , the perturbed occupied states $\{O'\}$ are determined by maximizing the total probability

$$P^{\text{occ}} = \sum_{i \in \{O'\}} P_i^{\text{occ}}, \quad (5)$$

with respect to the choice of $\{O'\}$ while keeping the total number of electrons (Z) the same for $\{O'\}$ and $\{O\}$. Since H^{st} is weak, this definition does not introduce any

ambiguities, i.e., the value of P_i^{occ} is either very close to one or nearly zero except for very few states with surface pair coupling (see next paragraph). The total probability, P^{occ} , determined in this state tracking scheme is less than but very close to Z . In this sense, the state tracking perturbed occupied states give almost the same spatial distribution of the charge and spin densities—which ensures the best possible application of the force theorem, and their difference reflects solely the physical effect of SOC, free from the above mentioned random fluctuations.

However, if a pair of occupied and empty states are so close that their energy separation is comparable to their SOC strength, strong mixing would exist between them. While a contribution from this quasidegenerate pair of states near E_F , so-called surface pair coupling (SPC), was emphasized strongly by Kondorskii and Straube [11], this term should not be so important because this coupling occurs only in very few and very small regions in the BZ (intersection or tangency of Fermi spheres of two bands). For example, in the two-dimensional BZ for ultrathin films, the area of the SPC region is

$$S_{\text{SPC}} \propto \left(\frac{\xi}{\partial E / \partial k} \right)^2. \quad (6)$$

With a maximum SOC shift of ξ , the SPC contribution is at most of the order of ξ^3 —which is at least an order higher in ξ than both the isotropic and anisotropic SOC induced change of total energy ($\propto \xi^2$ due to the reduced symmetry in the z direction). In addition, if a proper perturbative treatment is adopted which includes the electron-electron interaction between this quasidegenerate pair of states, the SPC contribution is of even higher order. Clearly the net contribution from SPC is very small. To evaluate this high-order term in a discrete integration, the mesh points should be dense enough to sample a reasonable number of k points in the vicinity of the intersection, S_{SPC} . The total number of k points should thus amount to ten thousand or so. Otherwise, for a limited number of k points (N_k), whenever SPC is encountered its contribution is enhanced, however, to ξ/N_k . This results in a large error in the MCA energy if $1/N_k$, the weighting factor, is larger than the actual S_{SPC} . Taking this property of the SPC contribution into account, it would obviously be a better approximation to eliminate this contribution by setting corresponding coupling matrix elements to zero in advance when using smaller N_k values, rather than increasing N_k to more than ten thousand. Practically speaking, the SOC matrix element between states ϵ_u (unoccupied) and ϵ_o (occupied) is set equal to zero if

$$\epsilon_u - \epsilon_o < 5\xi [|\langle \Psi_u | L_x | \Psi_o \rangle|^2 + |\langle \Psi_u | L_y | \Psi_o \rangle|^2 + |\langle \Psi_u | L_z | \Psi_o \rangle|^2]^{1/2}. \quad (7)$$

In a real calculation, surface pairs decoupled according to the above criterion are in fact very rare, but it improves the MCA results substantially.

As a test and also as the first application of our state tracking scheme, we calculated the MCA energy for free stand-

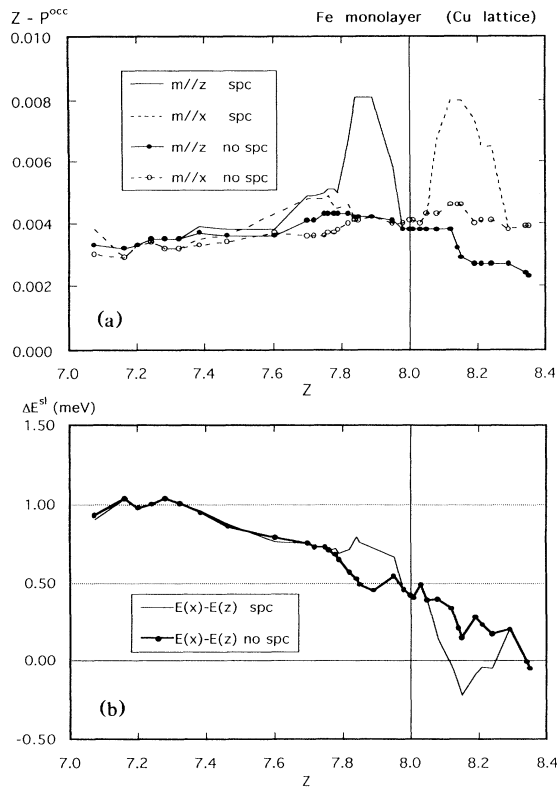


FIG. 1. (a) Probability of finding the SOC perturbed occupied state (as determined by state tracking method) in unperturbed occupied states, P^{occ} ; and (b) MCA energy (ΔE^{sl}) vs electron filling for the Fe(001) monolayer ($a=4.83$ a.u.). Plain and circled curves stand for results before and after elimination of the surface pair coupling, respectively.

ing Fe(001) monolayers. Three lattice constants [matching Cu(001), Ag(001), and W(001) surfaces, respectively] were used to investigate the effects of lattice strain on the MCA. For the unperturbed system, more than 100 plane waves are used as the FLAPW variational basis set to solve the semirelativistic Kohn-Sham equations. Within the muffin-tin spheres lattice harmonics with angular momentum l up to 8 are used to expand the charge density, potential, and wave functions. Integrations over k space are replaced by summations over 15 special k points in the $\frac{1}{8}$ irreducible 2D BZ (100 points in the full BZ). Convergence is assumed when the average root mean square distance between the input and output charge (spin) densities is less than $2.5 \times 10^{-4} e / (\text{a.u.})^3$. For the MCA calculations, 66 k points in the $\frac{1}{8}$ irreducible 2D BZ (421 points in the full BZ) are employed for different orientations of the spin moment (the SOC reduced symmetry in the x - y plane is considered by changing the direction of the magnetic moment in the plane). The total number of valence electrons, Z , is used as a parameter—which helps to reveal the SOC induced rehybridization over different energy regions.

Figure 1(a) plots the maximized total probability of

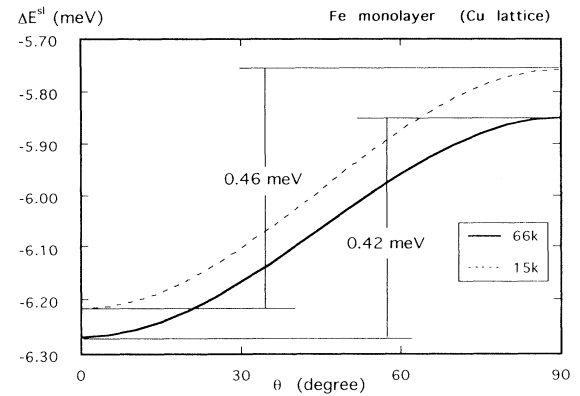


FIG. 2. The calculated angular dependence of the MCA energy for the Fe(001) monolayer ($a=4.83$ a.u.) using 15 and 66 k points in the $\frac{1}{8}$ irreducible BZ (100 and 421 k points in the full BZ, respectively). θ is the angle between magnetic moment and the normal of the layer plane.

the perturbed occupied states $\{O^i\}$ as a function of Z for the Fe monolayer with the Cu(001) lattice constant. As expected, P^{occ} (without SPC) is very close to Z (within 0.5%) in the whole Z range shown—indicating the distinct meaning of the state tracking. Two peaks ($\sim \frac{1}{2} \times \frac{1}{66}$) can be found when SPC exists, namely, $\langle d_{xz} | L_z | d_{yz} \rangle$ at the \bar{M} point of the spin minority band for the peak at $Z=7.9$, and $\langle d_{z^2} | L_x | d_{yz} \rangle$ at the point $(k_x, k_y) \approx (0.4, 0.0)\pi/a$ of the spin minority band for the peak at $Z=8.1$.

The calculated magnetic anisotropy energy, $\Delta E^{\text{sl}} = E^{\text{sl}}(x) - E^{\text{sl}}(z)$, is presented in Fig. 1(b). Obviously, it becomes a stable function with respect to electron filling over a wide range of Z (7.0 to 8.4 electrons) especially when the SPC is removed (solid circles). Furthermore, the randomness in the MCA energy distribution in the BZ is also completely eliminated. Both results are reasonable compared to experiment and, of course, indicate the advantage of our state tracking method over the blind Fermi filling. The elimination of SPC is somewhat important, since it would otherwise have a considerable effect on the MCA energy as shown in the region $Z \approx 7.9$ and $Z \approx 8.1$. Roughly, the influence of SPC on the MCA energy may reach $\xi/N_k \approx 0.5$ meV (assuming $N_k=66$) which is already as large as the MCA energy itself.

The angular dependence of the MCA energy for this Fe monolayer is plotted in Fig. 2, where $\theta=0$ denotes that the spin moment lies along the perpendicular direction (z). Clearly, for the first time, the calculated MCA energy can be well fitted by a $\sin^2\theta$ function. For the Fe(001) monolayer with the Cu lattice constant, the easy direction of the spin moment is along the z axis with an anisotropy energy $\Delta E^{\text{sl}}=0.42$ meV. Note that a value very close to this value can also be obtained by using an even smaller number of k points (100 in the full BZ). Importantly, calculations employing such a small number of

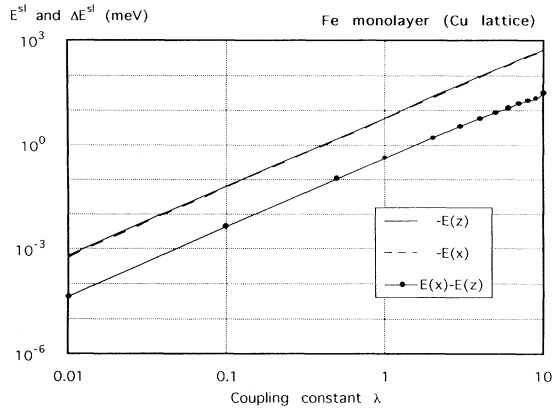


FIG. 3. Calculated SOC induced total energy changes (for both perpendicular and in-plane magnetization) and the MCA energy vs the scaling factor λ (in logarithmic scales) for Fe(001) monolayer ($a=4.83$ a.u.). SPC is included in the calculation.

k points (15 or 66 in the irreducible BZ) that yield the full MCA curve for the Fe(001) monolayer can be done in only a few minutes of Cray-YMP CPU time; taken together with its inherent stability, our state tracking method can be easily applied to a large variety of real systems of interest consisting of 10–20 atoms/cell.

As another critical check, we introduce a scaling factor λ to monitor changes in the strength of the SOC as $H=H^0+\lambda H^{sl}$. Physically, E^{sl} should be proportional to $\lambda^2 [\pm O(\lambda^4)]$ since the first-order term is always zero due to the time-reversal symmetry of H^{sl} ; ΔE^{sl} is also a second-order function of λ for the monolayer because of the lowered symmetry. Indeed, the calculated E^{sl} and ΔE^{sl} , as plotted in Fig. 3 (no neglect of SPC), exhibit a clear λ^2 relation in a wide range of λ from 0.01 (and even lower) to greater than 1. In principle, the smaller the λ , the smaller the effect of the SPC in a finite k -mesh calculation. Deviation from a λ^2 law exists only for λ much greater than 1 because of the strong SPC. Thus we can confidently say that our state tracking scheme has picked up only the SOC contribution without introducing noticeable spurious effects in the physical region spanned by λ .

Finally, the MCA energies for free standing Fe monolayers at lattice constants matching those for fcc Cu(001), Ag(001), and bcc W(001) ideal surface are compared in Table I. The results for the first two spacings agree approximately with the pioneering results of Gay and Richter [4,8], which had to be computed by using as many as 7744 to 14400 k points of integration in the Brillouin zone in order to obtain stable results. That the uncertainties from “blind” band filling and SPC can produce different results can be seen from Table I by comparing with Ref. [5]. The MCA energy constant is seen to decrease with increasing atomic spacing. A larger atomic distance leads to a narrower d band and less d band filling, as can be seen from the increase of the mag-

TABLE I. The MCA constant K_2 (in unit meV/atom) defined by $E^{sl}=E_0+K_2\sin^2\theta$ and magnetic moments m (in unit μ_B /atom) for the free standing Fe monolayers matching the fcc Cu(001), Ag(001), and bcc W(001) substrates.

Lattice constants (a.u.)	This work		Previous work		Reference
	K_2	m	K_2	m	
4.83 (Cu)	0.42	3.04	0.61		[8]
5.45 (Ag)	0.37	3.22	0.38	3.20	[4]
5.97 (W)	0.27	3.43	-0.033 to -0.043	3.11–3.13	[5]

netic moment also shown in Table I; this should lead to a slight increase in the anisotropy constant according to the band filling relation given in Fig. 1(b) if the band structure remained unchanged. However, the increase of the atomic distance makes the directionality (crystal-field) weaker, and the environment of every atom becomes more isotropic; this leads to the decrease of the MCA. Our results show that it is this environmental change that dominates the change of MCA energy in Fe monolayers. The mechanism will be explained in a forthcoming publication that includes realistic simulations on the interface MCA of Co-Cu systems for which good agreement with experiment is obtained.

Work at Northwestern supported by the National Science Foundation (Grants No. DMR89-06935 and No. DMR91-17818, and a grant of computer time at the Pittsburgh Supercomputing Center through its Division of Advanced Scientific Computing). One of us (D.S.W.) acknowledges the support of the National Science Foundation of China.

- [1] L. M. Falicov, D. T. Pierce, S. D. Bader, R. Gronsky, K. B. Hathaway, H. J. Hopster, D. N. Lambeth, S. P. Parkin, G. Prinz, M. Salamon, I. K. Schuller, and R. H. Victora, *J. Mater. Res.* **5**, 1299 (1990).
- [2] S. D. Bader, *Proc. IEEE* **78**, 909 (1990).
- [3] H. Brooks, *Phys. Rev.* **58**, 909 (1940); A. J. Bennett and B. R. Cooper, *Phys. Rev. B* **3**, 1642 (1971); N. Mori, Y. Fukuda, and T. Ukai, *J. Phys. Soc. Jpn.* **37**, 1263 (1974); P. Bruno, *Phys. Rev. B* **39**, 865 (1989).
- [4] J. G. Gay and R. Richter, *Phys. Rev. Lett.* **56**, 2728 (1986).
- [5] C. Li, A. J. Freeman, H. J. F. Jansen, and C. L. Fu, *Phys. Rev. B* **42**, 5433 (1990).
- [6] J. H. van Vleck, *Phys. Rev.* **52**, 1178 (1937).
- [7] M. Weinert, R. E. Watson, and J. W. Davenport, *Phys. Rev. B* **32**, 2115 (1985), and references therein.
- [8] R. Richter and J. G. Gay, *Mater. Res. Soc. Symp. Proc.* **151**, 3 (1989).
- [9] P. Strange, J. B. Staunton, B. L. Gyorffy, and H. Ebert, *Physica (Amsterdam)* **172B**, 51 (1991).
- [10] G. H. O. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, *Phys. Rev. B* **41**, 11919 (1990).
- [11] E. I. Kondorskii and E. Straube, *Zh. Eksp. Teor. Fiz.* **63**, 356 (1972) [*Sov. Phys. JETP* **36**, 188 (1973)].